Development in Wastewater Treatment Research and Processes

Removal of Emerging Contaminants from Wastewater through Bio-nanotechnology

Edited by
Susana Rodriguez-Couto
Maulin P. Shah
Jayanta Kumar Biswas

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CHAPTER

1 Nanoadsorbents for scavenging emerging contaminants from wastewater

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1.1 Introduction

Water is the most important and plentiful resource on earth. It plays a major role in the world economy. Almost 70% of the available fresh water is used in the agricultural sector. Water pollution is a major problem at present, which can potentially effect human health, plants, and animals. On the other hand water scarcity is another major environmental issue at present (Fereidoun et al., 2007; Yousefi et al., 2018). Because of the decreasing availability of fresh water resources, reuse and recycling of wastewater after proper treatment is being considered as a smart alternative for conserving fresh water resource. The reuse of wastewater has numerous benefits in diverse applications including irrigation in agriculture, aquaculture, manufacturing consumption, recreational and environmental practices, and artificial ground water recharging (Asano et al., 2007). Theoretically, wastewater can be applied to all purposes which are generally accomplished by using fresh water resources, if proper treatment is done to restore the water quality suitable for intended use. Except a small number of countries, wastewater reusing is strictly restricted for nonpotable purposes or maximum to indirect potable use. Hence, certain parameters like electrical conductivity, dissolved organic matter, and heavy metal concentration should be monitored before intended reuse of wastewater (Abedi-koupai et al., 2006).

Pure fresh water is very valuable for maintaining life on earth. Water sources can be contaminated in several ways and with different contaminants. Thus the process for remediation of polluted water is different depending on the type of contamination.

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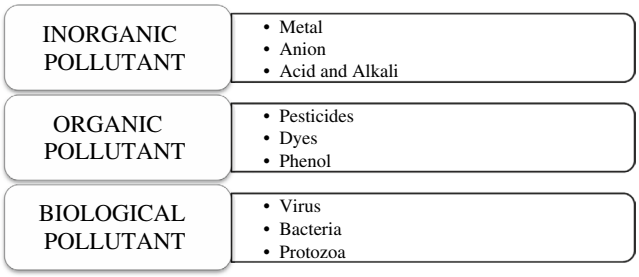

FIG. 1.1 Different types of water pollutants.

Wastewater is produced from different sectors like domestic, industrial, agricultural etc. The different types of contaminants present in wastewater can be broadly divided into three major categories—inorganic pollutants, organic pollutants, and biological pollutants. These categories are further illustrated in Fig. 1.1.

Apart from this general categorization of water pollutants the main concern lies over some pollutants which are categorized as persistent organic pollutant (POPs), heavy metals, and emerging contaminants. In the beginning of 1990s, the major concern about water pollution focused on heavy metals. But recently with the increase in use of pesticides and personal care chemical products the focus shifted from heavy metals to "emerging contaminants." Emerging contaminants include pharmaceutical and personal care products, disinfectants, surfactants, pesticides, dyes, paints, preservatives, food additives, microplastics, and nanomaterials. Emerging contaminants are natural or manmade chemicals that are not usually monitored in the environment but have the potential to enter different environmental sector and affect adversely (Rosenfeld and Feng, 2011). These emerging contaminants are hardly included in the international monitoring program indicating that the life of these contaminants, their fate and potential impact on ecosystem and living beings is still an unexplored area (Geissen et al., 2015). Recently the concern about the potential of these emerging contaminants to pollute rivers, lakes, and groundwater is rising (Adeleye et al., 2016; Dai and Mitch, 2013). Researchers have shown that the conventional technique of water and wastewater treatment cannot efficiently remove all the emerging contaminants present. So there is some need for progressive research aimed at developing some advanced water and wastewater treatment method (Qu et al., 2013). Among different methods that have been established for removal of emerging contaminants from wastewater, nanomaterials have ushered in a new hope. The aim of this chapter is to review the potentials of nanomaterials, especially nanoadsorbents in removing emerging contaminants from wastewater.

1.2 Emerging contaminants

Emerging contaminants (EC) are not new chemicals. They may be present in the environment since a long time but their presence and potential to adversely affect living organisms and environment has been recognized quite recently. According

Table 1.1 Categories of emerging contaminants and their examples.

Class of compound	Examples
Pharmaceutical and personal Care Products (PPCPs)	Antibiotics, anticonvulsants, mood stabilizers and cosmetic products
Flame retardant and their impurities	Polybromonated diphenyl ethers (PBDEs) and hexabromocyclododecanes (HBCDs)
Pesticides and biocides	Perfluororoctane sulfonates (PFOS) and perfluoroctanoic acid (PFOA)
Steroids and endocrine disruptors	Biogenic and synthetic hormones
Industrial and domestic wastes and food additives	PAH, bisphenol A, toluene, and saccharine

to Richardson (2009), emerging contaminants can be classified into two segments, either pharmaceutical and personal care products (PPCPs) or chemicals that are designated as endocrine disrupting compounds (EDCs). These contaminants are also referred to as contaminants of emerging concerns (CEC), persistent organic pollutants (POPs), organic wastewater contaminants (OWCs).

Endocrine disrupting compounds are those categories of emerging contaminants that interfere with the normal functioning of endocrine system in mammals resulting in cancer, birth defects, and developmental disorders. EDCs enhance cell mutation that ultimately leads to formation of cancerous cells. The effects of EDCs produce physiological deformities like learning disabilities, attention deficit, hyperactive disorders, and deformities in body parts like limbs. Exposing animals to low levels of EDCs produce similar effects as that of human beings. Xenoestrogens, alkyl phenols, and bisphenol-A are some of the endocrine disrupting compounds. Being nonbiodegradable organic pollutants, POPs persist in the environment and accumulate in human and animal body, posing great health risk. Most of the POPs are used as pesticide. Pharmaceutical and personal care products (PPCPs) are compounds that have already passed through the human body and transferred to drinking water and wastewater. These compounds cannot be removed by conventional treatment methods. They cause significant threat by promoting antibiotic resistant bacteria which later combine with other chemicals and form a complex chain (Focazio et al., 2008). Different classes of emerging contaminants can be elaborated in Table 1.1.

1.3 Occurrence of emerging contaminants in aquatic systems

Several researchers confirmed the presence of different categories of emerging contaminants in Indian water bodies. The main components of the ECs present have the following shares shown in Fig. 1.2.

According to a report of Delhi-based nonprofit Centre for Science and Environment (CSE) 78% of the sewage generated in India remains untreated and is discharged in water bodies like river and lakes (Mathew and Kanmani, 2020). These

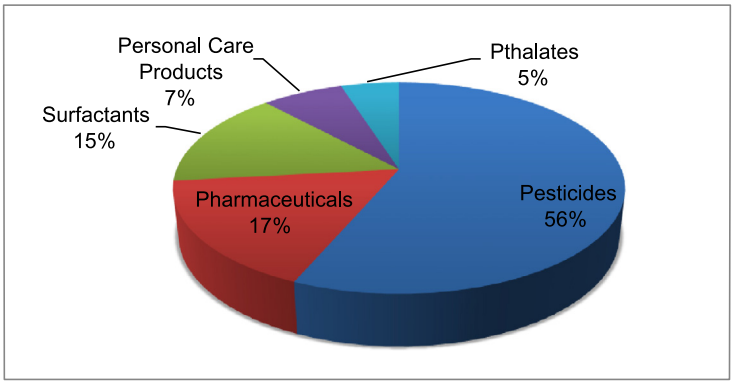

FIG. 1.2 Different components of emerging contaminants.

explain the reason behind high concentration of ECs in aquatic systems (Table 1.2). William et al. (2019) estimated the quantities of ECs present in a river named Ahar in Udaipur city and found 19 Active Pharmaceutical Ingredients (API), four of them were antibiotics. The river originated as a drinking water source and move through urban area while getting contaminated. It was observed that the concentration of API increased as it passed through densely populated regions. This phenomenon indicates the potential discharge of ECs in domestic sewages. Mutiyar and Mittal (2014) found occurrence of antibiotics in water of Yamuna River. Ramaswamy et al. (2011) investigated the presence of carbamazepine (CBZ), antiepileptic in the water of Kaveri, Vellar, and Tamiraparani rivers. Lapworth et al. (2018) demonstrated the presence of SMX and CBZ in river Ganga.

Triclosan, Triclocarban, and Paraben are some of the most important component found in personal care products (PCPs). These chemicals are used as antibiotic agents in shampoo, soap, hand-wash, sanitizers, etc. These compounds were found to be present in water samples drawn from Kaveri, Vellar and Tamiraparani rivers (Vimalkumar et al. 2018). Anumol et al. 2016 also demonstrated the presence of these compounds in influent coming into WWTP, Chennai. DEET another important compound of PCPs, used in mosquito repellents is found to be present in water of Ahar River, Udaipur city (William et al., 2019). The presence of PCPs in river water indicates discharge of untreated domestic wastewater into the river. It was also found that the concentration of these compounds increased as the river passes through densely populated regions. Benzotriazole ultraviolet stabilizers are compounds that are extensively used in shaving cream, sunscreen lotions, soaps, shampoos, etc. Presence of these compounds was detected in three main rivers of South India namely; Kaveri, Tamiraparani, and Vellar. Among the BUVSs, UV-329 and UV-9 were predominant (Vimalkumar et al. 2018). Table 1.3 demonstrates the commonly encountered PCPs in different rivers across India while Table 1.4 shows different pharma-chemical classes and their reported adverse effects.

Endocrine disrupting compounds is of major concern nowadays because of their ability to interfere with normal functioning of endocrine system in human being,

Table 1.2 Various APIs present in different rivers across India.

API	Class of drug	Sampling site	References
Carbamazepine	Anticeptic	Kaveri river Tamiraparani, TN Vellar, TN Pichavarom Mangrove, TN Ahar River, Udaipur Groundwater, Varanasi, UP Groundwater, Ramnagar, UP River Ganga, UP Stretch of River Ganga	Ramaswamy et al., 2011; Lapworth et al., 2018; Sharma et al., 2019
Acetaminophen	Analgesic	Stretch of River Ganga Groundwater near Ganga basin	Sharma et al., 2019
Atenolol	Beta-Blocker	Stretch of River Ganga Influent, WWTP, Chennai	Sharma et al., 2019; Anumol et al., 2016
Ketoprofen	NSAID	Stretch of River Ganga Groundwater near Ganga basin	Sharma et al., 2019
Ibuprofen	NSAID	Ahar River, Udaipur Stretch of River Ganga Groundwater near Ganga basin	William et al., 2019; Sharma et al., 2019
Diclofenac	NSAID	Ahar River, Udaipur Stretch of River Ganga Groundwater near Ganga basin Influent, WWTP, Chennai	William et al., 2019; Sharma et al., 2019; Anumol et al., 2016
Naproxen	NSAID	Ahar River, Udaipur Stretch of River Ganga Groundwater near Ganga basin	William et al., 2019; Sharma et al., 2019
Caffeine	Cosmetic, Psychoactive drug	Ahar river, Udaipur Stretch of River Ganga Groundwater near Ganga basin Influent, WWTP, Chennai Effluent, WWTP, Chennai	Williams et al., 2019; Sharma et al. 2019
Hydrochlorothiazide	Diuretics	Stretch of River Ganga Groundwater near Ganga basin Ahar River, Udaipur	Williams et al., 2019; Sharma et al., 2019
Trimethoprim	Antibiotics	Ahar River, Udaipur	Williams et al., 2019
Azithromycin	Antibiotics	Ahar River, Udaipur	Williams et al., 2019
Glibenclamide	Hypoglycemic drug	Ahar River, Udaipur	William et al., 2019

Table 1.3 Various PCPs commonly encountered in different rivers across India.

PCPs	Class of PCPs	Location of Occurrences	References
Triclosan	Antibacterial	Kaveri Tamiraparani Vellar Pichavarom Mangrove Stretch of River Ganga Groundwater near Ganga basin	Ramaswamy et al. 2011 Sharma et al. 2019
Triclocarbon	Antibacterial	Kaveri Tamiraparani Vellar Stretch of River Ganga Groundwater near Ganga basin	Vimalkumar et al. 2018 Sharma et al. 2019
UV-9	BUVs	Kaveri Tamiraparani Vellar	Vimalkumar et al. 2018
UV-329	BUVs	Kaveri Tamiraparani Vellar	Vimalkumar et al. 2018
DEET	Mosquito Repellent	Ahar river, Udaipur Stretch of River Ganga Groundwater near Ganga basin	Williams et al., 2019 Sharma et al. 2019
Benzotriazole	UV- Stabilizers	Ahar river, Udaipur	Williams et al., 2019

especially vulnerable group like children, pregnant mother, and elder age group. Several researchers have reported the presence of phthalates, polychlorinated biphenyls, plasticizer, perchlorate, etc. Polychlorinated biphenyls can enter into the environment from the leachate of poorly managed landfills or improperly discarded electronic wastes. William et al. (2019) found six steroid hormones in Ahar River, Udaipur such as estrone, 17α estradiol, 17α estradiol, androsterone, dihydrotestosterone, and testosterone. Das et al. (2014) measured 15 phthalates in drinking water from Jawaharlal Nehru University and the Okhla industrial area. Perchlorate is mainly used in fireworks, matches, etc. it is also applied in lubricating oil, aluminum refining, paint, rubber manufacturing and leather tanning etc. this compound can interfere with iodine transport and thereby result in reducing thyroid production (Fisher & McLanahan 2008). Researchers have documented the presence of pesticides such as chlorpyrifos, phenoxy acetic acid, diuron, and atrazine in river Ganga (Lapworth et al., 2018). Chakraborty et al., 2015 demonstrated the presence of organochlorine pesticides (OCPs) such as HCH, DDT, endosulfan, heptachlor, and aldrin in river Hooghly (RH) and river Brahmaputra (RB).

Table 1.4 Different classes of pharmaceutical chemicals and their adverse effects on various organisms.

Medicine Class	Reported effects	References
Anorexic treatments	Hormonal effect in crabs and crayfish	Daughton and Ternes, 1999
Estrogens	Endocrine disrupting effects on fish	Floate et al., 2005
Parasiticides	Effects on insect development and physiology; effect on rate of dung decomposition	Sommer and Bibby, 2002
Antibacterials	Selection of antibacterial resistance; Impacts on the structure of soil microbial communities; inhibition of growth blue-green algae and aquatic plants; biochemical effects in fish	Sengeløv et al., 2003 Pomati et al., 2004 Westergaard et al., 2001 Laville et al., 2004
Anti-inflammatory	Stimulation of growth of blue green algae and inhibition of growth of aquatic plants; effects on structure of fish hepatocytes	Pomati et al., 2004
Lipid regulator	Biochemical effects in fish	Laville et al., 2004
Analgesic	Biochemical effects in fish	Laville et al., 2004
Beta blocker	Biochemical effects in fish	Laville et al., 2004
Antianxiety drug	Effects on development of invertebrates	Pascoe et al., 2003
Cardiac glycoside	Effects on development of invertebrates	Pascoe et al., 2003
Calcium channel blocker	Effects on development of invertebrates	Pascoe et al., 2003

1.4 Exposure pathways of emerging contaminants in the environment

High levels of industrialization and urbanization along the river basin is the main reason behind the high concentration of EC in the river water. ECs usually go undetected into the environment (Petrie et al., 2015). Another important factor about these compounds is their high production, continuous consumption and consequent release into the environment. The pathways of their exposure and fate in the environment are illustraed in Fig. 1.3.

1.5 Treatment technologies for removal of ECs

Improvement in lifestyle, rapid urbanization, and industrialization has led to an enormous amount of emerging contaminant discharge in rivers and surface waters.

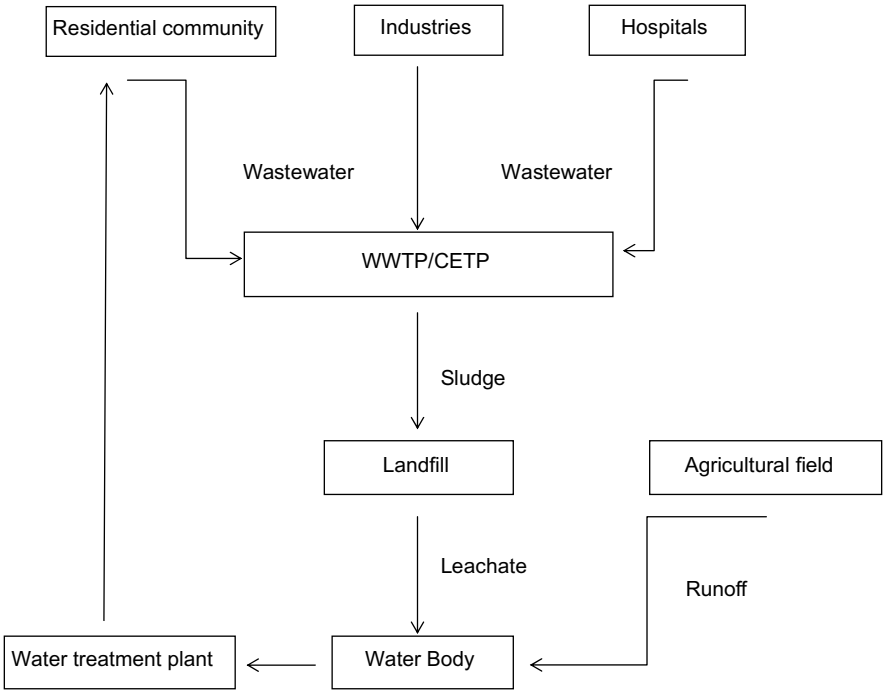

FIG. 1.3 Source and pathways of emerging contaminants in the environment.

Control of ECs is possible through application of efficient and cost-effective technologies. Some of the treatment methods are discussed below.

1.6 Conventional treatment methods

The present state of art of wastewater treatment involves activated sludge treatment. The efficiency of this process in removal of emerging contaminants and the disadvantages are discussed in Table 1.5.

1.7 Emerging methods

1.7.1 Biological treatment method

The biological treatment method makes use of constructed wetlands. This method has been evaluated by several studies. Ramprasad and Philip (2015) demonstrated the removal of surfactants and personal care products like sodium dodecyl sulphate (SDS), propylene glycol (PG), and trimethylamine (TMA) from grey water using a hybrid constructed wetland. In preliminary stage the system augmented with

Table 1.5 Different classes of EC and their removal through conventional treatment method.

Compound	Average Elimination (%)	Main Degradation Product	Observations	References
Non-ionic Surfactants Alkylphenol ethoxylates	90-99	APEC, CAPEC, AP	Primary degradation fast; ultimate degradation less than 40%, metabolites potential endocrine Disruptors	Lindström et al., 2002 Ternes, 1998
Pharmaceuticals			Rapid photodegradation	Petrovic and Barceló, 2003
Ibuprofen	65-90		Degradation product of lipid regulating agents	Öllers et al., 2001
Diclofenac	69-75			
Clofibric Acid	34-51			
Benzafibrate	83			
Naproxen	45-66			
Keptoprofen	69			
Gemfibrozil	46-69			
Carbamazepine	7			
Antiseptics Triclosan	44-92	Methyl triclosan	Possible photodegradation	Rodrıguez et al., 2003
Pesticides	-	-	Application period (mid March until mid May)	Stumpf et al., 1999

Phragmites australis and was fed continuously with grey water. It was found that the system was capable of removing SDS (94-98%), PG (95-98%), and TMA (95-99%). Tiwari and Guha, (2014) investigated the biotransformation of chlorpyrifos (CPF), organophosphate insecticide in aqueous medium. Although biological treatment is adopted as the best available treatment method but this method only facilitates partial removal of the ECs. This indicates that more efficient treatment technology is needed to ensure proper removal of ECs.

1.7.2 Advanced oxidation process

Advanced oxidation is another promising method for removal of Emerging Contaminant like pesticides and APIs. Glaze et al., 1995 studied for the removal of 1,2-dibromo-3-chloropropane (DBCP) pesticide using H_2O_2 and UV. It was observed that nitrate and carbonate/bicarbonate alkalinity, which is formed due to UV shielding and hydroxyl radical scavenging, have a detrimental effect on the oxidation of DBCP. H_2O_2 and UV is strong oxidizing agent. They act through the formation of

scavenging hydroxyl radical nut the residual H_2O_2 creates a problem. This problem can be overcome by adding smaller sized granular activated carbon namely GAC (Huang et al. 2018). Ternes et al. (2003) studied efficacy of ozonation in removing pharmaceutical products and he demonstrated that for optimum removal of the contaminant the concentration of ozone must be equal to the concentration of dissolved organic carbon.

1.8 Nanoadsorbents

In recent days, nanomaterials have received immense attention from scientists and engineers for addressing varied environmental issues due to their unique properties (Zhai et al., 2006; Mandal et al., 2018; Rai and Biswas, 2018; Biswas and Sarkar, 2019; Mukhopadhyay et al., 2021). One main reason for the unique physical and chemical properties of nanoscale material is the surface area of the materials (Gubin et al., 2005). Among the unique properties of nanomaterials, one is the adsorption capacity of various metal ions onto their surface (Kalfa et al., 2009). The surface atoms are unsaturated and are thus subject to combination with other element ions by static electricity (Türker, 2007).

1.9 Classification of nanoadsorbents

The nanomaterials are divided into four main groups based on their role in adsorption. Adsorption through nanoparticle is further a function of innate surface properties and external functionalization. Nanoparticles include metallic nanoparticles (e.g. gold nanoparticles), metallic oxide nanoparticles (aluminium trioxide or titatnium dioxide), nanostructured mixed oxides (nanostructured binary iron-titanium mixed oxide particles) and magnetic nanoparticles (iron di and trioxide). Carbonaceous nanomaterials (CNMs) are all together a different group of nanoparticles among which important as adsorbents are carbon nanotubes (CNTs), carbon nanoparticles (CNPs), and carbon nanosheets (CNSs) (Fig. 1.4). In silicon nanomaterials (SiNMs) these include silicon nanotubes (SiNTs),silicon nanoparticles (SiNPs), and silicon nanosheets (SiNSs). Other nanoparticles important for adsorption process are nanofibers (NFs), nanoclays, polymer-based nanomaterials (PNMs), xerogels, and aerogels.

1.10 Methods for preparation of nanoadsorbents

Synthesis of nanoadsorbents can be divided into two subdivision; the top-down approach, the bottom up approach. The top-down process uses a traditional approach for synthesis of nonabsorbent materials that reduces the particle size through erosion

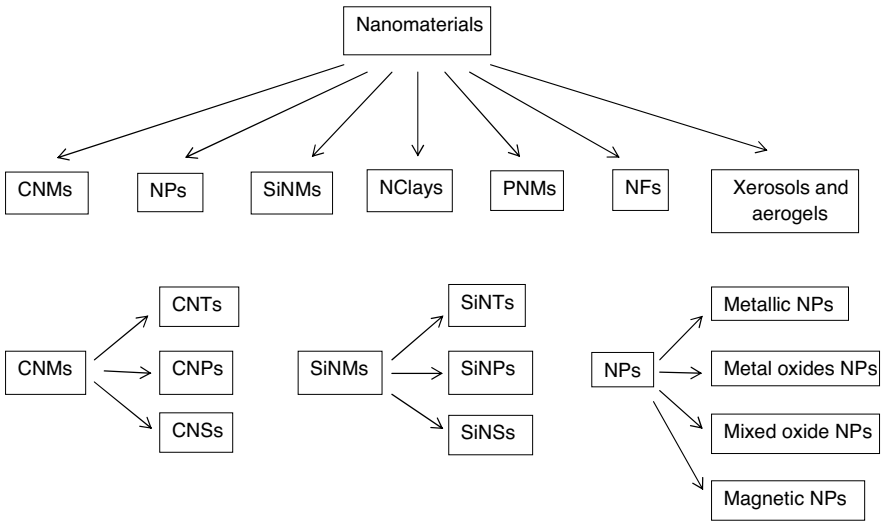

FIG. 1.4 Classification of nanomaterials as nanoadsorbents.

through different approaches such as mechanical alloying, reactive milling, high energy ball milling, etc. On the other hand, bottom up process is quite a new process for synthesis of nanomaterials. This process comprises of building a nanoadsorbents by atom, or molecule by molecule like molecular self-assembly, sol–gel, and chemical/physical vapor deposition. Both methods have their own advantages and disadvantages. The main problem associated with the top-down process is damage of crystallographic and surface structure during particle size reduction. In any case of the deficiencies created by top-down process, this process will still play an important role in the synthesis of nanoparticle. In bottom-up processes, the two main problems are that chemical purification is required and large-scale production is difficult. Despite this, the bottom-up process is considered the preferred technology at the present because it can produce materials that have specific properties tailored to the remediation need depending on the route chosen to fabricate them (Mansfield et al., 2017). Although, the chemical and physical processes of nanoadsorbents synthesis produce particles with a definite size and shape, these processes are not environmentally safe because of the use of harmful chemical agents (El-Sayed, 2020). Biological synthesis are needed to be more examined about particle size, shape etc. as in this process the particles are synthesized by biological synthesis (Ahmad et al., 2017). Microbial synthesis of nanoadsorbents is also possible through extracellular and intercellular mechanism. The biogenic synthesis of nanomaterials is more environment friendly. Moreover, the process takes place at normal temperature and pressure condition. For this reason, researchers are nowadays focusing on exploring biosynthesis of nanoparticles (Table 1.6).

Table 1.6 Methods of synthesis of nanoadsorbents.

Physical method	Biological method	Chemical method
High energy ball milling such as carbon nanoparticle, metal and metal oxide nanopartciles Inert gas condensation such as: metal nanoparticle, and intrametallic nanoparticles Pulse vapor deposition such as: metals and metallic alloys nanoparticles Laser pyrolysis such as: metals and non-metals nanoparticles Flash spray pyrolysis such as: ceramic nanoparticles Electro-spraying such as: metals and ceramic oxide nanoparticles Melt mixing such as: nanocomposition nanoparticles	Microorganisms assisted Biogenesis such as: metal, metal oxide, magnetic and quantum dots nanoparticles Bio-templates assisted biogenesis such as: Au, and Ag nanoparticles Plant extracts assisted biogenesis such as: Pt and Pd nanoparticles	Sol-gel synthesis such as: metal oxide, ceramic, and metal aluminates nanoparticles Micro-emulsion technique such as: semiconduction metal sulphate, metal salt, and organic nanoparticles Hydrothermal synthesis such as: metal, metal oxide and metal sulphide nanoparticles Polyol synthesis such as: magnetic, and metal hybrid nanoparticles Chemical vapor synthesis such as: Si/SiO2 and Al drop ZnO nanoparticles Plasma enhanced chemical vapor deposition such as: carbon and silicon nanoparticles

1.11 Properties of nanoadsorbents

Nanomaterials are effective as adsorbents because of their large surface area and multiple sorption sites, low temperature modification, short intraparticle diffusion distance, tunable pore size, and surface chemistry (Khin et al., 2012). The shape and morphology of nanoparticles play the key role in its efficiency as an adsorbent. Morphology, surface area and composition influence the nature of nanoparticles towards toxics (Gatoo et al., 2014). Furthermore, material, physical, and chemical properties are highly affected by innate surface properties, intrinsic compositions, apparent sizes, and external functionalization of nanosorbent materials (Khajeh et al., 2013). The chemical properties, location of active sorption site, volume to surface area ratio, and composition of functional group define the efficacy of nanomaterial as adsorbents.

1.12 Mechanisms of nanoadsorption

Due to vast diversity nanoadsorbents show wide spectrum of application potentials in removing diverse emerging contaminants as shown in Table 1.7. The efficacy of nanoadsorbents depend on their innate surface properties and external functionalities.

Table 1.7 Various emerging contaminants and their removal by different nanoadsorbents.

Nanomaterials Type	Nanomaterials	Pollutants	References
Carbon based	MWCNT	Triclosan	Zhou et al., 2013
		Norfloxacin	Yang et al., 2012
		Sulfamethoxazole	Kim et al., 2014
		Lincomycin	
		Ciprofloxacin	
		Tetracycline	
		Sulfonamides	
		Chloramphenicols	
	KOH activated MWCNT	Phenol	Ji et al., 2010
		Nitrobenzene	
		Sulfamethoxazole	
		Tetracylin	
		Tylocin	
	SWCNT	Sulfamethoxazole	Kim et al., 2014
		Tetracycline	
		Lincomycin	
	KOH activated SWCNT	Phenol	Ji et al., 2010
		Nitrobenzene	
		Sulfamethoxazol	
		Tetracyline	
		Tylosin	
	Graphite	Tetracycline	Ji et al., 2010
	Graphene Oxide	Levofloxacin	Moussavi et al., 2016
		Acetaminophen	
		Metformin	
Metal Organic Framework	Zeolitic imidazole framework–magnetic graphene oxide	Benzotriazole	Lin and Lee, 2016
	Chromium(III) tere-phthalat– MIL 101	Dimetridazole	Song and Jhung, 2017
		Metronidazole	
		Triclosan	
		Bisphenol A	
		Naproxin	
		Ketoprofen	
	Zeolitic imidazolate framework–8	1H–benzotriazole	Jiang et al., 2013
		5-tolyltriazole	Jiang et al., 2013
	Metal organic frame-work–porous carbon	Ibuprofen	Bhadra et al., 2017
		Diclophenac Sodium	
	Silver nanoparticle-modified MWCNT	Sulfamethoxazole	Song et al., 2016

(*continued*)

Table 1.7 Various emerging contaminants and their removal by different nanoadsorbents. *Continued*

Nanomaterials Type	Nanomaterials	Pollutants	References
	Mesoporous SBA-15	Carbamazepine Diclofenac Ibuprofen Ketoprofen	Bui and Choi, 2009
	Polyvinyl pyrrolidone –Fe_3O_4	Triclosan Ketoprofen Bisphenol A Estriol Ciprofloxacin	Fard and Barkdoll, 2018 Yan et al., 2017

Carbon-based nanomaterials which work as nanoadsorbents have strong affinity towards polar organic compounds. In this adsorption mechanism the adsorbates have a diverse interaction with adsorbents, which include hydrophobic effect, π-π interactions, hydrogen bonding, covalent bonding, and electrostatic interactions (Ersan et al., 2017).

1.13 The π-π interaction

The π–π interaction between compounds that accept π electrons and the π electron-rich regions of the grapheme surface of CNTs and graphite was observed during triclosan adsorption (Ji et al., 2010; Liu et al., 2016). Chen et al. (2008), reported a similar mechanism for the adsorption of sulfamethoxazole, tetracycline, and tyrosine by KOH activated CNTs. The π–π interaction is very dominant for the adsorption of chemical containing benzene rings on carbonaceous nanomaterials (Chen et al., 2008). Triclosan contains two aromatic rings that are favored for π–π interaction with the graphene structure on the CNT surface. In comparison, ibuprofen (IBP) contains only one aromatic ring in its molecular structure, resulting in weaker π–π interaction with the CNTs (Wang et al., 2015).

1.14 Electrostatic interaction

If the pH of the solution is different from that of the nanoadsorbents, the surface of the nanoadsorbents will carry either positive or negative charge. At the same time, ionizable emerging contaminants can also be protonated or deprotonated and become charged at different pH. Wang et al. (2015), described that the resulting electrostatic interactions between triclosan and IBP by CNTs may influence the removal of them in water. Due to the presence of oxygenated functional groups on PPCPs and CNTs,

the solution pH affects the protonation/deprotonation of these functional groups and alters the electrostatic interactions (Cho et al., 2011).

1.15 Hydrophobic interaction

Hydrophobic interaction is another mechanism for carbon materials to adsorb hydrophobic organic compounds (Nam et al., 2014; Pyrzynska et al., 2007). When the net charge on carbon nanoadsorbents is zero and the emerging contaminants present in the water are in molecular state then the hydrophobic interaction is largest and the adsorption capability is strongest (Lu et al., 2006). Yu et al., (2015) studied that hydrophobic interaction is the main reason behind the pH dependent adsorption of sulfonamides.

1.16 Hydrogen bonding

Hydrogen bonds can also be formed between the benzene ring on the surface of CNTs as the electron donor and organic compounds containing oxygen-containing functional groups (Pan and Xing, 2008). Sun et al. (2017), studied that hydrogen bonding plays the key role behind adsorption of 17β-estradiol (E2) and 17α-ethinylestradiol (EE2) on GO due to the high content of –OH groups on the GO surface.

1.17 Factors affecting adsorption process

1.17.1 pH

The pH of the solution strongly affects the adsorption process. It controls the surface charge of the adsorbents and also affects the protonation or deprotonation of the emerging contaminants based on their pKa. Increasing pH enhances dissociation of hydrophobic adsorbates into hydrophilic and negatively charged species, thus affecting the hydrophobic and electrostatic interactions between the adsorbent and adsorbate. Further, a higher pH can increase the π donating ability of the adsorbate, thus enhancing the π-π electron donor-acceptor interaction (Liu et al., 2014). Depending on the pH, PPCPs will be protonated or deprotonated, resulting in their electrostatic interaction with the CNTs (Nam et al., 2014).

1.17.2 Ionic strength

Increasing ionic strength also increases the adsorption process, when there is electrostatic repulsion between the adsorbent and adsorbate. Also, a high ionic strength can have a strong "salting-out" effect on hydrophobic compounds, increasing the tendency of organic molecules to precipitate from the aqueous solution and adsorb to the nanoadsorbent (Grover and Ryall, 2005).

1.17.3 Dissolved organic matter

The adsorption of sulfamethoxazole, thiamphenicol, and IBP was decreased with the increase of organic matter in the solution (Zhao et al., 2016). When the amount of dissolved humic acid was increased (up to 40 mg/L), the adsorption coefficients of the two sulfonamides decreased by 0.5–0.8 mg/kg, mainly due to direct competition for the adsorbent surface (Ji et al., 2009).

1.18 Conclusions

In case of removing emerging contaminant, there are several different techniques to treat the wastewater. But the adsorption is the most efficient, vital, and extensively used technique. The adsorption process can remove emerging contaminants without producing any harmful byproducts or toxic intermediates. Thus, adsorption process has a wider applications in treatment of wastewater. Nowadays nanoadsorbents are being introduced in the adsorption process. The unique properties of nanoadsorbents enhance its applications in this field making it a better tool for adsorption than other older adsorbents. Thus, nanoadsorbents are considered next generation adsorbents offering wide spectrum of applications and performing excellently in environmental remediation and pollution control owing to their unique properties like high surface area, stability, and antimicrobial effect. Future novel studies can focus on improvement of nanoadsorbent properties like chemical stabilization and improve surface adaptations as to improve its efficacy in wastewater treatment and to find out the disadvantages of nanoadsorbents to further overcome their shortcoming.

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CHAPTER

2

Treatment aspect of an emerging pollutant from Pharmaceutical industries using advanced oxidation process: past, current, and future trends

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2.1 Introduction

Quality water demand for drinking, sanitation, irrigation, and industrial use has been on continuous rise globally and there has been growing concern about treatment and reuse of water requiring the strictest standards. Water quality assessment mainly focused on investigation of heavy metal, priority pollutant, and microbial pollutant. Nowadays, presences of refractory organic pollutant in the range of ng/L to μg/L attracted attention of researcher due to their adverse effect on aquatic life even in such lower concentration (Pal et al., 2014). However, there are several emerging micropollutants that have not yet been regulated. In recent years, pharmaceutical compounds (PhCs) have provoked increasing concern, particularly as no legal requirements have been set for discharge into surface water bodies of these ubiquitous, persistent, and biologically active substances (Furhacker et al., 2008). Recent investigations document that PhC production and administration may vary both between countries and over time fluctuating not only on an annual basis, but also from one year to the next (Goossens et al., 2007). These unregulated chemical compounds commonly present in water bodies are now recognized as emerging contaminants (ECs). Classification of ECs include pharmaceutical, personal care products (PPCPs), pesticides, hormones, and having known or suspected undesirable effect on human as well as ecosystem. These group of compounds also responsible for disruption in endocrinal system of wildlife, therefore these groups are also known as endocrine disrupting compounds (EDCs) group. Due to the chemical composition and structure of Pharmaceuticals and PCPs can be easily dissolved in water and transported through the water cycle with high potential as a threat to aquatic organisms and humans. Indeed,

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several PhCs have been found in river biota, some at high levels (Rimkus et al., 1999), thereby evidencing the risk that environmental concentrations of PhCs can be higher than their predicted no effect concentrations (PNECs) (Santos et al., 2009), especially in effluent-dominant rivers whose dilution capacity and self-purifying processes are insufficient to temper the risk to aquatic life. International Conference on Chemicals Management (ICCM) 2015 prove that environment requires protection from pharmaceutical contaminants (Sharma et al.,2018) .General composition of wastewater released from Pharmaceutical industries varies as pH (3.9–9.2), BOD_5 (200–6000 mg/L), COD (375–32500 mg/L), BOD_5/COD ratio (0.1–0.6), TDS (675–9320 mg/L), TOC (860–4940 mg/L), TKN (165–770), NH_3-N (148–363), Cl^-(760–4200 mg/L) and $SO_4{}^{2-}$(890–1500 mg/L).

Intrinsic biological activity of pharmaceutically active compound (API) which leads to the fatal consequences are the emerging concern in recent years. Half of the pharmaceutical industries discard their wastewater without any specific treatment. The major pathway of pharmaceutical compound in the aquatic ecosystem through disposal of pharmaceutical industries, municipal and domestic influent, and human via faces or urine. Presence of these chemically active compound causes adverse effect on aquatic life such as development of antibiotic resistant microbes, retardation of nitrite oxidation, and methanogenesis. Most of the research found that presence of these potential toxic compound cause feminization in fishes and alligators, behavior and migratory pattern of salmon, and extinction of vulture in India. Thus, treatment through conventional process are not capable to remove these micropollutant from surface water, drinking water and wastewater and cause alteration in aquatic food web and human life due to their bioaccumulation behavior. Conventional treatments generate sludge, salts, syrups which require post treatment process which can increase capital cost, manpower, and dangerous, even though biological treatment are not enough for removal of recalcitrant aromatic containing compounds. The issue needs to be viewed in context of reusability of water with ECs, which is not only depend upon the availability of water but also its appropriate treatment. Although, in-depth investigation by scientific community for the treatment of ECs have been undertaken.

In fact, most WWTPs are designed to comply with generic pollutant thresholds, but they are not efficient at eliminating organic compounds at low concentrations ranging from ng/L to mg/ L (Verlicchi et al., 2012). More effective and specific advanced wastewater treatment is required to increase the elimination of PhACs from WWTPs (Rivera-Utrilla et al., 2013). Among all the technologies, group of advanced oxidation process (AOPs) are being used to oxidize recalcitrant organic pollutant in order to clean water for human consumption such as for drinking and other household use (Litter et al.,2005).AOPs was defined as in situ generation of powerful transitory species mainly hydroxyl radical (°OH), which oxidize organic contaminants to the permissible limit. AOPs can mineralize organic pollutant to carbon dioxide and water without any secondary sludge formation. From 1980s AOPs known for drinking water treatment technologies but later studies found it as useful technology for treatment of wastewater as well. Concentration of ECs before and after the treatment

process is the best way to estimate the removal efficiency of treatment technologies. Removal efficiency were taken directly form literature without any modification for briefing the efficiency of different technologies.

2.2 Treatment technologies

Wide array of treatment and disposal method of pharmaceutical wastewater has been employed by pharmaceutical industries, which is not only dependent on composition but also on quantity. Some of the treatment techniques for PCPs and pharmaceutical waste water are: i) recovery of APIs or drug present in wastewater, (ii) physical–chemical treatment by sedimentation or floatation, (iii) aerobic/anaerobic biological treatment in membrane bioreactors or bio aeration, (iv) inactivation of active substances by UV oxidation in conjunction with O_3 or H_2O_2, (v) sterilization and decontamination of infectious and bioactive substances from biotechnology, and (vi) new hybrid technologies specific to the pharmaceutical industry. Over time, nonconventional water treatment technologies have evolved as a result of the emergence of new techniques. These treatments can be widely divided into three major group such as phase changing treatment, biological treatment, and AOPs shows in Fig. 2.1. Among these treatment AOPs involved generation of hydroxyl radicals in enough quantity to treat PCPs and pharmaceutical waste with several advantages over conventional treatment technologies. Transformation of complex organic compound into simpler compound or mineralization into CO_2 or H_2O with no sludge production would be the major advantage of AOPs. AOPs proved as useful treatment technology for the treatment of refractory pollutant which is resistant to other conventional treatment technologies (Mota et al., 2009). In 1980s AOPs were first used for drinking water treatment and later well known for treatment of organic load (even in very low concentration) as well as dissolved organic compound which is difficult to remove from

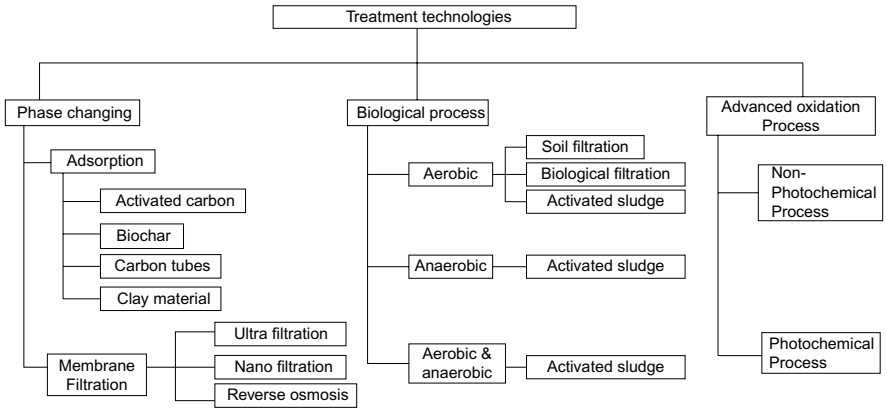

FIG. 2.1 Different treatment technology for ECs removal.

wastewater (Z.A. et al., 2012).High electrical energy consumption when UV light was applied, and high cost are the two main disadvantage of AOPs. For treatment of some recalcitrant pollutant AOPs can be used as pretreatment as well as posttreatment technology. AOPs has been employed a wide array of in situ generation of reactive oxygen species (ROS) via various process such as Fenton process, photolysis and ozonation etc. This ROS play important role in degradation of different type of PCPs and pharmaceutical compound from wastewater.

2.2.1 Recovery process

Pretreatment and recovery of PCPs, APIs, and pharmaceutical would be the best way to control the pharmaceutical waste from their source. Recovery of pharmaceutical is useful in reduction of waste disposal cost and operational cost. Recovered water could be reusable for various purposes which leads to improving the economic cost. Membrane filtration can be useful for recovery of pharmaceuticals and PCPs which are having molecular weight higher than 250 Da.Reverse osmosis, nanofiltration, and ultrafiltration can be very effective for recovery process based on economic benefit. Nanofiltration can be most developed and useful method for recovery of more than 80% of complex compound from wastewater. Ultrafiltration is also being used for recovery of organic compounds from fermentation waste.

2.2.2 Phase changing technologies

2.2.2.1 Adsorption

Adsorption is the best technology which have been used extensively for changing the phase of contaminants from one (liquid) to another(solid) in the removal of PCPs, Pharmaceutical and other ECs. Activated carbon, biochar, clay minerals, etc. are the most frequently used adsorbent for adsorption technologies. Physical property of AC such as high porosity, high adsorptive capacity, and specific surface area make it more effective in removing the range of contaminates from water (Yao et al., 2012). Removal efficiency of AC used as an adsorbent was found to be more than 90% which confirm that it will selectively use as an adsorbent for removal of PCPs, pharmaceutical, and other ECs. AC can be made from wood, coconut shell, sugar beet, pulp and peanut nulls, and most interestingly it can originate from waste also with different removal efficiency for PCPs and other different ECs. Charcoal-based material commonly known as biochar also used as an adsorbent. Through pyrolysis process biochar has been made by heating the biomass at high temperature in the absence of oxygen. Adsorption capacity and treating efficiency of biochar are highly dependent on its pyrolytic condition for the removal of PCPs, pharmaceutical, and other ECs via adsorption. Treatment efficiency of biochar is highly dependent on sources and production procedure in relation to ECs removal such as removal efficiency of biochar for sulfamethoxazole were in range of 12% for two types of wood as feedstock whereas its removal efficiency increases up to 21% when sugarcane used as feedstock (Esplagus et al., 2007). Clay minerals were also used as an

efficient adsorbent for the removal of PCPs, pharmaceutical and other ECs. Characteristic of adsorbent material, specific amount of nitrogen, iron, and minerals can be better dictating the removal efficiency of PCPs, pharmaceutical, and other ECs. Treatment performance of clay material used as an adsorbent for removal of ECs were dependent on the source of the clay. Pillared clay used as semiconductor for degradation of contaminants have been received considerable attention by enhancing the active surface area which can be use in AOPs. But treatment of PCPs and other ECs was not confirmed yet whether degradation of contaminants taking place first or adsorption process occurred first. Several other adsorbent materials such as zeolites, mesoporous, and microporous material were also used for adsorption of PCPs, pharmaceutical, and other ECs. It is evident that selection of adsorbent is the most important characteristic when choosing adsorption as removal process because it determines pore size, and ability to couple with a second treatment system. However, adsorption process and these materials used as an adsorbent have some application limitation for PCPs, Pharmaceutical and other ECs removal. A disadvantage of adsorption process is related to phase changing of contaminants, unable to degrade or mineralize the contaminants, feasibility of upscaling of process from laboratory to field, adsorption-based system can be used coupled with second treatment, high electrical consumption for thermal activation of biochar. The key knowledge gap is related to sustainable production of biochar, reusability of AC and use of clay prove to be unsustainable for long-term. This is an important area for further research.

2.2.2.2 Membrane technology

Nowadays membrane process is considered as promising technology for removal of PCPs, organic pollutant and other ECs by changing the phase of contaminants. Removal of suspended solid and high molecular weight without increasing disinfection byproducts are based on the use of hydrostatic pressure in membrane process so it is well known as low-pressure membrane technology whereas water and low molecular weight solutes allow to pass through it with the rules promulgated in response to the 1986 Surface Water Treatment Rule Amendments. There are different types of membrane filtration such as ultrafiltration (UF)-0.001-0.1μm, nanofiltration (NF)-10-100 Å, microfiltration (MF)-< 1μm, forward osmosis (FO), and reverse osmosis (RO)-< 10 Å or colloidal particles based on pore size. Due to the operating condition microfiltration (MF) can be used widely but it cannot remove contaminates with pore size smaller than 1 μm. Ultrafiltration (UF) shows higher removal efficiency than MF and can be used for significant removal of PCPs, pharmaceutical, and organics. Whereas removal efficiency of nanofiltration (NF) is better than UF and material of membrane influences the removal efficiency for treatment of PCPs and organics. Semipermeable membrane has been used in reverse osmosis (RO) and forward osmosis (FO) for separation of eater from dissolved solutes. During FO, movement of water through semipermeable membrane has been induced by gradient pressure working on high concentration solution. In case of RO hydraulic pressure is used for separation of colloidal particle from water.

This phase changing technology produces two effluent stream one is diluted, and another is concentrated phase and it will change the place of contaminants only. However, final disposal of treated water is the biggest challenge because it remains in the environment. As per the previous studies performance evaluation of phase changing process is dependent on type and source of material. There is very limited understanding of the basic principle of phase changing technology create significant knowledge gap and further research area.

2.2.3 Biological process

Meanwhile, increasing evidence showed that the biological treatment processes that widely applied in both urban wastewater treatment plants and Pharmaceutical wastewater treatment plant might have contributed to the proliferation of ECs in the process of wastewater treatment (Fatta-Kassinos et al., 2011; Manaia et al., 2016). There are different biological processes available which is widely used for removal of ECs from pharmaceutical wastewater. Depending on the type of contaminants aerobic or anaerobic processes of biological treatment can be applied or sequentially coupled with other tertiary system. The effectiveness of applying aerobic and anaerobic conditions related to the prevailing conditions of electron acceptance at the terminal. This also identify the presence of electron-acceptors in environment which play important role in biodegradation process. Biological treatment can be applicable for easily biodegradable PCPs whereas low biodegradable compound cannot eliminate at all. Applicability of biological process for the removal of PCPs is not efficient due to the lack of accurate analytical methodologies which is able to identify and quantify the complexity of these compounds.

But most of the PCPs having biological activity whereas toxicity of some of the antibiotics can cause adverse effect on microorganisms which play crucial role in conventional biological process. However, bio electrochemical systems (BES) emerging as an alternative of biological treatment process. Generation of in-situ energy occur in BES which reduces high energy consumption during conventional biological treatment. During BES oxidation of organic pollutant by bacteria takes place at anode simultaneously transfer of electron occur from microorganism and reduction of electron takes place at cathode by applying external electrical circuit. Activated sludge system technologies are not having efficient applicability due to the production of biosolids. When dealing with removal of pharmaceutical based ECs by conventional biological treatment lack of analytical methodologies for quantification, identification, isolation and extraction of transformed by-products from parent compound are the major concern. However, to date the comprehensive comparison of the fate of ECs in the wastewater treatment system that simultaneously using the conventional activated sludge treatment is still inadequate. Due to this, nowadays, membrane bioreactor (MBR) technology is a recommended alternative when remodeling the biological treatment of a WWTP is required. This technology, which relies on replacing the secondary settler in the CAS process with membrane filtration, is able to produce a high-quality effluent. In addition, MBRs can significantly improve

the removal of ECs with respect to the conventional activated sludge process, mainly due to the proliferation of more specific microorganisms promoted by a longer solid retention time (SRT) and the separation by membranes of CECs adsorbed in the sludge (Hamza et al., 2016).

2.3 Advanced oxidation process

Nowadays capability of AOPs for removal of recalcitrant pollutant in compared to conventional water treatment has grasped attention of researches. Types of AOPs and their mechanism for generation of reactive species given in Table 2.1. In this method complete oxidation of organic pollutant into CO_2 and H_2O takes place without formation of any by-products and secondary sludge. In case nitrogen, sulfur and chlorine present in targeted compound then formation of salts can occur through different treatment of AOPs. In-situ generation of hydroxyl radicals (OH°) with 2.8eV oxidation potential is the main characteristics of AOPs, which changes the level of organic contaminants into permissible limit in water for human consumption. Treatment of antibiotics, herbicides, insecticides, endocrine disrupting chemicals (EDCs), effluent organic matters, etc. have been done by AOPs. Fig. 2.2 shows the classification of AOPs into two main categories for the removal of PCPs, organic pollutant and some of other ECs.

2.3.1 *Nonphotochemical methods*

In monphotochemical method generation of hydroxyl radical (OH°) takes place in the absence of light.

2.3.1.1 Ozonation

Ozone-based AOPs commonly used for disinfection of PCPs loaded drinking water as well as wastewater. Due to the high oxidation potential of O_3 ($E_0 = 2.07$ V) it is widely being used in transformation of PCPs into smaller compound, CO_2 and H_2O. In-situ generation of O_3 take place by electrical discharge in the stream of oxygen (O_2) or air, without any odors and taste. Oxidation of complex PCPs through O_3 is highly pH dependent. Alkaline condition is more favorable for decomposition of PCPs and half-life of O_3 is 1 min.at pH 10.

In acidic condition, direct reaction of O_3 with PCPs is prohibited by the effect of proton (H^+) which itself reacts with O_3 to form O_2 and H_2O as shown in equation below:

$$O_3 + 2H^+ + 2e^- \rightarrow O_2 + H_2O \tag{2.1}$$

Ozone mediated oxidation of PCPs is initiated by hydroxyl ion (OH^-) which leads to the formation of hydroxyl radicals (OH°) through series of reaction. This OH° is well known short-lived oxidizing agent. Some other oxidizing agents such as ozonide anion radical ($O_3^{\circ-}$), superoxide anion radical ($O_2^{\circ-}$), and hydroperoxyl radical (HO_2°) were produced during O_3 mediated oxidation process.

Table 2.1 The different types of AOPs having different route of radical formation for removal of ECs from water.

S. No.	Types of AOPs	Oxidant	Mechanism of reaction	Efficiency	Ref.
Non-Photochemical Methods					
1.	Ozone (O_3)	OH°	Direct oxidation.	80-90%	A.Y.C. et al.,2012
2.	$H_2O_2 + O_3$	OH°	Direct oxidation.	96-98%	Rosal et al.,2008
3.	Catalyst + O_3	OH°	Direct oxidation.	40-50%	Borghi et al.,2015
4.	Fenton system	OH°/ Fe^{2+}	Iron coagulation Iron sludge -induced adsorption.	100 %	Y.Ji.et al 2016
5.	Heat/persulfate	SO_4^-	Persulfate oxidation.	75-80%	X. Gu et.al.,2013
6.	Fe (II)/persulfate	SO_4^-/ Fe^{2+}	Iron coagulation.	95-97%	F.S.Souza et al.,2015
7.	OH^-/Persulfate	OH°/ SO_4^-	Persulfate oxidation.	70-75%	A.Dulov et al.,2013
Photochemical methods					
1.	UV + O_3	OH°	UV photolysis.	95-97 %	F. Méndez-Arriaga et al.,2011
2.	UV + H_2O_2	OH°	UV photolysis.	90-95%	S.Sarkar et al., 2014
3.	UV + H_2O_2 + O_3	OH°	UV photolysis, direct oxidation, and H_2O_2 oxidation.	90-99%	I. Carra et al., 2015
4.	Photolysis	Light	UV photolysis	80-90%	N. Miranda-García et al., 2010
5.	UV/persulfate	SO_4^-	Persulfate oxidation, UV photolysis	70-80%	Pignatello et al., 2006
6.	Photo/Fenton	Fe^{2+}/ OH°	Iron coagulation, UV photolysis & iron sludge-induced adsorption.	70-90 %	Belgiorno et al.,2007
7.	UV/catalyst	OH°	UV Photolysis & direct oxidation.	85-90%	Herrmann et al.,1999

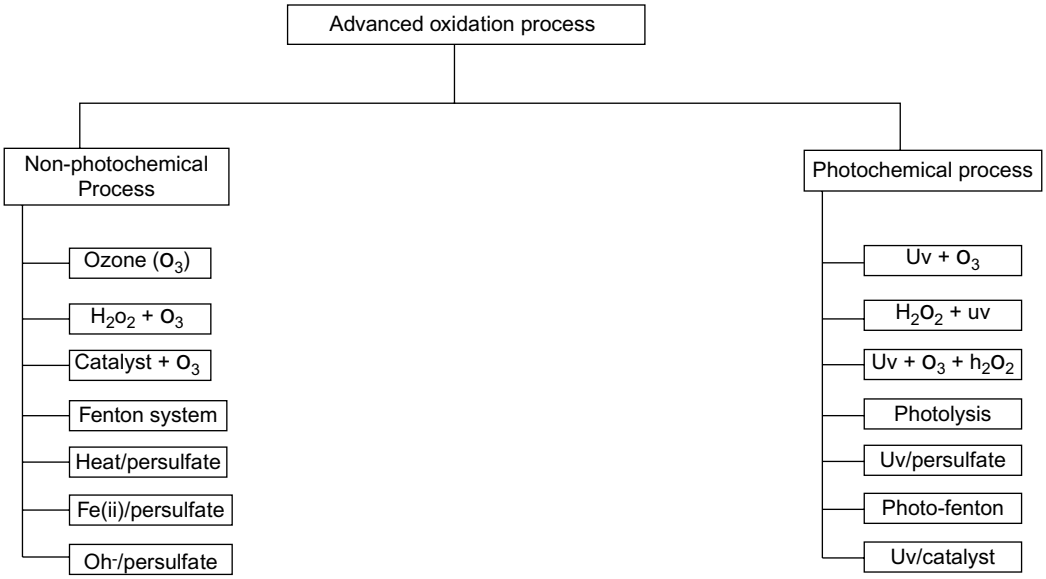

FIG. 2.2 Different types of advanced oxidation process for ECs removal.

In alkaline condition this hydroxyl ion (OH^-) can directly react with O_3 to generate hydroxyl radicals (OH°) as described below:

$$O_3 + OH^- \rightarrow O_3^{\bullet -} + HO^\bullet \tag{2.2}$$

$$O_3^{\bullet -} \rightarrow O^{\bullet -} + O_2 \tag{2.3}$$

$$O^{\bullet -} + H^+ \rightarrow OH^\bullet \tag{2.4}$$

Whereas some other less reactive radicals (HO_2°) generated by direction reaction between $OH^\bullet$& O_3 and this HO_2° itself reacts with O_3 for further production of $OH^\bullet$ given in equation below:

$$O_3 + HO^\bullet \rightarrow O_2 + HO^\bullet_2 \tag{2.5}$$

$$O_3 + HO_2^\bullet \rightarrow 2O_2 + HO^\bullet \tag{2.6}$$

Therefore, treatment efficiency of ozone mediated AOPs increases with increase in the amount of $HO^\bullet$generation in alkaline condition. The well-known$HO^\bullet$radical scavengers such as carbonate and bicarbonate present in the natural water bodies can suppress the chain reaction. Passive carbonate and bicarbonate would terminate the chain reaction as they do not react with $O_3$and PCPs. Capability of ozone based AOPs for the removal of ECs is 90% from water, so it is widely used for treatment of drinking water and wastewater.

2.3.1.2 Ozone and hydrogen peroxide (Peroxone)

H_2O_2 is having high oxidant potential ($E^0 = 1.77$ V) and its conjugate base known as perhydroxyl ions (HO_2^-) is formed through a series of reaction which directly reacts with O_3 resulting in the generation of OH°radical.Thus,O_3 induces indirect oxidation through electrophilic mechanisms in which O_3 attack on particular functional group of organic pollutants and PCPs. Successful utilization of combination of peroxide for removal of PCPs shows rapid generation of OH° radical than hydroxyl ion through decomposition of O_3 in the presence of conjugate base of H_2O_2 even at very low concentration. Formation of perhydroxyl ions (HO_2^-) takes place in alkaline condition as described in equation given below:

$$H_2O_2 \rightarrow HO_2^- + H^+ \tag{2.7}$$

$$HO_2^- + O_3 \rightarrow HO_2^{\bullet} + O_3^{\bullet -} \tag{2.8}$$

$$2O_3 + H_2O_2 \rightarrow 2OH + O_3^{\bullet -} \tag{2.9}$$

In acidic condition, oxidation of PCPs decreases by termination of series of reaction which do not lead to the formation of OH° radical. Treatment efficiency of AOPs increases by combining of ozone with hydrogen peroxide together and this combination process enhanced the COD removal.

2.3.2 Catalytic ozonation

Addition of catalyst in the medium where ozone is present has been employed to increase the generation of OH° radical and efficiency of treatment. This type of AOPs is known as catalytic ozonation. There are two types of catalytic ozonation: a) Heterogeneous and b) Homogeneous catalytic ozonation.

a) *Heterogeneous catalytic ozonation*: Mostly metal oxide such as iron oxides, titanium oxide, alumina and their combination used as catalyst for the treatment of PCPs based on their catalytic properties, surface area, pore size, pore volume, density and porosity. In this type of catalyst mediated ozonation, adsorption of ozone followed by decomposition and transfer electron from catalyst to O_3 occur which lead to formation of $O_3^{\bullet -}$& subsequently release of OH° radical (Pines et al., 2002).

b) *Homogeneous catalytic ozonation:* In this method generation of OH° radical takes place through series of reaction catalysed by transition metal ions for decomposition of PCPs. Oxidation of PCPs and other ECs through homogeneous catalytic ozonation occur in two ways: one transition metal ions decompose O_3 to generate $O_2^{\bullet -}$ which can cause inter-transfer an electron with O3 to form $O_3^{\bullet -}$, this series of reaction subsequently leads to the generation of OH° radical for oxidation process; another is complex formation between metal ions and PCPs which further reacts with O_3 to oxidise PCPs and other ECs (Tsitonaki et al., 2010).

2.3.3 Fenton system

This is one of the prominent AOPs process where ferrous ion (Fe^{3+}) and Ferric ion (Fe^{2+}) are used as activating agent of H_2O_2 to produced OH° radicals in acidic condition for decomposition of organic pollutant, PCPs and other ECs so it is well known as Fenton process. Since iron is known as abundant element on earth and can be easily available for heterogeneous catalytic reaction in which iron is used as catalyst. Generation OH° radical through Fenton mechanism involves several reactions given below:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{\bullet} + OH^{-} \tag{2.10}$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\bullet} + H^{+} \tag{2.11}$$

$$OH^{\bullet} + H_2O_2 \rightarrow HO^{\bullet}_2 + H_2O \tag{2.12}$$

$$OH^{\bullet} + Fe^{2+} \rightarrow Fe^{3+} + OH^{-} \tag{2.13}$$

$$Fe^{3+} + HO^{\bullet}_2 \rightarrow Fe^{2+} + O_2H^{+} \tag{2.14}$$

$$Fe^{2+} + HO^{\bullet}_2 + H^{+} \rightarrow Fe^{3+} + H_2O_2 \tag{2.15}$$

$$2HO_2^{\bullet} \rightarrow H_2O_2 + O_2 \tag{2.16}$$

Formation of OH° radicals occur through electron transfer as shows in Eq. (2.10). Excess of Fenton reagent can act as scavenger, so it is necessary to maintain the optimal molar ratio of $Fe^{2+}$and H_2O_2 for decomposition of PCPs and organic pollutant as represented in Eq. (2.11) and (2.12).Due to the pH dependency and high iron sludge production, Fenton process can be best applied as a pretreatment technology to convert the non-biodegradable organic pollutant and PCPs into biodegradable. Major advantage of Fenton system is easy to handle and working condition can be adjustable accordingly. Since previous studies showed that Fenton oxidation of PCPs based on homogeneous reaction system. Working pH of Fenton system which is quite low to avoid the precipitation of iron oxyhydroxide and recovery of dissolved ions in treated water are the two major drawback of Fenton oxidation process.

2.3.3.1 Sulfate-based AOPs

Sulfate-based AOPs can be better alternative of classical AOPs due to their treatment efficiency for oxidation of PCPs and other organic pollutant. During this process sulfate radicals are generated and used as an oxidizing agent instead of OH° radicals. Sulfate radicals are having high oxidation potential of (E^0 = 2.6 V) and longer half-life than OH° radicals based on reaction mechanism. In $SO^{\bullet-}_4$ mediated AOPs transfer of electron occur whereas in OH° radicals mediated AOPs abstraction of hydrogen atom occur which is less dominating. There are two types of sulfate mediated AOPs: persulfate and peroxymonosulfate process in which persulfate ($S_2O^{2-}_8$) is most frequently being used for oxidation of PCPs and organic pollutants due to their strong oxidizing potential (E^0 = 2.01 V),high solubility and long life time. Oxidation of PCPs and other organic pollutant takes place through electron transfer, addition, and hydrogen atom transfer mechanism. Persulfate have been classified based on

their activation: heat/persulfate; catalyst/persulfate and UV/persulfate. Activation of persulfate ($S_2O^{2-}{}_8$) through heat; UV and catalyst are given below:

$$S_2O^{2-}{}_8 \xrightarrow{\Delta/UV} 2SO^{\bullet-}{}_4 \tag{2.17}$$

$$S_2O^{2-}{}_8 + Mn^{n+} \rightarrow SO^{\bullet-}{}_4 + SO^{2-}{}_4 + M^{n+1} \tag{2.18}$$

In heat/persulfate process activation of persulfate occur within the rage of 30-130 °C of temperature and pH also play important role in persulfate mediated AOPs. Previous studies show that basic condition would be more favorable for oxidation of PCPs through persulfate based AOPs (Mishra et al., 2017). In alkaline condition, OH° radicals reacts to generate sulfate radicals:

$$SO^{\bullet-}{}_4 + H_2O \rightarrow OH^{\bullet} + SO^{2-}{}_4 + H^+ \tag{2.19}$$

$$SO^{\bullet-}{}_4 + OH^- \rightarrow OH^{\bullet} + SO^{2-}{}_4 \tag{2.20}$$

Whereas in catalyst mediated sulfate radical process, ferrous ion (Fe^{2+}) and ferric ion (Fe^{3+}) are most frequently used as catalyst for activation of sulfate radical.

2.3.4 Photochemical methods

Generation of OH° radicals initiated in the presence of light for oxidation of PCPs during photochemical method.

2.3.4.1 O_3 + UV Method

Combination of O_3 and UV is well known AOPs for the treatment of organic pollutant, PCPs and pharmaceutical pollutant. This treatment technology is more efficient than individual UV and O_3 technologies. Generation of OH° radicals increases using UV light in combination of O_3 this will leads to increase in oxidation of PCPs from water. O_3 is having high molar coefficient (3300 $M^{-1}cm^{-1}$) which results in quick absorption of UV light this would help in high productivity of OH° radicals. Mechanism of generation of OH° radicals from H_2O_2 through reaction between UV-light and O_3 are given in Eqs. (2.21) and (2.22):

$$O_3 + H_2O + h\nu \rightarrow H_2O_2 + O_2 \tag{2.21}$$

$$H_2O_2 + h\nu \rightarrow 2OH^{\bullet} \tag{2.22}$$

High concentration of O_3 are radical scavenger and quench the oxidation mechanism. Therefore, molar ratio of O_3 added in the aqueous medium with respect to pollutant should maintained. High UV light absorption capacity of phenolic compound such as phenol,xylenols, 5-methylresorcinol, etc. can increased the oxidation process by O_3 but complete conversion of these compounds into CO_2 and H_2O are not achieved. Whereas oxidation of some organic pollutant like oxalic acid, glyoxal, glyoxylic acid, and formic acid by O_3 to CO_2 and H_2O can be easily achieved. Various studies found that combination of O_3 and UV is efficient in reduction of TOC and COD besides its pollutant degradation capacity. Factors that affects the efficiency of

O_3 and UV AOPs are pH, initial pollutant concentration, turbidity of the solution, amount of O_3 dose, amount of UV dose, types of UV lamps used for the process, reaction time, and scavengers present in the water.

2.3.4.2 H_2O_2 +UV light Method

In this method exposure of UV light results in homolytic cleavage in peroxide linkage to generate OH° radicals. Treatment efficiency of H_2O_2 in combination with UV is highly dependent on absorption of UV light and molar extinction coefficient of peroxide (19.6 $M^{-1}cm^{-1}$) which is quite less as compare to PCPs present in aqueous medium. Quantum yield of H_2O_2 in combination with UV is high. Series of reaction involve in generation of OH° radicals are described as:

$$H_2O_2 + h\nu \rightarrow 2OH^{\bullet} \tag{2.23}$$

$$H_2O_2 + OH^{\bullet} + h\nu \rightarrow H_2O + HO_2 \tag{2.24}$$

$$H_2O_2 + OH_2 + h\nu \rightarrow H_2O + O_2 + OH \tag{2.25}$$

High concentration of H_2O_2can act as scavenger which react with OH° to form less reactive $HO°_2$ radical and decreased the degradation process of PCPs. Whereas in high pH of the solution presence of carbonate and bicarbonate ions can act as scavenger when react with OH° radical. Thus, operating condition should be maintained in such a way that enhance the formation of OH° radical and efficiency of oxidation process.

2.3.4.3 H_2O_2 +UV+ O_3 Method

This combination emerged as new dimension in treatment technologies which oxidize PCPs, other organic and inorganic pollutants effectively than standalone process. Generation of OH° radicals and oxidation of ECs enhanced by the combination of peroxone with UV light. Transformation of H_2O_2 to OH° by UV light are described below:

$$O_3 + H_2O_2 + h\nu \rightarrow 3O_2 + 2OH^{\bullet} \tag{2.26}$$

Conjugate base of hydrogen peroxide even at millimolar concentration could initiate the decomposition of ozone into hydroxyl radicals more quickly than hydroxide ion and this would enhance the reduction of COD. Basic pH of the solution favors the oxidation of PCPs and other organic pollutant such as almost 100% of degradation efficiency has been achieved by several researchers for oxidation of Phenol which is the most common organic pollutant in basic pH.

2.3.4.4 Photolysis

In this UV-based AOPs, UV is used to kill the microbes and also known as tertiary treatment process for degradation of PCPs and various organic compound which can absorb UV light (Ternes et al.,2002). In this AOPs excitation of electron in pollutant from ground state to excited state from where the electrons are transferred to an oxygen molecule, which converts both O_2 and the pollutant molecule into a radical

has been carried out by absorption of photon. This highly reactive radical oxidizes other molecules to attain a stable state. UV light can also cause homolytic cleavage in chemical bond of pollutant which leads to the generation of two radicals. Breakdown of the chemical bond is highly dependent on the intensity of the UV light such as wavelength of UV less than 190 nm can be effective in breakdown of C-F bond whereas wavelength in the range of 210-230 nm can be very effective in breaking of C-Cl bond. Radicals can also cause oxidation-reduction reaction with other dissolved molecules whereas water molecules photolyzed by UV light of high energy and low wavelength (190nm) to form hydroxy radicals. Mercury lamp with different UV light intensities are the mostly used for the generation of UV radiation. There are three types lamp: i) low-pressure lamp, ii) medium pressure lamp, and iii) high-pressure lamp. Medium and high-pressure lamp are having wide range of wavelength which leads to deep penetration of UV light in the pollutant resulting in efficient degradation process with high intensity and less time. Whereas former lamp is monochromatic in nature with 253.7 nm wavelength. Lamp is the main component of the UV reactor system where mercury arc lamp is used as UV irradiation. Photolysis is ecofriendly because it does not require any chemical and no residual are left after treatment. Shorter treatment time is also an advantage of photolysis process. This process involves the induction of photochemical reaction through interaction between artificial or natural light and target compound such as organic pollutant, PCPs and other ECs. This will lead to direct degradation of target compound into intermediate compound and then further decomposition occur to obtain the end-products. To regulate the formation of byproduct disinfection of drinking water has been done by UV-treatment instead of chlorination. Treatment efficiency of photolysis increases when it takes place in the presence of some strong oxidant, photocatalyst, or O_3. The major disadvantage of photolysis is the limited formation of hydroxyl radical which leads to the partial degradation of pollutant and produces intermediate products instead of carbon dioxide and water. Photolysis lags the treatment of higher concentration total suspended solid and particulate matter. Photolysis process is expensive and require higher energy than other tertiary treatment process.

2.3.4.5 UV/persulfate

Previous studies show that highly reactive species such as OH° radicals and $SO^{\bullet-}_4$ produced by persulfate, UV can enhance the decomposition of PCPs, and generation of reactive species.

$$S_2O^{2-}_8 + h\nu \rightarrow 2SO^{\bullet-}_4 \tag{2.27}$$

In oxidation of PCPs and organic pollutants through sulfate based AOPs addition of OH° radicals to C=C bonds and abstraction of H-atom from C-H bond occur. Various transition metal and metal oxide has been used as a catalyst to activate persulfate to generate sulfate radicals in the presence of UV radiation. Zero valent iron is the most common transition meta used as a catalyst for the oxidation of organic pollutant and PCPs. Treatment efficiency of persulfate mediated AOPs found to be high at basic pH than acidic or neutral pH.

2.3.4.6 Photo-Fenton Method

Photo-Fenton method is known as combination of Fe^{2+}/Fe^{3+} and H_2O_2 in the presence of UV-light ($\lambda < 600$) for the removal of ECs from water. Presence of UV-light enhance the generation of OH° by photoreduction of Fe^{3+} to Fe^{2+}, which again reacts with H_2O_2 as shows in the equations below (Herrmann et al.,1999):

$$Fe^{+3} + H_2O + h\nu \rightarrow Fe^{+2} + H^+ + OH^{\bullet} \tag{2.28}$$

Oxidation rate of PCPs and organic compounds through photo Fenton system is accelerated as compared to the Fenton system. In photo Fenton process total iron consumption and sludge production decreased due to the high oxidation rate with respect to Fenton system. Conventional method is not effective in treatment of PCPs, Pharmaceutical, and other organic pollutant. Presence of inorganic ions, such as chloride, carbonate, bicarbonate, sulfate, etc. may alter the oxidation rate of PCPs and organic compounds. Previous studies show that photo Fenton system could be effective in treatment of PCPs, organic compounds, and pharmaceuticals under moderate condition of without pH adjustment. Even though effectiveness of photo Fenton system for the treatment of recalcitrant compound including PCPs, organic compound, and pharmaceutical has been proved by TOC removal within the range of 9–71% and COD conversion in the range of 37–91%.

2.3.4.7 Photocatalysis

The mechanism in which light and catalyst concurrently used to accelerate the chemical reaction. Photocatalyst classified into two categories i) Homogeneous photocatalysis in which higher oxidation state of metal ion complexes used to generate hydroxyl radical under photon and thermal condition, and ii) Heterogeneous photocatalysis in which semiconductor material used as photocatalyst to generate hydroxyl radicals. Photocatalysis is an emerging technology for the treatment of PCPs, Pharmaceutical and other organic pollutant in which heterogeneous semiconductor used as photocatalyst with some benefits such as ambient operating conditions and use of catalyst which are inexpensive, nontoxic, photochemically stable and commercially available in various particle size or crystalline form. In photocatalytic oxidation, generation of OH° radicals take place by UV light (300 nm < λ < 390 nm) on the surface of catalyst which act as an oxidant. Metal oxide which are RO type of semiconductors are used as catalyst in the oxidation process of PCPs, Pharmaceuticals and other ECs. In the photocatalytic process, illumination of aqueous suspension of catalyst through UV light greater than band gap of semiconductor used as catalyst leads to the excitation and movement of electrons or holes on the surface of catalyst shows in Fig. 2.3. Recombination of electrons and holes liberating heat or make their own way to the surface of photocatalyst where they can react with adsorbed species. This process produces h_{VB}^{+} which are able to react with water and hydroxide ion under alkaline condition to generate OH° radicals and $e^{-}CB$ react with adsorbed molecular oxygen reducing it to produce superoxide radicals anion which in turn react with proton to form OH° radical this leads to the oxidation of PCPs, Pharmaceuticals and other ECs to carbon dioxide and water due to their extremely oxidation potential

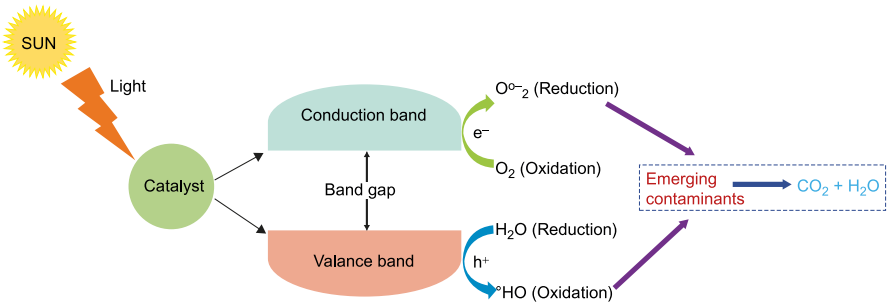

FIG. 2.3 Schematic representation of photocatalysis process.

(Verlicchi et al.,2012). Steps involved in oxidation mechanism of PCPs and organic compounds are given in the equations below:

$$\text{Catalyst} + h\nu \rightarrow e_{CB}^{-} + h_{VB}^{+} \tag{2.29}$$

$$e^{-} + O_2 \rightarrow O^{\bullet -}{}_2 \tag{2.30}$$

$$h^{+} + OH^{-} \rightarrow OH^{\bullet} \tag{2.31}$$

$$OH^{\bullet} + RH \rightarrow^{\bullet} RHOH \tag{2.30}$$

$$OH + RH \rightarrow R^{\bullet} + H_2O \tag{2.33}$$

$$h^{+} + RH \rightarrow^{\bullet} RH^{+} \tag{2.34}$$

$$H_2O + h^{+} \rightarrow OH^{\bullet} + H^{+} \tag{2.35}$$

Operating parameters such as catalyst concentration, wavelength or intensity of light and pH of the solution can affect the performance efficiency of photocatalyst.

$$R + h^{+} \rightarrow R^{+\bullet} \rightarrow \text{intermediate(s)/Final degradation products} \tag{2.36}$$

$$\text{Protonation of superoxide}: O^{-\bullet}{}_2 + OH^{\bullet} \rightarrow HOO^{\bullet} \tag{2.37}$$

$$\text{Co-scavenging of } e^{-}: HOO^{\bullet} + e^{-} \rightarrow HO_2^{-} \tag{2.38}$$

$$\text{Formation of } H_2O_2: HOO^{-} + H^{+} \rightarrow H_2O_2 \tag{2.39}$$

Eq. (2.36) & (2.37) shows protonation of $O^{-\bullet}{}_2$ radical to form the hydroperoxyl radical ($HO^{\bullet}{}_2$)and subsequently H_2O_2. Most important feasibility of application of Photocatalysis for the treatment of various PCPs and organic pollutant is complete mineralization of parents and their intermediate compounds without secondary pollution and low operating costs. Post separation of catalyst from treated water is the major obstacle for industrial implementation of photocatalytic system. This $HO^{\bullet}{}_2$ radicals are having scavenging property and can prolong the recombination time of holes in photocatalysis process (Mishra et al., 2017). However, occurrence of these facts in photocatalysis attributed to presence of water molecules and dissolved

oxygen (DO).Generation of $OH^{\bullet}$ is not possible in the absence of water molecules and impede photodegradation of PCPs and organics. Hydroxylation of aromatic compounds can be employed by the reactive $OH^{\bullet}$ radical that leads to successive oxidation/addition and eventually ring opening. The resulting intermediates, mostly aldehydes and carboxylic acids will be further carboxylate to produce innocuous carbon dioxide and water. The overall photocatalysis reaction shown in Eq. (2.39):

$$\text{Organic contaminant} + \text{photocatalyst/h}\nu \rightarrow \text{intermediate} \rightarrow CO_2 + H_2O \quad (2.40)$$

Mechanisms of photocatalysis involves five independent steps which are given below [28]:

1. Mass transfer of the organic contaminant(s) (e.g. A) in the liquid phase to the TiO2 surface. Adsorption of the organic contaminant(s) onto the photon activated TiO2 surface (i.e. surface activation by photon energy occurs simultaneously in this step).
2. Photocatalysis reaction for the adsorbed phase on the TiO2 surface (e.g. A/B).
3. Desorption of the intermediate(s) (e.g. B) from the TiO2 surface.
4. Mass transfer of the intermediate(s) (e.g. B) from the interface region to the bulk fluid.

2.3.4.8 Other AOPs

Some other AOPs are wet air oxidation (WAO), super critical wet oxidation process (SWOP) process and electron beam radiation**.** During wet oxidation process molecular oxygen or air has been used as oxidizer in high pressure and temperature environment which leads to the generation of free radicals that decomposes the waste. Thus, temperature and pressure are the controlling factor for WAO process. Most of the organic acids excluding acetic and propionic acid are converted to CO_2 at high temperature. Maintenance of the WAO system require huge operational expenditure and investment because it handles an extreme reaction environment. In SWO water changes its polarity and became a nonpolar solvent to get miscible with the organic part under supercritical condition such as extreme high temperature and pressurized. Under supercritical condition homogeneous mixture is formed by water and oxygen, which is perfect medium for organic degradation. Above critical point organic compound and oxygen dissolved in water and brought into intimate molecular contact in a single homogeneous phase. At sufficiently high temperatures the kinetics is fast, and the oxidation reaction proceeds rapidly to completion without any limitation of interface transport. This supercritical water oxidation (SCOW) is also known as hydrothermal oxidation (HTO). In hydrothermal oxidation process hydrogen peroxide used to oxidize the toxic effluents above the critical point of water. In the heterogeneous catalytic SCOW organic material required in solid phase. SCOW is most efficient method in case of environmental remediation because complete removal of oxidizable material and conversion of inorganic substances like ammonia or cyanides to CO_2, H_2O, and $N_2$was achieved by this process. Steps involved in SCOW process are: i) starting from pressurizing the reagent, ii) reaction, iii) salt separation, and iv)

depressurization. In SCOW waste water mixed with oxidant and fed in the reactor, this oxidant is normally heated before reaction which allows an exothermic reaction between the waste and oxidant. Heat produced in during exothermic reaction between waste and oxidant which leads to activate the reagent for further oxidation process. As a result, solubility of salt reduced and get precipitated in the SCOW reactor after treatment. Thus, SCOW requires high energy, which can be recovered by utilization of this hot stream for preheating or energy production. Several works that study the organic reactions in SCW, focusing on the influence of the properties of water and in the kinetics modelling, has been developed over the last few years. Electrochemical oxidation is also one of the efficient AOPs for degradation of PCPs and pharmaceuticals which is based on in situ generation of hydroxyl radicals (E° (•OH/H2O) = 2.8 V vs SHE). Various studies showed satisfactory removal of TOC and COD through Electrochemical oxidation. Efficiency of Electrochemical oxidation of Pharmaceuticals and PCPs are based on thickness of electrode, synergistic effect of dissolved iron and doping of electrode. Ultrasound is also one of the efficient treatment techniques for removal of organic pollutant, also known as sonochemical oxidation. Not much literature is available on sonochemical degradation of PCPs and Pharmaceuticals based on high intensity acoustic radiation at frequency (25kHz) results in cavitation. This cavitation concentrates the diffused energy of ultrasound and leads to production of radicals for further oxidation-reduction reaction. Use of this technique can be best for two-phase treatment of less soluble organic compounds.

2.4 Future prospects

The major health concern is the presence of PCPs and organics as an Emerging contaminant in aquatic ecosystem which can cause long term effect on aquatic ecosystem even though in trace amount. Major issue related to the treatment of PCPs from drinking water as well as wastewater. Phase changing or conventional treatment technology are likely not the best approach for the removal of PCPs from wastewater and drinking water. Photocatalysis mediated AOPs has gained more attention as effective technology for treatment of trace number of PCPs due to its complete mineralization aspects in the presence of UV or Solar light. Recalcitrant organics such as PCPs, Pharmaceutical and some other ECs are mineralized completely rather than transformation of phase. There are several technical issues that need to be further investigated which constrained the applicability of heterogeneous photocatalysis for water treatment. One of the key issues related to the consideration of photocatalysis process as pre-treatment or standalone system. Photocatalytic system can be used as pretreatment prior to biological treatment which would reduce the residence time and reaction volume of the biological system. Photocatalytic system used as standalone treatment system would mineralize the PCPs and organics within the less residence time. Utilization of solar energy instead of artificial UV light need to implement to reduce electricity cost and it would also promote the feasibility of photocatalytic

based AOPs in pilot scale. Finally, a large-scale photocatalytic treatment process with high efficacy, solar-driven and low site area requirements can be realized in the short future with rapid evaluation of different possible pilot plant configurations.

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CHAPTER

3

Membrane bioreactor (MBR) as an advanced wastewater treatment technology for removal of synthetic microplastics

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3.1 Introduction

Synthetic microplastics are particles smaller than 5 mm in size and have been identified in different environmental samples worldwide. Environmental pollution caused by these micro debris symbolize a universal trouble that, due to the undeviating effect on the ecosystem (Bouwmeester et al., 2015). Microfibers are mainly consists of Rayon, nylon, and polypropylene (Gago et al., 2018). The resilience and sluggish time of degradability make these micro fibers, to resist the marine atmosphere for hundreds of years (Song et al., 2014), and signify a potential menace for aquatic life (Rochman et al., 2013,Yang et al., 2015). Synthetic microplastics are identified from different sources, including laundering of synthetic fabric, degraded debris of larger plastics like bottles, fishing nets, vehicle rubber abrasives, or cosmetics including micro beads (Napper et al., 2015). It has been also investigated that these micropollutants can also be produced from our daily activities such as by opening of plastics baggage. The quantity is reliant on the circumstances such as rigidity, width, concentration of synthetic polymers and their dimension. Microplastic can be distinguished into two types as "primary" and "secondary" to differentiate on the basis of their sources (Arthur et al. 2009). The microplastics that are released into the direct use or abrasions of cleaning products produced as microbeads from cosmetics (Costa et al. 2010). Microplastics which are produced by the disintegration of larger plastic materials are generally regarded as secondary (Cole et al. 2011). On the basis of our present technology, microplastic sources can be categorized into 4 types: (i) larger plastic waste particles, (ii) personal care products, (iii) pharmaceutical products, and (iv) synthetic

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fabric (Kang et al., 2018; Li et al., 2018; Mishra et al., 2019). Appropriate and scientific research on of the exact sources and transmission routes by scrutinizing the data can combine the progress in spectroscopic techniques with experimental and statistical designs. The fragmentation and degradation rate of larger microplastics is unidentified even for many types of environments (Law and Thompson, 2014). Microplastics in aquatic ecosystem endure much physical and environmental degradation (Andrady, 2011, Ivar do Sul and Costa, 2014). Free et al. (2014) showed that plastic fragments may undergo comparatively more rate of disintegration due to elevated ultraviolet saturation in lakes (Mishra et al., 2020; Mishra and Das, 2021). However, on the whole method of microplastics degradation in freshwater and marine ecosystem was investigated to be alike (Zbyszewski and Corcoran, 2011). In oceanic environments, characteristics of microplastic particles such as their tiny size and low-density facilitate their transport in the gyre via ocean currents (Ballent, et al., 2016).

Due to their miniature size, a bulk of released microfibers directly enters the aquatic stream bypassing waste water treatment plants and reaches rivers, lakes, and oceans. In the marine environment, these micropollutants are transported throughout the ocean by sea currents, as a result these tiny plastics are found in each marine environment (Cole et al., 2011, Ballent, et al., 2016). A recent report estimated around 35,000 tons of plastic debris present ocean (Cózar et al., 2014; Eriksen et al., 2014). Another investigation suggested that approximately five trillion microplastic pieces are presently floating in the marine water (Obbard et al., 2014; Eriksen et al., 2014). More than 7 million micro fibers are released from single clothes through domestic machine washing and 1900 fibers per washing cycle. It is anticipated that leading plastic producing countries contribute more than 62% of the plastic in the marine system annually. Microplastics in aquatic systems are the key basic of diverse problems like, entanglement (Kanhai et al., 2019; Mishra et al., 2021; Singh et al., 2020; Das and Singh, 2011, Das and Mishra, 2008, 2010). In a similar report, 80% of fish caught from a river in Brazil reported microfibers (Silva-Cavalcanti et al., 2017). More terrible reality is that micro fleeces were detected in approximately 80-85% of water samples that we are drinking directly (Kosuth et al., 2018). When the airborne micro particles of these pollutants are inhaled by human, gets deposited in the lungs and leads to harmful respiratory diseases (Lamichhane, 2018).

At present there is no stringent regulation on the limit of microplastics in water, neither any management techniques have been developed for their removal. Waste water treatment plants are working to improve water quality so as to meet human demands, and a prospective barricade for these micro pollutants from drinking water for human use. Microfibers generated from domestic washing machine clothes containing detergents, chemicals, and cosmetics are entering natural aquatic environments without treatment due to their microscopic size and deserve outmost consideration. This present chapter summaries present information on microfiber pollution, reviews the existing knowledge on synthetic microfiber treatment by different, elaborately discusses membrane bioreactor (MBR) technology for removal of synthetic microplastics and identifies the future investigation requirements concerning the microfiber removal technologies.

3.2 Microplastic generation and pollution

Microplastics are the most important type of oceanic pollutants on seashores and suspended on surface of water, which is always uncovered to UV rays. Then due to extensive weathering it goes through disintegration and steadily degrades and smaller particles formed. During later stages of degradation, the plastic polymers characteristically start losing its color additives, increased surface textures, developing into fragile and weak over the time. Microplastic pollutants have originated mainly from the corrosion of fragments of larger plastic products or from any personal care products (Napper et al., 2015). Another foundation of contaminants is the household laundering method or textile and fiber industries (Mishra at al., 2019, Singh et al.,2020). Due to their small size, a greater part in discharged microplastics cannot be captured by WWTPs, and enter into in this rivers and oceans (Magnusson and Wahlberg, 2014). In spite of the augmented worldwide awareness, the build-up of these materials in the atmosphere is regarded as the most challenging situation due to the ever-increasing universal plastic manufacture. The ever increasing production, application and generation of synthetic microfibers is mounting surprisingly, thus creating a universal problem. The major fabric producing countries are United States, India, China, and Africa (Boucher and Friot, 2017). Due to our increased dependency on polyester clothes with newest style, it is considered as the major polluting industrial sector as compared to its huge production and the growing environmental pollution. (Brodde, 2017). In a single wash a synthetic cloth is reported to release more than 2000 microfiber particles so, if we sum up the total released amount annually into aquatic system, it is more than billions and trillions. Presently, it is of immense importance to identify the main causes of these micro pollutants in a range of aquatic bodies. A major portion of these microfiber particles shift toward nearby water bodies from close by landfills situated (Cole et al., 2011).

In water, microplastics are present in the sediments, surface water and floating throughout the water, thus making various sources of possible problems for aquatic species (Fig. 3.1). The microfibers causes' physical, biological and physiological health effects when ingested, by the marine species. These micro pollutants are also reported to alter the food chain level at different stages. The huge amount of these pollutants, along with their microscopic size and closeness to aquatic organisms, permit them for direct uptake by these species at different food webs. At present, enormous amount of microplastic wastes are being deposited in the marine waters (Jambeck et al., 2015). In the ocean the synthetic fibers are subjected to chemical, physical exposure along with and solar heat, leading to fragmentation of the pollutants. Andrady (2011) reported various factors of physical forces, including marine waves; environmental parameters such as sunlight, salinity, water temperature; pH of the water to play a crucial function in aquatic plastic fragmentation. Factors that have wide impact on plastic degradation are extreme weathering conditions in poorly nourish water condition. This present form of global microfiber pollution symbolize a menace to environment, since these minute particles are mixing with the food sources and getting accidentally ingested by the species (Garth et al., 2021;

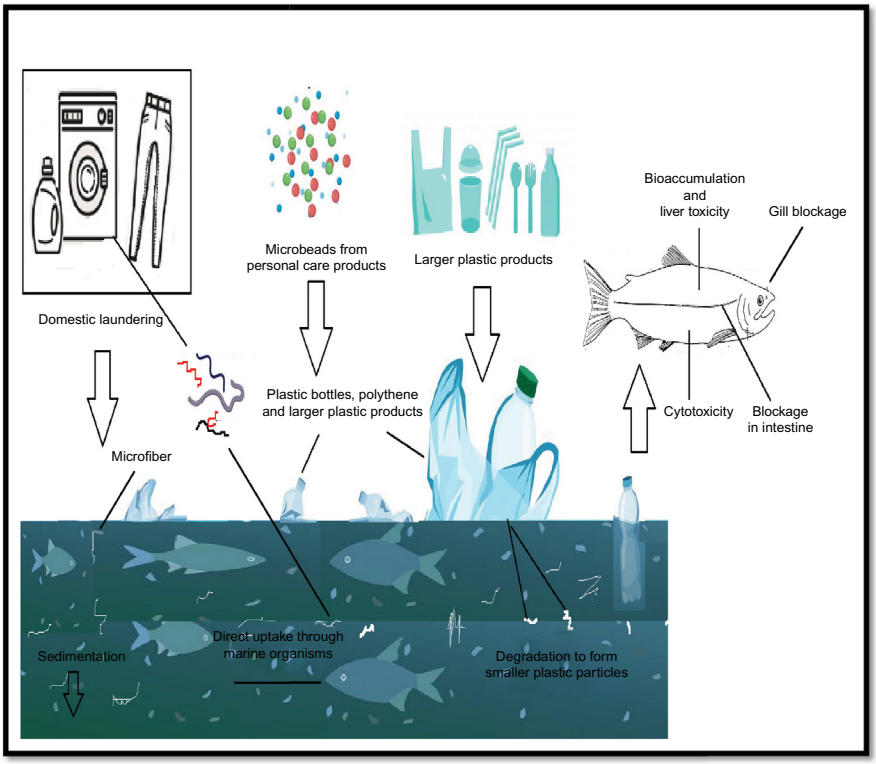

FIG. 3.1 Distribution of microplastics in the aquatic environment with various sources and possible problems for aquatic organisms.

Das et al., 2014a, 2014b; Das et al., 2015). Even though microfiber pollution research has improved recently, the verification of lethal effects of these particles non human health is still scarce (Koelmans, 2016; Ghosh et al., 2015, 2018a). Various research investigations have reported cellular damage, with harmful consequences for and reproductive disorders in organisms exposed to micro plastic pollution (Rochman, 2015; Wardrop et al., 2016; Ghosh et al., 2018b). Similarly the uptake of the particles results in potentially lethal health consequences, such as blockages in digestive tract, tissue deposition, and cellular damage (Wright et al., 2013). Thus, micro plastic can enter the whole food chain and disturb the natural food web. India has shoreline of 7500 km, which is exposed to quick industrialized growth and rapid urbanization as a major source of plastic pollution to the ocean water and is a matter of, immediate intervention (Naidu et al., 2019).

A correlation is developed between the site specific micro plastic at particular location and human activities in those specific areas including the plastic type and their concentration with their generation. Although plastic pollutants are reported globally in all oceans, recently synthetic fibers, and micro plastics are suggested to be a major

source of marine microplastic pollution. It is also vital to recognize their spread, circulation and deposition in the aquatic system. Microplastics are reported to come out from larger plastics particles or from fragmented plastic debris. Once it reaches the ocean, these particles are spread throughout the ocean as a result microplastics are reported in every habitat universally (Cole et al., 2011). Microfibers are the major abundant source of plastic pollution reported in the environment and are released by the extensive use of synthetic garments. The most plentiful of apparatus of aquatic waste is synthetic plastics and fibers and because of the simplicity with which it can be transported, it can be originated amongst garbage gathered from even the farthest sites (Ryan et al., 2009). Together with these regions, marine surfaces become visible to be more deeply contaminated, whereas pollution has been noticed even in the polar region. Unmanageable abandoned synthetic pollutants and bare areas have been predicted as the most causative land-based sources of aquatic pollution (Barnes et al., 2009; Kumar et al., 2016a, 2017), whereas less causative sea based contributors are associated to commercialized actions linked to the ocean like fishing, oil production, and to inhabitants gathering on seashore areas. Dilapidated fish nets have been recognized as the dangerous ecological trouble, because it has harmful effects on aquatic organisms (Watson et al., 2006; Cheshire et al., 2009).

Microplastic pollutants have been identified on seashore and in sub tidal sediments globally (Song et al., 2014) and signify a menace for aquatic organisms especially marine (Wright et al., 2013) as they can be consumed by aquatic algae, small fish, large fish ultimately enter the human body (Mishra et al., 2019). Numerous investigations described that these particles transport other pollutants, and synthetic colors (Collard et al., 2015) to ecosystems also. Additionally, these particles can also absorb and when engulfed by aquatic organisms, could be relocated to the food chain and finally to human (Bakir et al., 2014).

3.3 Effect of Synthetic microplastic pollution

Microplastic pollution is almost devoured the whole world in its invisible arms, especially the marine environment due to its buoyancy and durability properties. These synthetic materials are hazardous for all type of environments as it is processed with many chemical additives including flame retardants (such as polybrominated diphenyl ethers), UV stabilizers, heat stabilizers, pigments, and antimicrobial agents to provide specific properties (Smith et al., 2018). Due to the phenomenon of photodegradation and weathering these materials broken into tiny pieces and dispersed in the terrestrial and aquatic ecosystems (Smith et al., 2018). These synthetic materials are then ended up in the oceans via directly the river systems or indirectly by the WWTPs. Rivers act as a potential pathway for all these debris; since it acts as the first line sink of the contamination; it is reported that approximately 1.15 to 2.41 million ton of microplastic wastes presently enters into the marine environment annually (Lebreton et al., 2017; Mato et al., 2001; Rochman et al., 2013). The persistent and small size characteristics make these MPs bioavailable to many marine animals such

as zooplanktons, corals, lobsters, sea urchins, fish, etc. If these synthetic particles are ingested by the marine animals got deposited in the tissues, bloodstream, and different internal organs of the body. Ultimately bioaccumulated in the food chain up to the higher rank or trophic level animals causing a number of physical, physiological effects and even death (Sharma and Chatterjee, 2017; Ziccardi et al., 2016). The ingestion and bioaccumulation of microplastics by many marine animals reported in recent research articles are represented in the Table 3.1.

Moreover, other cellular, molecular, oxidative stress, and neurological disorders are also reported (Jeong et al., 2016; Jeong et al., 2017). However, this synthetic pollution is not only restricted to the marine animals, but the general human population also exposed to these particle from a variety of sources including, sea based foods and drinks, synthetic clothes, and personal care products. Among these sources, the increasing evidence of the presence of MPs in commercially important seafoods (such as fishes, shrimps and mussels) in are reported which indicating a possible risk to human health through biomagnification and become a potential route of exposure to human via diet (Walkinshaw et al., 2020; Devriese et al. 2015; Cauwenberghe and Janssen 2014). In a recent scientific study on the commercially important fish from Western Arabian Gulf, about 58.58% of synthetic textile fibers (most prominently polyethylene and polypropylene) were recovered from the gastrointestinal tracts of the fish (Baalkhuyur et al., 2020; Kumar et al.,2016b; Mohanty et al., 2017, 2018). Similarly, in case of mussels, approximately 2.6-5.1 microfibers per 10 g of commercial mussel sample ranging from 200-1500 mm were reported from Belgium stores (De Witte et al., 2014). There are some foods and drinks also reported the occurrences of the MPs in the food chain such as, table salt, honey, beer, sugar and in canned fish which are used in diet regularly in human life (Karami et al., 2017, 2018; Abassi et al., 2018; Andrady, 2011; Arthur et al., 2009; Baalkhuyur, 2018; Bakir et al., 2014; Ballent et al., 2016; Baresel et al., 2017; Boucher and Friot, 2017; Bouwmeester et al., 2015; Catarino et al., 2018; Chae et al., 2011; Chang et al., 2020; Cheshire et al., 2009; Cheung et al., 2018; Cole et al., 2011, 2013; Collard et al., 2015; Costa et al., 2010; Cózar et al., 2014; da Silva Mendes et al., 2015; De Witte et al., 2014; Desforges et al., 2015; Devriese et al., 2015; Eriksen et al., 2014; Free et al., 2014; Gago et al., 2018; Imhof and Laforsch, 2016; Ivar et al., 2014; Jambeck et al., 2015; Jeong et al., 2016, 2017; Kang et al., 2018; Kanhai et al., 2019; Karami et al., 2017, 2018; Kosuth et al., 2018; Lamichhane, 2018; Lattemann and Höpner, 2008; Law and Thompson, 2014; Lebreton et al., 2017; Lehner et al., 2019; Li et al., 2018; Liebezeit and Liebezeit, 2013, 2014; Lithner et al., 2011; Magnusson and Wahlberg, 2014; Mato et al., 2001; Mishra et al., 2019; Murphy et al., 2016; Naji et al., 2018; Napper et al., 2015; Obbard et al., 2014; Padervand et al., 2020; Poerio et al., 2019; Prata et al., 2019; Rochman et al., 2013a, 2013b; Ryan et al., 2009; Santos et al., 2015; Sharma and Chatterjee, 2017; Silva-Cavalcanti et al., 2017; Singh et al., 2020; Smith et al., 2018; Song et al., 2014; Talvitie et al., 2017; Tanaka and Takada, 2016; Van Cauwenberghe and Janssen, 2014; Walkinshawa et al., 2020; Watson et al., 2006; Wright et al., 2013; Yang et al., 2015; Zbyszewski and Corcoran, 2011; Ziccardi et al., 2016; Brodde, 2017, 2014). However, depending on the

Table 3.1 The ingestion and bioaccumulation of microplastics by marine animals reported in recent research articles.

Organisms	Level of synthetic MPs	Size range	Type of debris	Location	Reference
Acanthurus gahhm (Fish)	10 particles/ individual	2700 μm (mean)	fibers	Red Sea coast, Saudi Arabia	Baalkhuyur et al. (2018)
Mugil cephalus (Fish)	30 particles/ individual	<2000 –>'5000 μm	fibers,	Hong Kong Coast	Cheung et al. (2018)
Lutjanus kasmira (Fish)	10 particles/ individual	2160 μm (mean)	fibers, fragments of fishing net	Saudi Arabian Red Sea coast	Baalkhuyur et al. (2018)
Engraulis japonicus (Fish)	2.3 ± 2.5 particles/ individual	150-1000 μm	fibers	Tokyo Bay, Japan	Tanaka et al., 2016, Naji et al. (2018)
Chelonia mydas (Sea Turtle)	Not specified	>500-<1000 μm	Fibers, film, fishing thread	Brazilian coast, Ubatuba	Da Silva Mendes et al. (2015)Catarino et al. (2018)
Chelonia mydas (Sea Turtle)	47.5 particles/ individual	Not specified	Fibers, fragments	Brazilian coast, Ubatuba	Santos et al. (2015); Abassi et al. (2018)
Crangon crangon (Marine invertebrates)	Not specified	300-1000 μm	Fibers, fragments	Belgium	Devriese et al. (2015)
Euphausia pacifica (Marine invertebrates)	0.058 ± 0.01 particles/ individual	816.1 ± 107.7 μm	Fibers, fragments	Northeast Pacific Ocean	Desforges et al. (2015)
Neocalanus cristatus (Marine invertebrates)	0.026 ± 0.005 particles/ individual	555.5 ± 148.7 μm	Fibers, fragments	Northeast Pacific Ocean	Desforges et al. (2015)

exposure and susceptibility, these synthetic micropollutants possibly lead to oxidiative stress, cytotoxicity, neurotoxicity, disruption of immune system, and even cause cancer by bioaccumulating in the tissues of organisms (Prata et al., 2019; Chang et al., 2020; Lehner et al. 2019).

The synthetic microplastic pollution became a significant global concern due to its omnipresence in various ecosystems and environmental regions. Presently there is economic alternative yet to remove these pollutants from ocean. Marine pollution due to plastics particles symbolize a universal problem that has become more alarming in present situation, due to the direct effect of these pollutants on the atmosphere and living organisms. Recent findings have proved that plastics leads the amount of waste available in the marine and inland waters (Eriksen et al., 2014; Mato et al., 2001). In these circumstances, to prevent this pollution, a strong need has arisen for developing strategies for removing and recycling the plastic microfibers. However, these strategies are still in the budding phase of research with very few numbers of addresses till now (Bouwmeester et al., 2015).

3.4 Technical implementation of membrane bioreactor (MBR) for elimination micro plastic pollutants

Existing worldwide principles are not integrated and local experimental techniques are too costly and prolonged process in their capability to control the pollution caused by microplastics within various aquatic environments. As this area of research is comparatively latest, lacking of relevant researches and a scarcity of investigation of the biodegradation of these synthetic polymer pollutants in the environments (Murphy et al. 2016; Mishra et al, 2019). The technical execution follows the aim of ever-increasing the working life of the existing treatment plants by filtering the microplastic fragments primarily in pretreatment, which cause obstacle of the filters. Contrarily, the lifecycle of the micro porous filters can be thus enlarged and the operational expenses reduced and sustainably eradicate these pollutant particles from the aquatic environment. But when the elimination is base on a chemical treatment technology, it is not restricted by dimension of the microplastic fragment as in physical process. The process reagent can attach to these polymer fragments of all size and shape, the aquatic environment will be enhanced through the lessening of the microplastic particle load (Lattemann and Höpner, 2008). The microplastic pollutants along with waste waters is drain using the membrane bioreactor filtration method can filter contaminated water leaving pure water into the environment as depicted in Fig. 3.2.

Recent years, these bioreactors based on membrane system get widespread educational attention and a very quick development in on site implementation. The immense triumph is given by the important enhancement provided by this machinery, as it is related to conventional way of management, such as elevated sewage excellence, effortless scale-up. The most recent technique are associated with automatic ventilation cleaning, chemical cleaning using chemical reagents and bacterial

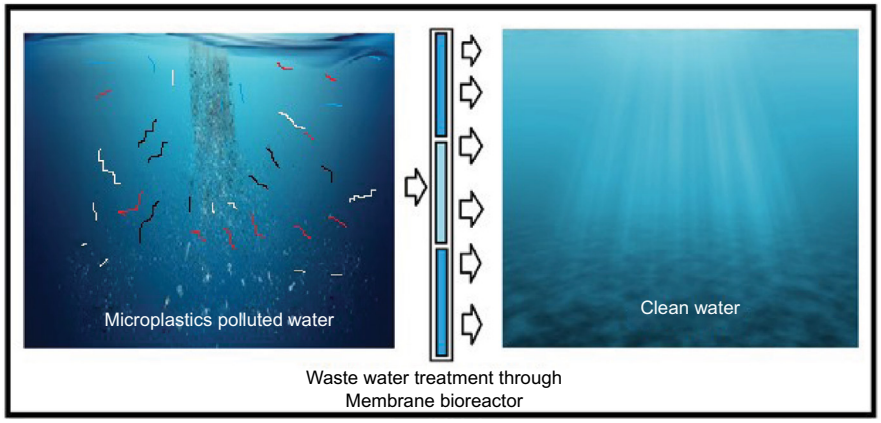

FIG. 3.2 Microplastic removal by waste water treatment using membrane bioreactor.

degradation and nano material-assisted membrane system. The manifestation of the increasing attention of this tool is the considerable augment on both large and super large-scale treatment plants universally. MBR technique merges the biological triggered method with film separation, which offers additional benefits over other methods. Benefits comprise a considerably improved discharge quality concerning fragments, ability due to the membrane filter size, and process elasticity towards influx modification. Even the management of MP may be more competent using these reactor techniques as contrast to conventional executive systems. This has been partially clarified plastic polymers can be disintegrated in an effective way due to superior biological action in a MBR method (Baresel et al.,2017). The role of this technique in the management is the lessening of solution difficulty by the biological degradation of the biotic pollutants; this will allow trouble-free cleansing of plastic fragment and its additional handling (Murphy et al. 2016). The procedure usually begins when a pre-treated tributary enters into the bioreactor, where the method of degradation of natural pollutants is taking place. The discharged blended fluid is then forced along with filtration system for the elimination process.

This technology can reduce 99% of these micro pollutants from waste water and results in the decrease in MP concentration in the ultimate runoff. The gravity or sand filters can remove 97%, where as dissolved air flotation and disc filters 94-98% of the MPs from the discharge released after primary treatment (Talvitie et al.,2017). As a huge amount of effluents are continuously released into the water systems, MP pollution should be considered, when scheming superior ultimate step of the treatment technologies and employing them in treatment plants. The management can also eradicate all shapes of MPs. The most negligible sized plastic and microfibers were the most widespread and frequently observed type of MP and also after the tertiary step of treatment technology (Mishra et al., 2019). Investigation of the microplastic removal efficiency using advanced final-stage treatment technologies from wastewater treatment plant are represented in Table 3.2.

Table 3.2 Removal efficiency of different treatment technologies for microplastic removal.

Sl. No.	Removal methods	MP/L in untreated water	MP/L after treatment	Removal Efficiency	References
1	Disc filter	0.5- 2.0	0.03-0.3	40–98.5%	Talvitie et al.,2017
2	Rapid sand filter	0.7	0.02	90-97%	Padervand et al.,2020
3	Dissolved air flotation	2.0	0.1	95%	Talvitie et al.,2017
4	Membrane bioreactor	7.0	0.005	99.9%	Talvitie et al.,2017; Chae et al.,2011

Membrane bioreactors (MBR) are method in which catalysis endorsed microbes or microbiological products is coupled to a micro filtration process, activated by a membrane system. Numerous partitions which created by the film, a gradient is developed in the reaction system. The treatment stages can be kept apart; otherwise they can be dissolved into each other. In addition, the usefulness of the method facilitates an effortless combination with other methods such as reverse osmosis. This method can be employed without producing any harmful byproducts, which present novel and supplementary prospect with product quality enhancement, uniqueness in the method and ecological affability (Poerio et al., 2019). At the present time, MBR is considered as the most dominant technology for skillful urban sludge treatment worldwide. These new rising fields of research and function are immensely developing such as food, medicine, and biological refineries. This technique has been employed for a many years but achieve more interest only in the previous decade for the management of both urban and polluted water released from industries. This is chiefly due to a noteworthy low cost membranes and technology improvement lessening power prerequisites.

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CHAPTER

4 Strategies to cope with the emerging waste water contaminants through adsorption regimes

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4.1 Introduction

Due to the teeming millions and simultaneous urbanization there has been a fear-mongering of depletion of clean-water supplies which can, in future affect one third of world population (Schwarzenbach et al., 2010). Waste water contains inorganic and organic contaminants as an outcome of geogenic or anthropogenic activities and can be of potential risk to human, livestock, and aquatic organisms. There are several categories of pollutants with different degrees of toxicity, bioaccumulation potential, and persistence. These include heavy metals, biocides, pesticides, dyes, pharmaceuticals, fluorides, arsenic, and micropollutants also called emerging contaminants (EC's) (Schwarzenbach et al., 2010). These pollutants results in various health issues like cancer, kidney failure, memory disruption, oxidative stress, hypertension, cardiovascular disorder, reproductive disorders, nervous system disorder, and anemia (Fig. 4.1). Some of the emerging pollutants can mimic the natural hormones which can be very dangerous for endocrine system and these chemicals are called as EDC or endocrine disrupting chemicals (Shi et al., 2012; Nghiem and Fujioka 2016).

In order to meet the growing demands of clean drinking water the conventional waste-water treatment techniques (WWTT) (on-site: physical, chemical and biological; off-site: activated sludge, constructed wetlands, stabilization ponds, trickling filters, and membrane bioreactors) must be supplemented with modern techniques (electrochemical treatment, evaporation, ion-exchange and incineration, membrane bioreactors, membrane separation, oxidation, and solvent extraction). Certain novel uptake methods (adsorption onto nonconventional solids, advanced oxidation, biomass and nanofiltration and biosorption) are also available. Among these technologies, adsorption through conventional adsorbents (commercial activated carbons, inorganic materials, ion-exchange resins, etc.) and nonconventional adsorbents

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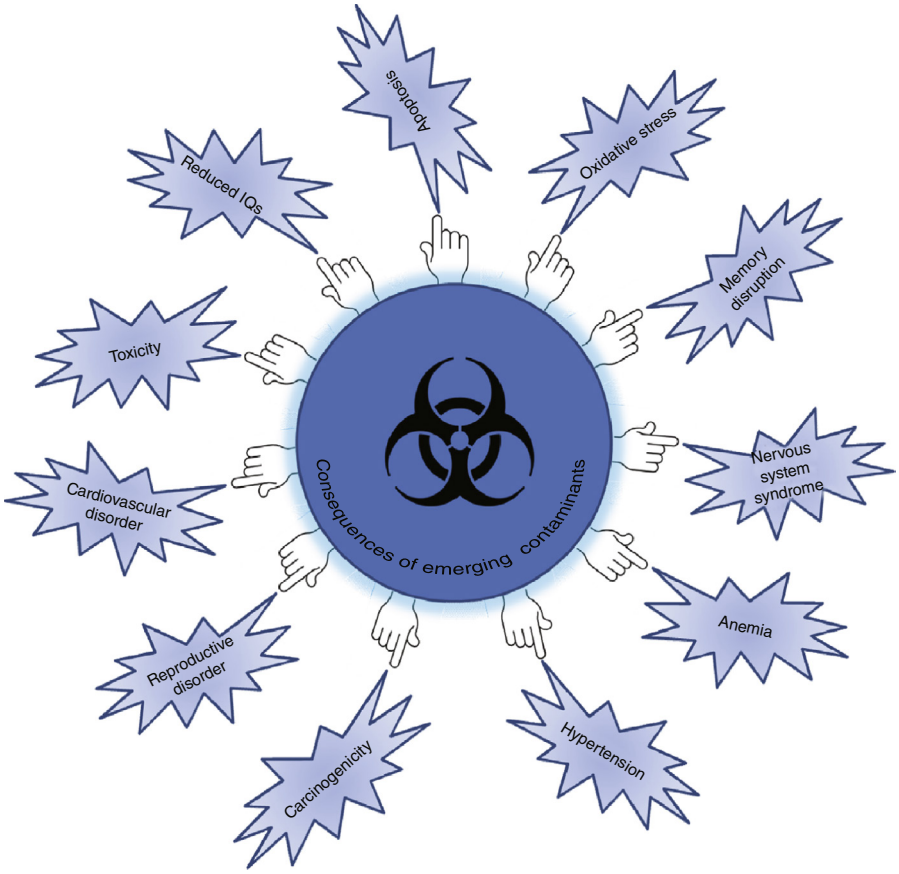

FIG. 4.1 Advers effects and major disorders caused by ECs on human beings.

(activated carbons from solid-wastes, agricultural wastes, biosorbents industrial by-products, natural materials, etc.), is a viable-alternative and has a promising future for the remediation of industrial effluents, wastewaters (WW), groundwater, and including the generation of drinking water (DW). The mechanisms involved in adsorption-oriented removal of pollutants are physisorption (hydrophobic interactions, hydrogen bond, surface adsorption, Van der Waals interaction, Yoshida's interaction), chemisorption (electrostatic interactions, complexation, chelation, covalent binding, inclusion complex formation, oxidation/reduction, and proton displacement), ion-exchange (reversible exchange of ions) and precipitation (microprecipitation, surface precipitation, and proton displacement) (Crini and Badot, 2008).

However, choice of a specific method for WWT relies upon different factors such as the type of waste, its concentration, heterogeneity level, percentage of cleanup required, feasibility of technique, its efficiency, practicability, operational difficulties, environment impact, and treatment cost involved. However, every WWT technique/technology has its own limitations (technical and economic) in real-life situations. This chapter

focuses on various strategies to cope with the emerging waste water contaminants through adsorption regimes, including their merits, demerits, and future prospects.

4.2 Uptake of pollutants from water via adsorption

Adsorption is recognized as a viable technology for sanitation water and extensively utilized for the production of drinking water, treatment of industrial effluents, groundwater, and wastewaters. Adsorption process possesses many advantages over other processes as it is cost-effective, requires less energy, flexible, easy to use with versatile designs and can be operated in different scenarios for water purification. The technical feasibility and economic viability of adsorption processes is governed by many factors such as pollutants to be removed, fluid properties, types of adsorbent, waste disposal, regeneration, process configuration, and operating conditions. Various types of adsorption methods can be used for eliminating the pollutants from contaminated water. For instance, batch and continuous adsorption systems offer different capabilities for the treatment of water. Batch adsorption system (batch reactors) can be employed for determining thermodynamic parameters, adsorbate(s)-adsorbent interactions, maximum adsorption capacities, and adsorption rates. Packed-bed columns are more effective for the decontamination of huge quantity of water in less time. However, the batch processes are more effective than continuous adsorption systems in terms of removal effectiveness.

4.3 Adsorbents and there use in purification of waters

Different types of adsorbents are used during adsorption process depending upon the cost, availability and types of pollutant to be removed. It has been observed that activated carbon can be used commercially for liquid phase purification and as universal adsorbent for water purification (Rivera-Utrilla et al., 2011; Bhatnagar et al., 2013). But for the adsorption of pollutants from liquid phase many other types of adsorbents have been proposed and produced. For instance, Table 4.1 shows different types of adsorbents used for the removal various geogenic and anthropogenic pollutants from waste waters.

There are several strategies for purification of contaminated or polluted waters (Fig. 4.2). Till date many studies have been conducted on the adsorption of water pollutants using one adsorbate in solution but for remediation of groundwater, contaminated water, wastewaters, and industrial discharge, multi-component adsorption processes are more relevant. The use of many adsorbates at a time during adsorption may cause synergistic effect, antagonistic effects or noninteraction effects. The adsorption process may also be impacted by different types of pollutants to be absorbed, their number, their concentrations, and fluid properties like pH, and temperature. The existence of many pollutants in a liquid may remarkably the affect performance of an adsorbent. For example, the characteristics and quantity of co-ions in a multimetallic system significantly affect the removal of heavy metal ions (Choy and McKay, 2005). On the other hand in a mixture of metal and dye, the removal

Table 4.1 Different types of adsorbents used for purification of water.

Adsorbent	Pollutant absorbed	Reference(s)
Alumina	Pharmaceutical products, toxins, metals, heavy metals, metalloids, dyes, and halogens	Kasprzyk-Hordern (2004)
Activated carbon	Pharmaceutical- products, toxins, metals, heavy metals, metalloids, dyes, halogens, organic contaminants, and radioisotopic contaminants	Alhashimi and Aktas (2017)
Biological materials	Halogens, dyes, metals, heavy metals, metalloids, and organic contaminants	Ahluwalia and Goyal (2007) Davis et al. (2003) Volesky (2007) Wang and Chen (2009)
Biochar	Pharmaceutical products, toxins, metals, heavy metals, metalloids, dyes, halogens, and organic contaminants	Alhashimi and Aktas (2017)
Clays	Pharmaceutical products, toxins, metals, heavy metals, metalloids, dyes, halogens	Vinati et al. (2015)
Composites (zeolites)	Pharmaceutical products, metals, heavy metals, metalloids, dyes, halogens, organic contaminants, and radioisotopic contaminants	Koshy and Singh (2016)
Graphene-based adsorbents	Pharmaceutical products, toxins, metals, heavy metals, metalloids, dyes, halogens, organic contaminants, and radioisotopic contaminants	Peng et al. (2017)
Agricultural biomass, waste materials from industries and other by-products as cheap adsorbent	Pharmaceutical products, metals, heavy metals, metalloids, dyes, halogens, organic contaminants, and radioisotopic contaminants	Adegoke and Bello (2015) Ahmed and Ahmaruzzaman (2016) Bhatnagar et al. (2015) Bhatnagar and Sillanpaa (2010) De Gisi et al. (2016)
Nano adsorbents	Pharmaceutical products, metals, heavy metals, metalloids, dyes, halogens, organic contaminants, and radioisotopic contaminants	Zhang et al. (2011) Santhosh et al. (2016)
Polymeric materials and metal-organic frameworks	Pharmaceutical products, metals, heavy metals, metalloids, dyes, halogens, organic contaminants, and radioisotopic contaminants	Kumar et al. (2017)

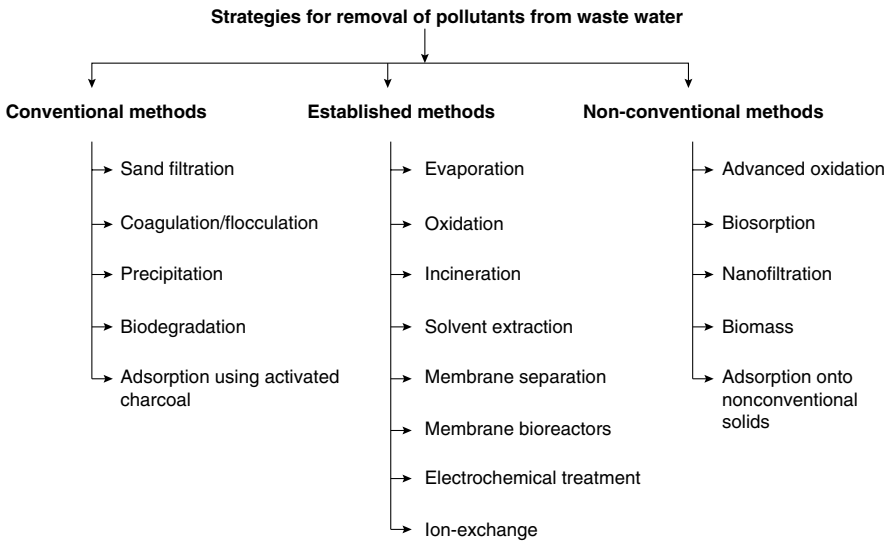

FIG. 4.2 Different methods available for uptake of pollutants from waste waters.

of metal from the mixture is promoted by the existence of dye (Hernandez-Eudave et al., 2016). Although adsorption is cost effective, robust and ecofriendly process for purification of water, however, there are chances for the improvement of its performance for solving the recent problems of polluted-drinking water, wastewater, groundwater, and industrial effluents.

4.4 Various emerging pollutants and their effects

There are many types of water pollutants and emerging contaminants having different toxicological profiles and physicochemical properties added to the waters from various sources (Fig. 4.3). These pollutants include geogenic pollutants, anthropogenic chemicals, and persistent compounds. Some of the most important water pollutants are pesticides, biocides, metalloids, heavy metal ions, organic and inorganic compounds, and pharmaceuticals (Schwarzenbach et al., 2010). Due to their persistence, toxicological profile, and bioaccumulation in the environment these contaminants are of major concern towards water pollution. Some of the major water pollutants are discussed below:

4.4.1 Heavy metals

Industrial effluents contain a large proportion of metallic and heavy metal ions which are major water pollutants and a big threat to environmental because of their nonbiodegradable and noxious nature (Mouni et al., 2009). Due to their toxicity cadmium, mercury, zinc, copper, lead, nickel, cobalt, chromium, and aluminium are considered as major water pollutants (Dias et al., 2007; Fu and Wang 2011). Heavy metals and their compounds are highly noxious to animals, humans and form compounds with

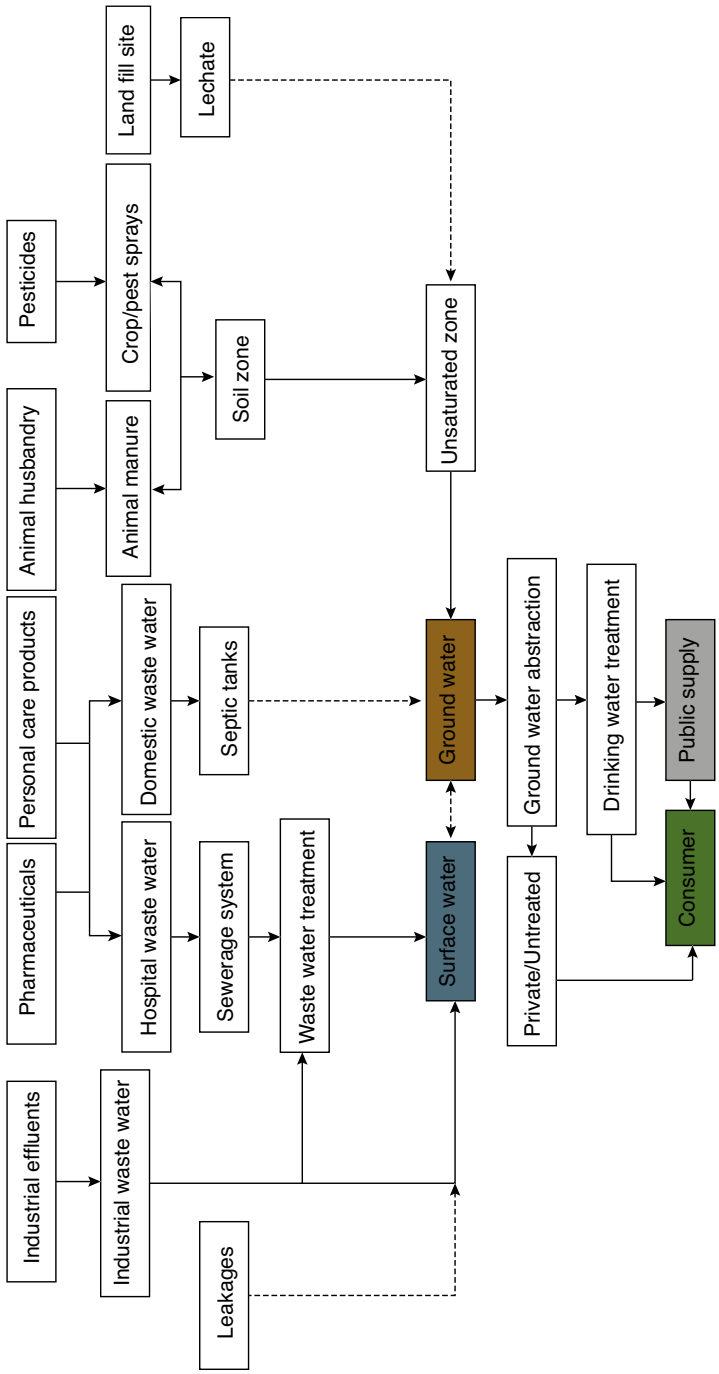

FIG. 4.3 Sources of emerging pollutants in the water supply chain.

cellular components which are rich in oxygen, nitrogen, or sulphur, modify the protein structures inhibit, the enzymes functions which culminate in cellular dysfunctions (Ibrahim et al., 2006). Heavy metals toxicity causes various disorders such as heart disease, kidney disorders, memory loss, neural disorders and damages in the gastrointestinal (Ibrahim et al., 2006).

4.4.2 Dyes

The dyes and pigments are produced from industrial wastes of cosmetic, food, paper, rubber, pharmaceutical, textile, and automotive factories (Gong et al., 2008; Ghodbane and Hamdaoui, 2010). Around 10,000 different dyes are used in industries and approximately 7×10^5 tons of synthetic-dyes are being produced per year across the world (Chequer et al., 2013). The industrial discharge contains an array of dyes which can be classified as disperse, acidic, reactive, direct, and basic (Ghodbane and Hamdaoui, 2010). These compounds are highly recalcitrant and persistent in nature due to their high molecular weights and complex structures (Hernandez-Montoya et al., 2013; Qui and Zheng, 2009). Moreover, these are highly toxic, carcinogenic and mutagenic to various living forms (Al-Ghouti et al., 2003).

4.4.3 Pharmaceuticals

Pharmaceutical contaminants are found in trace amounts in wastewaters, surface waters, drinking water, and groundwaters (World Health Organization, 2011). Pharmaceutical compounds such as analgesics, antibiotics, painkillers, anti-inflammatory, and hormones are known to be one of the most hazardous emerging contaminants of waters (Sarici-Ozdemir and Onal, 2010; Bagheri et al., 2014). They inhibit the hormone receptors and metabolic processes of liver and kidney in animals and humans (World Health Organization, 2011). (Baccar et al., 2012; Bagheri et al., 2014). Traditional sewage treatment plants are not sufficient for eliminating pharmaceutical contaminants and are unable to remove or degrade these compounds (Baccar et al., 2012; Bagheri et al., 2014). Hence, these pharmaceutical wastes are continually adding into water resources thereby presenting enormous environmental risk for both human beings and the ecosystems (Onal et al., 2007; Yu et al., 2008; Sarici-Ozdemir and Onal 2010; Baccar et al., 2012).

4.4.4 Fluoride

Fluoride is also recognized as a toxic geogenic pollutant by the World Health Organization which accumulates in groundwater naturally (Jadhav et al., 2016). Around 260 million people across the globe are consuming groundwater containing higher levels of fluoride (Sani et al., 2016). The use of water having higher levels of fluoride (>1.5 mg/L) may cause many disease like cancer, thyroid disorder, dental problems, skeletal fluorosis, arthritis, osteoporosis, and endocrine dysfunction, Alzheimer disease, kidney disorders, gastric irritation, gastrointestinal disorders, and infertility (Das et al., 2005; Gupta et al., 2007; Ozvath 2009; Tomar and Kumar 2013; Jadhav et al., 2016). This halogen may also cause disruptions of important biochemical

processes by interfering with carbohydrates, proteins, vitamins, and enzymes which are involved in glycolysis, coagulation, neurotransmission, and oxidative phosphorylation (Tomar and Kumar 2013; Kut et al., 2016).

4.4.5 Arsenic

Arsenic is extensively scattered in rocks and soil of Earth crust and hence a geogenic pollutant (Mandal and Suzuki, 2002). The use of water containing arsenic may results in many disorders like keratosis, melanosis, arterial hypertension, skin cancer, renal disorders, reproductive, and respiratory disorders (Shankar et al., 2014). The levels of this pollutant decides the technical suitability and feasibility of a water purification technique that must be used.

4.4.6 Other emerging pollutants

In last few decades, analytical instrumentation and techniques have been improved to such an extent that even trace amounts of contaminants found in wastewaters and groundwater can be detected very easily (Nghiem and Fujioka, 2016). The advancements in technology lead to the detection of emerging chemicals, which are present in waters since many years but they are now reported as potential water contaminant (Jeirani et al., 2016; Nghiem and Fujioka 2016). These emerging pollutants may be organic or inorganic in nature and include phytoestrogens, hormones, pesticides, beauty products, disinfection byproducts, and hydrocarbons (Nghiem and Fujioka, 2016). As aforementioned, these pollutants can cause long-term adverse effects on humans and animals and act as endocrine disrupting chemicals that can cause lethal disease like cancer (Shi et al., 2012; Nghiem and Fujioka 2016).These micro-pollutants cannot be removed by conventional treatment processes.

However, the adsorption techniques are successfully used for elimination of these pollutants. Heavy metal remediation have been reported in many studies using adsorption processes (Rao et al., 2010; Barakat 2011; Gupta and Bhattacharyya, 2012; Malik et al., 2016; Shah et al., 2016; Yu et al., 2016; Uddin 2017). Dye polluted fluids have been effectively treated using adsorption regimes and more researches are being done to understand and check the removal of dyes by various new adsorbents (Allen and Koumanova, 2005; Demirbas, 2009; Chincholi et al., 2014; Yagub et al., 2014; Adeyemo et al., 2015; Seow and Lim 2016; Vital et al., 2016). The pharmaceutical-based contaminants are also being eliminated from contaminated waters with satisfactory results using adsorption techniques. Ibuprofen, naproxen, erythromycin, diclofenac, carbamazepine and atenolol are some of most studied pharmaceuticals using adsorption processes (Kim et al., 2014).Various adsorbents like activated carbons, zeolites, and silica have been used for removal pharmaceutical-based pollutants (Fukahori et al., 2011; Baccar et al., 2012; Martucci et al., 2012; Kim et al., 2014; Kyzas and Deliyanni, 2015). Fluorides can also be removed using adsorption processes (Mohapatra et al., 2009; Bhatnagar et al., 2011; Miretzky and Cirelli, 2011; Jagtap et al., 2012; Loganathan et al., 2013; Velazquez-Jimenez et al., 2015; Vinati et al., 2015). But, it has been observed that traditional adsorbents including

activated carbons are unable to completely remove the fluoride and are insufficient for purification of water containing higher amounts of fluoride. There are many report where different adsorbents have been used for the elimination of arsenic from contaminated waters (Mohan and Pittman, 2007; Gallegos-Garcia et al., 2011;Verma et al., 2014; Baig et al., 2015; Habuda-Stanic and Nujic, 2015; Jadhav et al., 2015). However, the adsorption of arsenic from water is economically and technically a challenge. The pro and cons of adsorption process used for the purification of water containing arsenic have been analyzed by many authors (Verma et al., 2014; Baig et al., 2015). For the remediation of emerging contaminants from waste waters various adsorbents have been used which includes hydrothermal carbon (Liu and Zhang, 2009), activated carbon (Jeirani et al., 2016; Zhang and Hofmann 2013), Agricultural waste adsorbent (Velazquez-Jimenez et al., 2013), zeolites (Sprynskyy et al., 2006) and clays (Gupta and Bhattacharyya, 2008).

4.5 Adsorption strategies for removal of emerging pollutants from waste waters

The emerging pollutants can be removed using the adsorption regime (Fig. 4.4) which includes different strategies depending upon the nature and concentration of emerging pollutants. Different adsorption strategies for removal of emerging water pollutants have been discussed below:

4.6 Adsorption of pollutants using hydrothermal carbonization: an environment safe procedure using carbon adsorbents

The hydrothermal carbonization process is an environment safe method for obtaining carbonaceous adsorbent and in recent years it has attracted the interest scientific community. In this method an organic material along with water is heated at temperatures above 100 °C in a sealed vessel. This method of carbon based adsorbent production is different from the conventional pyrolysis due to its low pollutant emission, lower power consumption and higher yield. Hydrothermal carbons (HTCs) are basically chars having higher number of functional groups with high oxygen content and less porous nature. The carbonaceous materials are used as fuel and as adsorbent. Activated carbon that is used as adsorbent for purification of contaminated waters is obtained from charcoal (or biochar). Pyrolysis is the conventional technique of carbonization of biomass, which requires heating (temperatures 400–1000 °C) of lignocellulosic material for long durations. Pyrolysis is an environment unfriendly process and has many disadvantages like high temperatures of heating, higher energy requirement, release of poisonous gases, production of large quantity of pyroligneous acid, and production of corrosive material. Moreover, the yield of pyrolysis is poor and not constant.

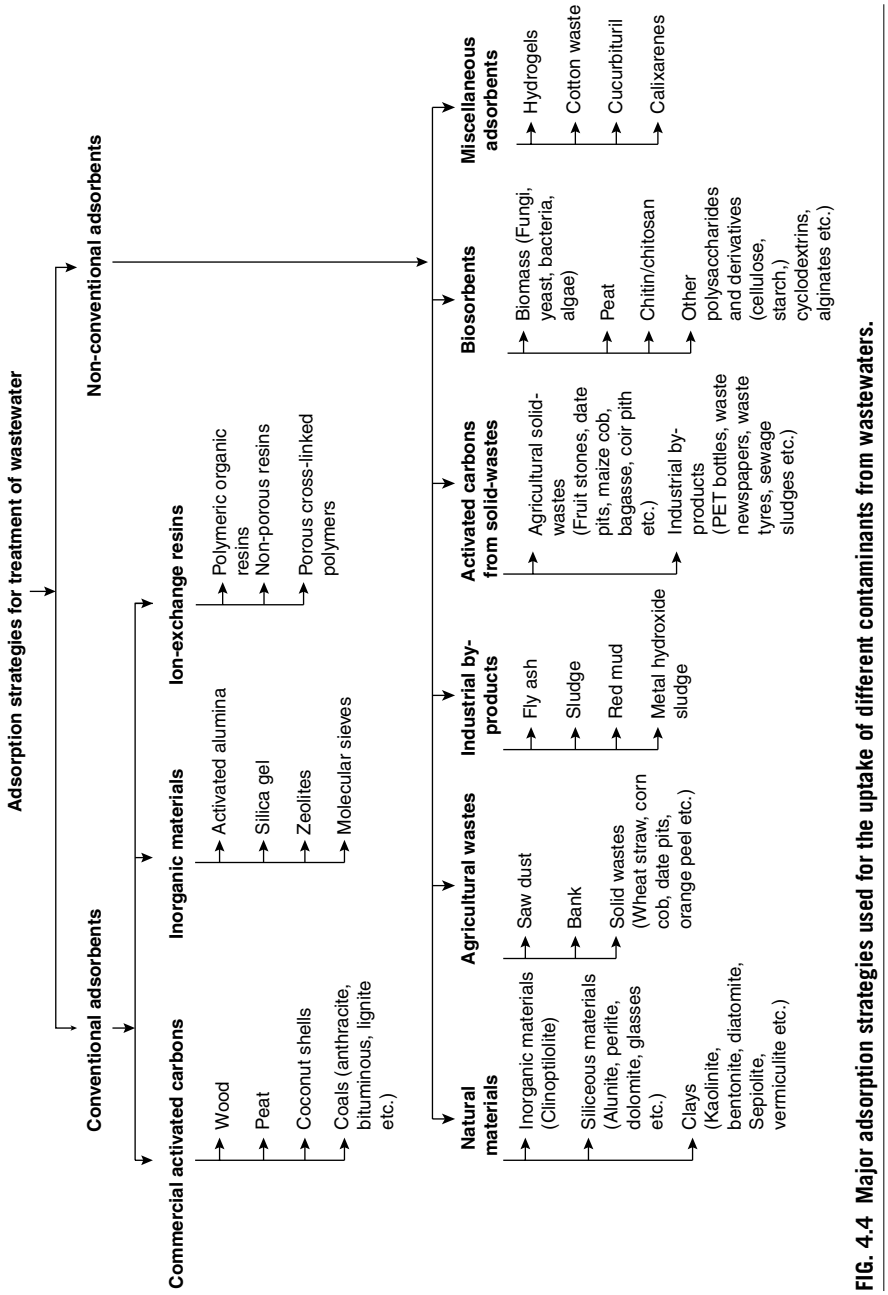

FIG. 4.4 Major adsorption strategies used for the uptake of different contaminants from wastewaters.

However, the hydrothermal carbonization (HTC) is an eco-friendly method that requires low temperatures (up to 200 °C) and under water-generated pressure carbonization can be done from biomass and water. The HTC has many advantages over conventional pyrolysis such as no need of drying the raw material, requires mild temperatures, less energy requirement, no gases, acids and tar is generated and its yield is around two fold higher than that of pyrolysis (Kumar et al., 2011). Hence, HTC can be a method of choice for carbonization and synthesis of ACs (activated carbons) adsorbents for eliminating various pollutants from the contaminated water.

4.7 Use of hydrothermal carbonization (HTC) in adsorption

The HTCs can be effectively used for eliminating waste water pollutants through adsorption process. The use of HTCs in removal of various contaminants is discussed below:

4.7.1 Dye adsorption

Dyes are highly persistent pollutants which are very difficult to remove from waters as they are non biodegradable and highly toxic chemicals. These pollutants are of large size and hence adsorbent of large pore size are required for effective removal. Alatalo et al. (2016) have reported that methylene blue dye could be effectively removed through adsorption. Fructose was used as adsorbent with a $ZnCl_2$-LiCl template and 2-thiophene carboxaldehyde. However better adsorption capacity was obtained when the adsorption cycle was performed several times. Martin-Jimeno et al. (2015) have used KOH activated hydrothermal carbons made on templates to adsorb three dyes (methyl orange, rhodamine B, and fuchsin basic).The templates of HTCs without activation with KOH exhibits narrow microporosity and hence adsorb the dye methyl orange due to its narrowest nature amongst the three while those hydrothermal carbons which were activated using high KOH ratios adsorbed a higher amount of fuchsin basic and rhodamine B as the HTCs activated by KOH developed broader porosity. Roldan et al., (2016) analyzed the uptake of methylene blue and rhodamine B using glucose + HTC mixed with nitrogen or sulfur and by adding thiopene carboxaldehyde and pyrrole carboxaldehyde alone or together. Hao et al. (2014) have used the chemically activated AC (activated carbons) from beer waste and investigated the removal of methylene blue from water via adsorption technique and reported that the maximum uptake efficiency of the activated carbon was 341 mg/g. They also concluded that the removal of the dye depends on the pH values. Lower pH values inhibit the adsorption process and higher pH values favor the adsorption of dye. This is because higher pH values create negative charge on the exterior of the adsorbent and favor the uptake of dye (methylene blue molecule is positively charged).

4.7.2 Pesticide(s) adsorption

Much water pollution is caused by pesticides run off from agricultural fields. Only a few reports on adsorption of pesticides with HTCs are available. Zhao et al. (2016) have reported the elimination of pesticide paraquat (1, 1'-dimethyl-4 and 4'-bipyridyl dichloride) using hydrothermally activated PAN fibers and glucose solution as adsorbent. Hydrothermally activated PAN fibers HTC adsorbent was then activated with 1M NaOH for removal of paraquat. It was observed that when PAN fibers were used alone, the adsorbed amount was practically zero while it increases to about 50 folds when PAN fibers were subjected to hydrothermal treatment and it was further increased by three times after activation with NaOH.

4.7.3 Antibiotics/drugs adsorption

There are only limited reports available on the adsorption of drugs using HTCs. Zhu et al. (2014) have conducted the work of tetracycline adsorption using heat-activated HTC. This antibiotic is extensively used in veterinary medicine and aquaculture for the improvement of feed efficiencies and growth rates. It is released in environment as unmetabolized compound which results in the development of resistant bacterial strains which cannot be treated with present day antibiotics. Char has been observed to remove tetracycline quite efficiently at 700 °C temperature. The adsorptions of antibiotics were due to specific surface of HTC and not due to the functional groups as the functional groups were not sufficient in this HTC (Zhu etal. 2014).

4.7.4 Endocrine disrupting chemicals (EDC)

Municipal discharge and waste water in sewage treatment plants are major sources of EDC. These chemicals act like natural hormones and cause dysfunction of endocrine system. These compounds are mostly eliminated by degradation. Hydrothermal carbons have been used as adsorbents for removal of EDC bisphenol A, 17α-ethinylestradiol, and phenanthrene (Sun et al., 2011). The authors observed that during adsorption of EDC, the polar HTC can effectively remove the polar compounds than pyrolytic carbons.

4.8 Metals and metal ions adsorption by HTCs

Adsorption is one of the common methods for removing metal and metal ions from contaminated waters. HTCs have a more surface area than the activated carbons and have specific characteristic features which allow them to act as an efficient adsorbent of metal ions and metals. These characteristics include presence of higher number of functional groups, polarity, specific interaction with the metallic ions and acidic in nature. These features allow HTCs to attract positively charged metal ions and change the pH of solution due to higher functional groups on the surface so that it increases uptake of metals from aqueous phase. The metals like chromium, lead,

cadmium, and copper are considered as top priority toxic pollutants of water. These metals reach the waters through industrial effluents and wastes. Many reports are now available regarding removal of these metals and their ions using HTCs.

Shen et al. (2016) have used hydrothermal carbon made from chitosan for elimination of lead, chromium and cadmium. The chitosan (2-glucosamine and N-acetyl-2-glucosamine) is a promising adsorbent than the other adsorbent materials reported so far. Hydroxyl and amine groups of chitosan adsorb the metals and this makes it a good scavenger of metals. Chitosan is unstable in an acidic solution but adsorb lead and cadmium when pH levels are high, while adsorb chromium when pH levels are low. However, chitosan is unable to remove Cr (VI) as its removal is dependent over pH levels as it mostly found in anionic forms (CrO_4^{2-}, $HCrO^-_4$, and $Cr_2O_7^{2-}$), which can only be attracted towards the positively charges of the surface. Chitosan is chemically stable due to presence of hydroxyl and amino groups. However, this stability can be maintained with low temperature (140–220 °C) carbonization process which is only possible with HTC method. The hydroxyl and amino groups maintain the positive charge over chitosan HTC and can be used as adsorbent of Cr (VI). Shen et al. (2016) have obtained the highest removal capacity for chromium (343 mg/g) at a pH 4.0 followed by a saturation effect due to the availability of the favourable active sites on the adsorbent. The adsorbent was easily recycled by centrifugation followed by washing with NaOH. After recycling the adsorbent retain around 92% adsorption potential even after five cycles. However, the HTCs prepared at higher temperatures (200–220 °C) showed lower adsorption capacity due to destruction of functional groups.

Regmi et al. (2012) have conducted work on uptake of copper and cadmium using adsorption technique. Promising results of uptake of these metals were obtained in some of the experimental situations. They found that at low pH level (less than 5.0) the uptake of metal is very low due to presence of other similar cations in aqueous solution. This is due to protonation of HTC surfaces which cause the positively charged cations to repel away. The adsorption of copper and cadmium was pH dependent and copper was precipitated at a pH 7 while cadmium precipitated at basic pH(pH 10). However, both the metals were eliminated using HTCs mediated adsorption at pH 5. Similarly Liu and Zhang (2011) observed the same results when activated HTC was used for adsorption of Cu (II). They reported that copper has been adsorbed more with increasing levels of pH. Sun et al. (2015) investigated the removal of Cd(II) using HTCs remodeled using KOH. The results obtained in this work showed that the modified carbons exhibit higher adsorption capacity for cadmium and removed around 90% of cadmium while the HTCs which were not modified with KOH eliminate only 10% of cadmium from solution. This effect may be due to the availability of higher quantity of oxygenated ligands on the exterior of remodeled carbon. As described above (Regmi et al., 2012) the adsorption of metal using HTCs is pH dependent. Hence, it can be concluded that when pH levels are low the HTC surface gain positive charge which results inlow adsorbtion capacity of HTC while at higher pH levels the HTC surface gain negative charge which results in a higher adsorption capacity.

The HTCs prepared from acrylic acid and glucose having higher quantity of carboxyl ligands have been used for the adsorption of bivalent cadmium and lead (Demir-Cakan et al., 2009). In this study, it was observed that the rate of adsorption of both metals was higher when acrylic acid is used in higher quantity during the HTC synthesis. In a report by Chen et al., (2011) the bivalent cadmium and lead were adsorbed using activated HTC HTCs were activated by oxidation at 300 °C temperature to obtain the carboxyl groups. Due to the use of oxidized HTC the amount of metal adsorbed increased many folds and it was observed that in comparison to other common adsorbents, the oxidized HTC was found to be more superior with regard to the adsorbtion of bivalent lead while for bivalent cadmium it showed almost similar adsorption capacity as shown by other adsorbents.

Liu and Zhang (2009) have worked on removal of Pb(II) using HTCs. In their study it was observed that at very low pH levels (acidic pH) the removal of metal was low while at pH around or equal to 5, the rate of adsorption was maximum which further decreases when pH was further increased. At higher pH (more than 5) lead formed the hydroxylated compounds which led to the weakening of the association between metal and the negatively charged surface of HTC that resulted in a drop in metal adsorption. However, oxidizing the HTC with hydrogen peroxide greatly improved the adsorption of Pb(II) (Xue et al., 2012). It can be concluded from the above experiment that the surface of the HTC are rich in oxygen atoms which are active sites for the interaction with the metal (adsorption of bivalent lead).

4.9 Adsorption of metal(s) from mixture of metals

There are a only few reports available on removal of one or more than one metal from a mixture of metals via adsorption using HTCs (Sun et al., 2015). The rate of adsorption is higher when cations have smaller radii and HTCs have higher oxygen content. However, as the numbers of active sites on the exterior of HTCs are limited, the competition between different metal species for the active sites has been observed during the uptake process. Hence, the removal of a metal from a mixture of metals is very low than its removal from its pure solution. Similar results have been also observed by Xue et al. (2012) for the adsorbtion of heavy metals using HTC in columns from a blend of heavy metals in aqueous phase.

4.10 Adsorption of heavy metals using HTCs

Being a radioactive element uranium is one of the most important heavy metal studied for its recovery using HTCs as it is a nonrenewable resource and used for the generation of electricity. Due to the stability of carbonaceous materials from heat, acids, bases, and effect of radiation, they are most suitable adsorbents for heavy metal uptake. Yang et al. (2014) found that these materials can tolerate the radioactive radiation. For instance, when these materials were irradiated with gamma rays with a dose between 1 to 100 kGy it was observed that the maximum dose of gamma

radiation only slightly decreased the adsorption capacity which hardly affected the adsorption of U(VI). However, unmodified carbons show poor uptake of uranium due to presence of fever functional groups while on the other hand modified HTCs have higher quantity of oxygenated groups on its surface and hence have more affinity towards adsorbates like U(VI). Uranium is soluble at low pH (acidic pH up to 4.5) in moderate concentrations and found as uranyl cation (UO_2^{2+}). Many types of HTCs have been deployed for uptake of tetravalent uranium from its aqueous solutions which are discussed in the literature below.

Carbon microspheres HTCs were synthesized using *S. cerevisiae* cells using hydrothermal processes followed by their chemical recasting using the 'Hummers method' for increasing the quantity of functional ligands on HTC surface (Li et al., 2016). In contrast, Li et al. (2014) used polyphenols compounds used as an antidote against acute poisoning of uranyl cations. They obtained higher quantity of functional ligands (phenol groups) on stable HTC material surface by cross-linking polyphenols from bayberry tannins and glyoxal. Yang et al. (2014) reported the use of glyoxal with acrylonitrile to obtain large number of -CN groups which were allowed to react with NH_2OH -HCl to produce amidoxime groups at the surface of HTC to bind U(VI) efficiently.

Uranium has a tendency to form complexe with phosphates. Yu et al. (2014) used this characteristic of uranium and used another strategy to synthesize HTCs having phosphates groups. They synthesized the HTC from glucose and oxidized it at 300 °C in air. For obtaining the active functional site on the surface, the newly formed HTC was allowed to react with o-phosphoethanolamine and N, N^0-dicyclohexylcarbodiimide. Similarly, HTCs with phosphate groups were synthesized in one step process by blending phosphoric acid and glucose (Zhang et al.2014). Song et al. (2012) also used the same process for synthesis of a multidentate ligand which showed good selectivity towards actinides during a separation process involving 5-azacytosine column-actinide/lanthanide.

Liu et al. (2013) have reported better adsorption of U(VI) using HTC synthesized from pine needles. This HTC was obtained using a two-stage synthesis process followed by oxidation with 2 M HNO_3 for obtaining higher number of carboxyl groups. Zhang et al. (2013) have synthesized a new HTC using glucose and oxidized it at 150 °C and 300 °C and found that quantity of carboxyl ligands on the surface of HTC influences the adsorption capacity of uranium produced by the oxidation. Production of this functional group was directly proportional to the oxidation temperature and independent of time. Kumar et al. (2011) have also used much simpler processes to obtain HTC using biomass from switchgrass and *Panicum virgatum*. This HTC obtained from lignocellulosic material in one step process is not modified further for adsorption of uranium. Zhang et al. (2014) have synthesized HTC with chitosan which is rich in amino groups, easily available and a cost effective material for HTC synthesis.

It has been observed that the uptake of uranium is greatly influenced by variations in the pH (from 1 to 4.5). At highly acidic pH the rate of uptake is low while it is higher at a pH of 4. This is because at acidic pH the functional groups exist on the exterior of HTC get protonated and this positively charged exterior of HTC repelled the UO_2^{2+} ion resulting low adsorption rate at acidic pH. While, the positive charge

on HTC surface decreases with increase in pH which results in decreased repulsion and increased uptake of UO_2^{2+} ion. Some of the studies have used pH up to 8 for adsorption of UO_2^{2+} ion. If CO_3^{2-} ion forms a coordination compound with uranyl cation then uranyl cation can be soluble in aqueous solutions (Kumar et al., 2011) and the maximal adsorption is possible up to pH 6.0. It has been observed that if pH is more than 6.0, the UO_2^{2+} ion have a negative charge in the solution while at pH less than 6.0, U have a positive charge. The two factors which are responsible for adsorption of U are prevention of prolonged diffusion process due to the absence of developed porosity and the strong affinity between UO_2^{2+} ion and the active sites on the surface of HTC. It has also been observed that active sites present on the surface of HTC for adsorption of tetravalent uranium are less and their number is independent from the value of the specific surface of HTC (Liu et al., 2013). The adsorption capacities of some HTC for removal of uranium are shown in Table 4.2.

The various studies conducted by different workers on the uptake of tetravalent uranium ion using adsorption processes is given in Table 4.3. It can be observed from different reports that the uptake of uranium ion via adsorption strongly relies on the relative concentrations of tetravalent uranium ion and type of HTC used. Its uptake via adsorption also influences by the pH levels of aqueous solutions and the better adsorption rates are reported when the pH level is less than 5.0.

Another ion which has similar environmental effect is Th (IV). It is frequently found in sewage as it is used in many industrial applications and released in industrial discharge (Syed, 1999). This heavy metal is used in alloy synthesis and it is a chief source of energy production and is used in atomic reactor as nuclear fuel. Hence, it needs to be recovered. The similar char which was used for uptake of tetravalent uranium (Zhang et al., 2013) has been used by Zhou et al. (2015) for adsorption of Th (IV). The char was oxidized at medium temperatures in air for increasing the oxygenated functional ligands on its exterior and this activated char was used to remove maximum amount of Th (IV) at pH levels 3.5. A higher adsorption rate of Th (IV) was observed as the positive charge on the exterior of HTC declined and resulted in sedimentation of $Th(OH)_4$. The consequences of rise in temperature were also observed and it was found that the quantity of thorium removed was improved as the

Table 4.2 Reports on adsorption of tetravalent uranium.

S. No.	Adsorbent used	Time taken for adsorption (min)	Maximum adsorption capacity (%)	Reference(s)
1	5-azacytosine-functionalized HTC	5	90	Song et al. (2012)
2	Salicylideneimine-functionalized HTC	1	80	Wang et al. (2012)
3	Catechol-like phenolic ligand-functionalized HTC	1	88	Li et al. (2014)
4	Microorganism-derived carbon microsphere	10	80	Li et al. (2016)

Table 4.3 Adsorption of U (VI) by HTCs and adsorption capacity of HTCs at different parameters.

S.N.	Name of the sample	Conc. of HTC used (mg/L)	Initial conc. of tetravalent uranium (mg/L)	U (VI) uptake (mg/g)		Time (h)	pH	Temp. (°C)	Reference(s)
				Langmuir[a]	Experimental[b]				
1	HTC	5000	30	2.1	4.0	34	3.9	25	Kumar et al. (2011)
2	5-azacytosine-HTC	500	-	-	408.4	2	4.5	60	Song et al. (2012)
3	Salicylideneimine-HTC	500	119	292.8	261.8	-	4.3	-	Wang et al. (2012)
4	HTC	200	50	62.7	55.9	1	6.0	35	Liu et al. (2013)
5	HTC-COOH	200	50	205.8	176.0	1	6.0	35	Liu et al. (2013)
6	HCSs250	200	50	-	169.9	25 min	7.0	-	Zhang et al. (2013)
7	HCSs300	200	50	-	180.0	25 min	7.0	-	Zhang et al. (2013)
8	HTC-btg	400	400	332.2	307.3	2	4.5	25	Li et al. (2014)
9	HTC	200	-	80.0	-	2	6.0	25	Yu et al. (2014)
10	HTC-PO_4	200	-	434.8	-	2	6.0	25	Yu et al. (2014)
11	HCSs-PO_4^{-3}	200	≥110	285.7	261.8	1	5.0	25	Zhang et al. (2014a)
12	HCSs	200	≥110	80.0	64.9	1	6.0	25	Zhang et al. (2014b)
13	HCC	-	-	264.6	-	-	-	-	Zhang et al. (2014b)
14	HTC-AO	50	300	-	1021.6	2	4.5	25	Yang et al., (2014)
15	Oxy-HTCM	400	100	184.8	160.0	12	4.5	25	Li et al. (2016)

[a] *Langmuir isotherm model data of adsorption.*
[b] *Experimental data of maximum adsorption.*

temperature increased. This is due to the fact that as the temperature rises, the HTCs have more oxygen content to adsorb thorium.

From above information it can be concluded that the hydrothermal carbonization method can be used as an alternative to the classical pyrolysis method. This procedure is included in Green Chemistry and has many advantages over classical methods, such as better yield, cost effective, energy efficient, requirement of low temperature and use of wet raw materials. The HTCs obtained have more active sites on their surface due to presence of higher quantity of oxygenated functional groups and different templates can also be used to activate the HTCs to increase its porosity. Due to these characteristics HTCs can be used for adsorption of a wide variety of pollutants. However, they also require some specific reaction conditions such as pH and temperature. The work on HTCs still requires indepth investigations and they have a wide range uses in adsorption regimes.

4.11 Use of cost-effective adsorbent for adsorption of heavy metals

Heavy metals are released through almost all modern economic activities and have been deployed in various processes since many years. But now these elements like zinc, cadmium, lead, copper, and nickel are found in waste water streams. These heavy metals ions have been released in water resources from battery manufacturing, mining operations, smelting industries and electroplating industries. Theses ions have several adverse effects on human health and hence these heavy metals required to be removed from effluent using available technologies like coagulation, precipitation, electrochemical treatment, membrane filtration, adsorption and ion exchange. In the present section use of cost-effective adsorbents for uptake of these elements, such as cadmium, lead, and zinc will be discussed.

4.12 Uptake of metals using low-cost adsorbent materials

Waste materials can be reprocessed and reused as low cost resource and can be used for synthesis of adsorbents which can be used to make whole adsorption process economically viable. The materials such as wastes from agricultural processes, industries, mineral wastes, and marine materials can be deployed for synthesis of cost-effective adsorbents. The use of these materials in adsorption process has been discussed in details as under:

4.13 Use of agricultural residues as adsorbents

Waste materials from agriculture are environment safe and economic sources for synthesis of low-cost adsorbent materials. These materials are easily and abundantly available. Various agricultural wastes can be recycled and used for removing many

types of contaminants from waste discharge. The composition of agricultural wastes mainly includes starch, cellulose, lignin, hemicelluloses, simple sugars, lipids, proteins, and hydrocarbons. These components of agriwaste are rich in functional groups which can act as potential materials for uptake of heavy metal via adsorption. These materials can be recycled to develop adsorbent of desired particle size and can be used directly, after pre-treatment or after modification for uptake of contaminants from waters. The pre-treated agriwaste adsorbent have been extensively studied. Pre-treatment of these materials results in development of more active sites on their surface due to the activation of functional groups which leads to development of higher affinity towards pollutants to be removed. Table 4.4 shows the application of agricultural wastes as adsorbent, for uptake of lead, cadmium, and zinc.

Lignocellulosic material of sugarcane bagasse consists of a wide variety of active sites due to its complex configuration. An efficient adsorbent can be prepared from modified sugarcane bagasse for removal of heavy metals (Orlando et al., 2002; Karnitz et al., 2007). Similarly, succinic anhydride can be modified as an effective adsorbent of metals after pretreatment. The chemical introduction of polyamine create amide and carboxylic functions in succinic anhydride and the wastewater containing heavy metals can be effectively treated with this modified succinic anhydride. The metals like lead, zinc, cadmium, and copper are attracted towards the succinic anhydride-polyamines adsorbent due to its chelating nature (Bianchi et al., 1991).

The *Agave salmiana* bagasse was successfully modified to be used as adsorbent of heavy metals with different modifying agents viz. tartaric acid, oxalic acid, citric acid, HNO_3, HCl, and NaOH (Velazquez-Jimenez et al., 2013). The remodeled bagasse were then used to uptake Pb(II), Cd(II), and Zn(II) ions from their solutions at pH = 5.0.The desorption was conducted at 25 °C and pH 2.0 and 4.0. The main functional group responsible for metal uptake was carboxylic groups. It was observed that the metal removal capacities of untreated bagasse were 36, 14 and 8 mg/g for lead, cadmium, and zinc, respectively. The bagasse was then treated with various modifying agent mentioned above and it was observed that the treatment of oxalic, citric, and tartaric acid did not improve the adsorption capacity of raw bagasse. However, when bagasse treated with HNO_3 and NaOH, the adsorption capacity of bagasse was improved up to 27–62%.

Demiral and Güngor (2016) converted the grape bagasse to activated carbons using phosphoric acid. It was observed that at carbonization temperature of 500 °C, this activated carbon had maximum surface area (1455 m^2/g) and pore volume (0.88 cm^3/g). The activated carbon was then applied as an adsorbent for removal of copper from waste water. The highest removal capacity (43.47 mg/g) of this adsorbent was observed at 45 °C. Gurgel and Gil (2009) have used succinylated sugarcane bagasse (MMSCB 1) for preparation of new adsorbents, MMSCB 3 and MMSCB 5. The maximum adsorption capacities for copper, cadmium, and lead were observed as 59.5 and 69.4, 86.2 and 106.4, and 158.7 and 222.2 mg/g, for MMSCB 3 and MMSCB 5, respectively.

In a study, the grafted copolymerization-modified orange peels were used for the uptake of cadmium, lead, and nickel (Feng et al., 2011). As compared to the

Table 4.4 Different low cost adsorbents used for remediation of Pb, Cd, and Zn.

Metal ion	Adsorbent material	Adsorption capacity (mg/g)	Reference(s)
Pb^{2+}	Activated NMF	3.2 mmol/g	Xu et al. (2015)
	Agave bagasse (HCl)	42.31	Velazquez-Jimenez et al. (2013)
	Agave bagasse (HNO_3)	54.29	Velazquez-Jimenez et al. (2013)
	Agave bagasse (NaOH)	50.12	Velazquez-Jimenez et al. (2013)
	Agave bagasse (raw)	35.60	Velazquez-Jimenez et al. (2013)
	Banana peel	2.18	Anwar et al. (2010)
	Black liquor	18.65	Srivastava et al. (1994)
	Blast furnace sludge	64.17–79.87	Lo´pez-Delgado et al. (1998)
	$Ca(OH)_2$-modified muskmelon peel	0.81 mmol/g	Huang and Zhu (2013)
	Cancrinite-type zeolite from fly ash	2.53 mmol/g	Qiu and Zheng (2009)
	Chitosan	0.036 mmol/g	Rangel-Mendez et al. (2009)
	Clinoptilolite	27.7	Sprynskyy et al. (2006)
	Cross-linked chitosan with epichlorohydrin	34.13	Chen et al. (2008)
	Fly ash	76.06%	Hegazi (2013)
	Kaolinite	5.3	Gupta and Bhattacharyya (2008)
	KCl-modified orange peel	141.84	Guo et al., (2011)
	Lentil husk	81.43	Basu et al., (2015)
	Mercerized garlic peel	109.05	Liu et al., (2014)
	Montmorillonite	21.7	Gupta and Bhattacharyya (2008)
	NaCl-treated clinoptilolite	122.40	Günay et al. (2007)
	Native garlic peel	51.73	Liu et al. (2014)
	Natural zeolite	1.71 mmol/g	Peric´ et al. (2004)
	Natural zeolite	99.9%	Wingenfelder et al. (2005)
	Olive pomace	0.074 mmol/g	Pagnanelli et al. (2003)
	Orange peel xanthate (XOP)	218.34	Liang et al. (2010)
	Padina pavonica (brown algae)	210	Jalali et al. (2002)
	Ponkan peel	112.10	Pavan et al. (2008)

Table 4.4 Different low cost adsorbents used for remediation of Pb, Cd, and Zn. *Continued*

Metal ion	Adsorbent material	Adsorption capacity (mg/g)	Reference(s)
	Raw clinoptilolite	80.933	Günay et al. (2007)
	Red mud	64.79	Lo´pez et al. (1998)
	Rice husk	87.18%	Hegazi (2013)
	S. natans (brown algae)	224	Jalali et al. (2002)
	Sargassum hystrix (brown algae)	265	Jalali et al. (2002)
	Sargassum sp.	1.16	Sheng et al. (2007)
	Seaweed	1.78 mmol/g	Ahmady-Asbchin et al. (2009)
	Sulfured orange peel	164.00	Liang et al. (2011)
	$ZnCl_2$-activated grapefruit peel	12.73	Pei and Liu (2012)
Cd^{2+}	Activated NMF	2.1 mmol/g	Xu et al. (2014)
	Agave bagasse (HCl)	12.50	Velazquez-Jimenez et al. (2013)
	Agave bagasse (HNO_3)	13.50	Velazquez-Jimenez et al. (2013)
	Agave bagasse (NaOH)	18.32	Velazquez-Jimenez et al. (2013)
	Agave bagasse (raw)	13.27	Velazquez-Jimenez et al. (2013)
	Alkali-pretreated *Ulva onoi* (green algae	90.70	Suzuki et al. (2005)
	Bagasse fly ash	1.24	Gupta et al. (2003)
	Banana peel	5.71 mg/L	Anwar et al. (2010)
	Bentonite	0.084 mmol/g	Purna Chandra Rao et al. (2006)
	Blast furnace slag	18.72	Gupta et al. (1997)
	Blast furnace sludge	6.74–10.15	Lo´pez-Delgado et al. (1998)
	Ceramium virgatum (red algae)	39.7 mmol/g	Sarı and Tuzen (2008)
	Chemically modified chitosan	357.14	Sankararamakrishnan et al. (2007)
	Chitin	13.00	Benguella and Benaissa (2002)
	Chitosan	85.47	Sankararamakrishnan et al. (2007)
	Chitosan	0.016 mmol/g	Rangel-Mendez et al. (2009)
	Citric acid-modified orange peel	0.90 mmol/g	Li et al. (2007)

(*continued*)

Table 4.4 Different low cost adsorbents used for remediation of Pb, Cd, and Zn. *Continued*

Metal ion	Adsorbent material	Adsorption capacity (mg/g)	Reference(s)
	Clinoptilolite	4.22 mg/L	Sprynskyy et al. (2006)
	Fly ash	73.54%	Hegazi (2013)
	Grapefruit peel	42.09	Torab-Mostaedi et al. (2013)
	HCl-modified *Cucumis sativus* peel	58.14	Pandey et al., (2014)
	Illite	350 mmol/kg	Echeverrı´a et al. (2002)
	Jatropha oil cake	85%	Garg et al. (2008)
	Kaolinite	4.00	Gupta and Bhattacharyya (2008)
	KCl-modified orange peel	125.63	Guo et al. (2011)
	Laminaria japonica (brown algae)	1.85 mmol/g	Liu et al. (2009)
	Maize corncob	99%	Garg et al. (2008)
	Montmorillonite	21.6	Gupta and Bhattacharyya (2008)
	Natural zeolite	85.8%	Wingenfelder et al. (2005)
	Olive pomace	0.062 mmol/g	Pagnanelli et al. (2003)
	Orange peel xanthate (XOP)	76.57	Liang et al. (2010)
	Red mud	10.57	Lo´pez et al. (1998)
	Rice husk	67.92%	Hegazi (2013)
	Sargassum sp.	0.76	Sheng et al. (2007)
	Sawdust	94.5%	Naiya et al. (2009)
	Seaweed	0.85 mmol/g	Ahmady-Asbchin et al. (2009)
	Sugarcane bagasse	99.5%	Garg et al. (2008)
	TBA-derivative kaolinite	6.31	Gupta and Bhattacharyya (2006)
	TBA-derivative montmorillonite	43.47	Gupta and Bhattacharyya (2006)
	Ulva onoi (green algae)	61.90	Suzuki et al. (2005)
	Unmodified rice straw	13.90	Ding et al. (2012)
	Wheat stem	0.10 mmol/g	Tan and Xiao (2009)
	ZrO-derivative kaolinite	5.27	Gupta and Bhattacharyya (2006)
Zn^{2+}	Activated NMF	2.0 mmol/g	Hadi et al. (2014)

Table 4.4 Different low cost adsorbents used for remediation of Pb, Cd, and Zn. *Continued*

Metal ion	Adsorbent material	Adsorption capacity (mg/g)	Reference(s)
	Agave bagasse (HCl)	12.40	Velazquez-Jimenez et al. (2013)
	Agave bagasse (HNO_3)	14.43	Velazquez-Jimenez et al. (2013)
	Agave bagasse (NaOH)	20.54	Velazquez-Jimenez et al. (2013)
	Agave bagasse (raw)	7.84	Velazquez-Jimenez et al. (2013)
	Bentonite	0.141 mmol/g	Purna Chandra Rao et al. (2006)
	Bifurcaria bifurcate (brown algae)	30.3	Freitas et al. (2008)
	Black liquor	95.0	Srivastava et al. (1994)
	Blast furnace slag	17.66	Gupta et al. (1997)
	Blast furnace sludge	4.25–9.25	Lo´pez-Delgado et al. (1998)
	Cancrinite-type zeolite from fly ash	1.532 mmol/g	Qiu and Zheng (2009)
	Cross-linked chitosan with epichlorohydrin	10.21	Chen et al. (2008)
	Fucus spiralis (brown algae)	34.30	Freitas et al. (2008)
	KCl-modified orange peel	45.29	Guo et al. (2011)
	Laminaria japonica (brown algae)	1.42 mmol/g	Liu et al. (2009)
	Mango peel	28.21	Iqbal et al. (2009)
	Nano-porous-activated neem bark	11.90	Maheshwari et al. (2015)
	NaOH-treated *Eucalyptus sheathiana* bark	250.00	Afroze et al. (2016)
	Natural zeolite	0.812 mmol/g	Peric´ et al. (2004)
	Natural zeolite	93.6 %	Wingenfelder et al. (2005)
	Orange peel xanthate (XOP)	49.85	Liang et al. (2010)
	Raw *Eucalyptus sheathiana* bark	128.21	Afroze et al. (2016)
	Red mud	12.59	Lo´pez et al. (1998)
	Rice husk ash	7.15	El-Said et al. (2011)
	Seaweed	0.71 mmol/g	Ahmady-Asbchin et al. (2009)
	Sulfured orange peel	80.00	Liang et al. (2011)
	Ulva fasciata sp. (green algae)	13.50	Prasanna Kumar et al. (2007)

unmodified orange peel, adsorption of lead and cadmium using modified material increased to 4.2 and 4.6 folds respectively. The highest uptake for lead and cadmium were reported to be 476.1 and 293.3 mg/g respectively using modified orange peel. Afroze et al. (2016) have recently used base-modified and unmodified bark of *Eucalyptus sheathiana* to test the removal of zinc ions from industrial discharge. The results of zinc removal were quite comparable with other types of adsorbent materials. The maximum adsorption capacity for removal of zinc from effluent using modified eucalyptus bark at 30 °C was reported as 250.0 mg/g. Basu et al. (2015) have used lentil husk as cost effective adsorbent and observed the highest removal capacity (81.43 mg/g) for lead at 30 °C and pH 5.0. Rice husk has silica as the major component and some portion as alumina. These compounds can be used for synthesis of zeolite and alumina coated carbon nanotubes which are good scavenger of metals from aqueous solutions (Gupta et al., 2011). Zeolite was synthesized from rice husk ash (RHA) and used in cadmium-contaminated wastewater for removal of cadmium (Santasnachok et al., 2015). At dosage of 0.25 g/L of adsorbent, maximum cadmium removal capacity of 736.38 and 684.46 mg/g were observed using manufactured zeolite Na-A and Na-X, respectively.

4.14 Uses of industrial wastes as adsorbents

Industrial wastes are very difficult to manage. Fly ash generated from combustion processes is a major waste material of power plants and allied industries. It has been used for production of bricks, cement and road construction. Fly ash has good quantity of silica and alumina and can be used as raw material for synthesis of adsorbent like zeolite (Bhatnagar and Sillanpaa, 2010). Several reports are available in which fresh fly ash, modeled fly ash and dispersed TiO_2-fly ash are used for uptake of metals ions from contaminated or waste waters (Gupta and Ali 2004; Harja et al., 2012; Shyam et al., 2013).

A byproduct released from the aluminum industry is known as 'red mud' which is used as adsorbing material for water treatment. It is composed of small fragments of aluminum, silicon, iron, hydroxides, and titanium oxides. Due to its high alkaline nature, red mud is required to be neutralized before its conversion to an adsorbent. Zhu et al. (2007) have used granular red mud (GRM) as a good adsorbent for cadmium and observed the maximum uptake capacities as 38.2 mg/g Cd at 20 °C, 43.4 mg/g Cd at 30 °C, and 52.1 Cd mg/g at 40 °C from aqueous solutions.

In another study, Gupta et al. (2001) have prepared a cost-effective adsorbent from red mud and utilized it for uptake of lead and cadmium from blended waters. The red mud was oxidized by treating with H_2O_2, washing with distilled H_2O and then its activation at 500 °C for 3 hours in a muffle furnace. Using this activated adsorbent the highest elimination of lead was seen at pH level 4.0. The major waste from steel industries, basic oxygen furnace (BOF) slag, was used to study the uptake of metal like copper, cadmium, lead, and zinc from waste waters (Xue et al., 2009; Xue et al., 2013). Black liquor is a waste from the paper industry which is produced

in large amount. From this material lignin can be extracted which can be modified and used for uptake of lead and zinc from waste waters (Srivastava et al., 1994). The adsorbent synthesized from black liquor has been used for uptake of lead and zinc and it was observed that the metal uptake increases with the rise in pH, and lead was more efficiently removed than zinc.

Animal skins obtained from the leather industry have been utilized for removal of iron and chromium (Fathima et al., 2005). They have high protein content which can make complexes with iron. The iron treated fleshing is then used for elimination of chromium (VI) from solutions. The iron-treated material shows improved adsorption capacity, i.e. 51 mg of chromium (VI)/ g of treated fleshing in comparison to untreated flesh with 9 mg/g. However, till date, adsorbent derived from animal skin have not been used for uptake of other metals. The adsorption capacities of other adsorbent synthesized from industrial waste for uptake of zinc, cadmium, and lead have been mentioned in Table 4.4.

4.14.1 Marine materials

Chitin is a polysaccharide found in large quantity in the the exoskeletons of marine animals like crabs and arthropods. Chitin is a waste material from sea food processing industries and can be used for synthesizing adsorbent(s) (Rinaudo, 2006). It has large amount of polysaccharides, which is easily available from sea food packing and processing industries. Chitin can be modified as good adsorbent of metal ions from aqueous solutions (Benaissa and Benguella, 2004; Karthik and Meenakshi, 2015).

Chitosan is a biopolymer of acetylated glucosamine which can be synthesized from deacetylation of chitin. It is one of the most important derivatives of chitin due to its biodegradability, hydrophilicity, and antibacterial property (Rinaudo, 2006). It has been found that chitosan develop amino groups on its surface during deacetylation process and therefore adsorb six fold more metals than chitin. The adsorbents made from chitosan have been used for uptake of heavy metals from wastewaters (Pandey and Tiwari, 2015; Chen et al., 2017). The capacities of chitosan microcapsules synthesized via cross-linking have been tested for uptake of various metals and metallic ions including cadmium, copper, and zinc (Sargın and Arslan, 2015). The effects of different reaction conditions like amount of adsorbent used, contact time, reaction temperatures, pH etc. on adsorption of these metals have also been studied. The uptake capacity of microcapsules for cadmium and zinc was reported as 0.15mmol/g and 0.25mmol/g respectively. The removal/adsorption capacities of adsorbents synthesized from marine material for uptake of heavy metal have been given in Table 4.4.

4.14.2 Clay and zeolite

Zeolites, clays, soil, and sediment are costeffective materials available easily for synthesis of adsorbent and can be used as precursors of adsorbent or low-cost adsorbent materials. Soil and sediments can be used for uptake of organic contaminants like glyphosate (Morillo et al., 2000) and other herbicides (Kibe et al., 2000) from

contaminated solutions. Similarly, clay and zeolite are cost- effective adsorbent and have good uptake capacities for metal and metal ions. The use of clay and zeolite as adsorbent for uptake of cadmium, lead, and zinc are listed in Table 4.4.

Zeolites are highly porous naturally occurring minerals of aluminosilicate. They have diverse cavity structures and can also be synthesized commercially. Zeolites can chelate various cations like calcium, sodium, magnesium, potassium and other ions due its porous structure. They possess ion-exchange abilities because the cations are loosely attached to the zeolite. Hence, it is possible to exchange adsorbed ions with rest of metal ions. Clinoptilolite is the most investigated zeolite out of more than 40 natural species. Sprynskyy et al. (2006) have used fresh and pretreated clinoptilolite to study the uptake of lead and cadmium and observed that the highest removal capacities of clinoptilolite material were 4.22 mg/g and 27.7 mg/g for Cd^{2+} and Pb^{2+}, respectively when starting concentration of metal was set 80mg/L. Similar study has also been conducted by Wingenfelder et al. (2005) for uptake of metal ions (Pb, Cd, and Zn) from mine waters using native zeolite. They observed that the elimination of zinc and cadmium is pH dependent and decline in their uptake was observed at low pH while the uptake of lead was independent of pH change. Hence lead was removed from mine waters at both acidic and neutral pH.

Clay is a negatively charged fine silicate mineral having large surface area. It shows higher uptake of metal ions due to negative charge on its surface. The metals ions have high affinity towards negative charge of clay which can be compensated by uptake of positively charged metal cations (Ali et al., 2012). Different variety of clay materials have been explored, modeled and used to synthesize adsorbent having high efficiency of metal uptake. The two most important clay material used for removal of heavy metals are montmorillonite and kaolinite. Gupta and Bhattacharyya (2008) have studied removal cadmium and lead from water using kaolinite and montmorillonite. They observed that the metal uptake by clay adsorbent is pH dependent and increase with increase in pH, while it slows down when insoluble metal hydroxides are produced. The rate of adsorption was observed to be very fast and lead was maximally adsorbed within 180 min while cadmium was adsorbed in 240 min. The uptake capacities of other zeolite, clay derived adsorbents used for uptake of lead, zinc, and cadmium have been listed in Table 4.4.

Heavy metals can be effectively and efficiently removed from effluent using adsorption process. The most popular adsorbent material for waste water treatment is activated carbon which has been used extensively for the treatment of impure water since many years. However, the cost of its production and low efficiency for heavy metal uptake are some of the major drawbacks of commercial activated carbons. Hence, some costeffective suitable alternatives are required to replace traditional activated carbon. In this situation the costeffective adsorbent from agriculture and industrial wastes along with lowcost natural adsorbent can be a solution of this problem. However, the cost effective adsorbent have low adsorption capacity which is requires scale up using cheap and effective modification methods. By developing low-cost treatment methods, activation methods and analyzing the composition of these materials, they would become better adsorbent for removal of pollutants.

4.15 Adsorption/biosorption of antibiotics from waste water

Novel contaminants are constantly added to the ecosystem and their maximum allowable concentrations are not governed by any regulations which lead to various illeffects on ecosystem (Halling-Sorensen et al., 1998; Calamari 2002; Adler et al., 2008; Cooper et al., 2008; Rivera-Utrilla et al., 2013). Different compounds like domestic products (glass cleaners, degreasants, and detergents), cosmetics (makeup products, creams, and perfumes), and pharmaceuticals products are such materials which are due to their wide varieties and extensive uses are of great concern (Adler et al., 2008; Cooper et al., 2008; Rivera-Utrilla et al., 2013). Now days, the most extensively used medical drugs are antibiotics used for human and animals. Antibiotics and their byproducts have been added to the environment through excreta which reaches to waste water through municipal discharge. Very high concentrations of antibiotics and their derivatives are now observed in wastewaters, affecting its quality and hence required to be removed for safe use. These compounds are highly toxic (Kümmerer, 2001), less biodegradable (Al-Ahmad et al., 1999; Kümmerer et al., 2000) and can even cause health hazardous (Bendesky et al., 2002).

Antibiotics such as tetracyclines (TCs) and nitroimidazoles are most important group of such materials which have been spotted in waters (Halling-Sorensen et al., 1998; Calamari, 2002; Rivera-Utrilla et al., 2013). They inhibit the bacterial protein synthesis and destroy the good bacteria in waste waters. Hence, waste waters containing these compounds requires urgent treatment. As aforementioned, activated carbon is one of the most commonly used adsorbent for uptake of contaminants. So, it is extensively used for the treatment of waste waters and removal of contaminants. Granular activated carbons (GAC) and powdered activated carbons have such chemical and textural characteristics that makes it useful for uptake of organic and inorganic pollutants from contaminated waters (Radovic et al., 2001; Moreno-Castilla 2004; Dias et al., 2007; Rivera-Utrilla et al., 2011; Beita-Sandi et al., 2016). The activated carbon has the capability of removing the toxic pharmaceutical-related pollutants from solution, hence it has fascinated the attention of workers (Snyder et al., 2007; Choi et al., 2008; Simazaki et al., 2008; Yu et al., 2008; Calisto et al., 2015; Vidal et al., 2015; Zhu et al., 2015).

Snyder et al. (2007) have studied the uptake of many pharmaceuticals and hormones using granular and powdered activated carbons and observed promising results with around 90% removal of most of the pharmaceuticals studied. Maximum uptake results observed were triclosan (90–96%), fluoxetine (91%), acetaminophen (73–84%), and carbamazepine (74–86%) while only 50% for removal percentage was observed in case of gemfibrozil, diclofenac, naproxen, ibuprofen, and sulfamethoxazole. They observed that the existence of natural organic matter (NOM) with pharmaceutical products block the porosity and reduces the effectiveness of activated carbon by occupying the active sites on the carbon. Many reports are also available where uptake of tetracyclines has been reported using adsorbents like soils and clays (Figueroa et al., 2004; Kulshrestha et al., 2004; Jones et al., 2005; Basakcilardan-Kabakci et al., 2007; Turku et al., 2007; Parolo et al., 2008; Gu and Karthikeyan 2008; Chang et al., 2012) and apatites (Misra, 1991).

Jones et al. (2005) have observed that the soils which have organic carbon content (0-4%), in such soils the uptake of tetracyclines is largely influenced by the factors such as soil texture, existence of iron oxide and cation exchange capacity. Parolo et al. (2008) investigated the results of pH and ionic strength on the elimination of tetracycline on montmorillonite and found that the tetracycline can be inserted in the space between two layers of montmorillonite. The highest elimination of tetracycline was reported at pH 4.0 due to cationic nature of tetracycline at this pH which favors the cation exchange. However, the uptake by montmorillonite was observed to be reduced in the presence of sodium ions.

Different carbon materials like multiwalled carbon nanotubes (Zhang et al., 2011), graphene oxide (Gao et al., 2012), and $MnFe_2O_4$/activated carbon composites (Shao et al., 2012) can also be employed for uptake of tetracycline from waste or contaminated waters. However, only a few researches has been done on uptake of tetracycline using activated carbon. Choi et al. (2008) have obtained 90% removal of tetracycline using activated carbon columns and found it very effective adsorbent for seven types of tetracycline. The adsorption capacity of these compounds varied according to the type of tetracycline, concentration of natural organic matter, and characteristics of the water. It is also observed that irrespective of the greater hydrophobicity of sulfonamide, the activated carbon has more affinity towards tetracycline.

Carrales-Alvarado et al. (2014) have studied the uptake of nitroimidazoles using some new carbon compounds having variable textural and chemical properties. These properties have major role in the removal of metronidazole (MNZ) from contaminated waters. Nitroimidazoles was effectively removed from aqueous solution using carbon materials having low content of carboxylic groups and large surface area. The uptake of MNZ on carbon adsorbent is remissible, hence after the adsorption process the used carbon adsorbents were regenerated by washing them with water. Ahmed and Theydan (2013) analyzed adsorption kinetic data of metronidazole (MNZ) and concluded that the uptake of MNZ with activated carbon synthesized from agricultural by-products pursues a pseudo second order and from heat production data it has been observed that the uptake of MNZ via adsorption was endothermic.

4.16 Elimination of heavy metals via adsorption/biosorption

Adding of heavy metals to the environment through anthropogenic activities has severe effect on environment and on animals and humans. Heavy metals released from various industrial activities get accumulated in groundwater and surface waters. Various methods for uptake of heavy metals from water include reverse osmosis, chemical precipitation, ion exchange by resins, and evaporation. These methodologies are costly due to use of expensive materials and equipments, and are not sufficient for uptake of heavy metals to maintain the threshold values (10–100 ppm) of heavy metals in water as per current regulation.

In present situation biosorption is a competitive technological solution for above mentioned problems (Wang and Chen, 2009). In this method biomolecules or biomasses are used to attach metal ions and enhance their uptake from water.

For instance, bacteria, algae, fungi, and yeasts are some biomasses investigated for the uptake of heavy metals from contaminated water (Davis et al., 2003; Ahluwalia and Goyal, 2007; Volesky 2007; Wang and Chen, 2009). The major benefits of this method is uptake of metal ions even from low concentrations (0–100 ppm) using biodegradable, cost-effective, and efficient adsorbent materials (Ahluwalia and Goyal, 2007; Wang and Chen, 2009).

4.17 Heavy metals uptake using activated sludge and sludge-derived materials

Biosorption is the process of removal of pollutants from waste water using biological material or organisms. In last few years, biosorption has been used for removal of pollutants from waste waters and it is an efficient and cost-effective method of water purification (Miretzky et al., 2011; Wu et al., 2011). Several types of nonliving biomass have been used as biosorbent development and studied for their capacity of heavy metal removal. These different biomasses used as biosorbent includes bacteria (Ahluwalia et al., 2007), marine algae (Vijayaraghavan et al., 2005), and others (Singh et al., 2007) and these biomaterial or biopolymers are used as sorbent. The activated sludge is a process in which masses of microorganisms like bacteria, fungi, and protozoa are suspended in loose clumps by stirring (Rajasulochana and Preethy, 2016). Todd and Josephson (Todd and Josephson, 1996) have treated sewage water using biological methods. The microbes can remove the contaminants by consumption of organic material, adsorption and assimilation. The biofilm of microbes can remove the organic matter, heavy metals, nitrates, phenol, quinoline, pentachlorophenol, trichlorophenol, and sulfates (Rajasulochana and Preethy, 2016).

Heavy metals are non-biodegradable hence, their removal from contaminated water is a big challenge. Therefore, there is need to devise some low cost technologies which can efficiently adsorb the heavy metals from waste water. Heavy metal ions can be removed from aqueous solutions using several active and inactive organisms as biosorbents. Biosorbents are rich in the functional groups or organic ligands (like sulfate, carboxyl, phosphate, hydroxyl, and amine groups), which play major roles in removal of heavy metal contaminants. The current technologies and processes used for purification of contaminated water are reduction, precipitation, adsorption, membrane filtration, and coagulation. These methods have several drawbacks, especially they are unable to remove heavy metals from waste waters when concentrations are very high. Hence, for uptake of heavy metals from water, agricultural wastes and activated carbon adsorbent synthesized from agricultural residues can be used as costeffective material (Babel and Kurniawan, 2003; Ahalya et al., 2005; Wang et al., 2009). Algal biomass is one of the most promising biomaterial used for uptake of heavy metals (Gupta et al., 2001; Volesky, 2001; Zeroual et al., 2003; Kalyani et al., 2004;Vijayaraghavan et al., 2005; El-Sikaily et al., 2007; Han et al., 2008; Deng et al., 2009; Gupta and Rastogi 2009; Ncibi et al., 2009; Zakhama et al., 2011). Marine algae polysaccharides have carboxylic (–COOH), sulfonic

($-SO_3H$) and hydroxyl (–OH) groups, which play major role for heavy metal uptake by marine algae (Mckay et al., 1999; Davis et al., 2003). Harja et al. (2015) investigated the uptake of cadmium in batch and column studies using oil extraction from algaal waste. The oil extraction was done by alkaline treatment and the treated algae were effective for uptake of cadmium II. Mashkani and Ghazvini (2009) have used chemically modified Azolla as biosorption material to remove the Cs (Cesium) and Sr (Strontium) solutions and the highest elimination was obtained at pH 8.8. The dried algae culture was used as bisorption material to remove the heavy metals from solutions in batch and continuous reactors (Zakhama et al., 2011). EI Nemr et al. (2011) studied the uptake of chromium (VI) using both normal and activated carbon from marine red alga *Pterocladia capillacea* obtained by acid dehydration. Soltmann et al., (2010) used the silica sols to immobilize or encapsulate the algaal biomass of micro algae (*Spirulina* etc.) and macro algae (*Fucus*) and studied the efficiency of the immobilized algae for uptake of chromium, nickel, lead, and copper from drinking water. Chao et al. (2013) prepared chars from the macro brown algae *Undaria pinnatifida* using physical and chemical methods and tested this material for uptake of copper and observed that the small amount of char has the highest efficiency to remove the metals even at low concentration. However, this study was not for industrial application as preparation of chars requires costly equipment and the growth of macro algae is very slow. Daniel et al., (2005) used the algal and bacterial biomass together for uptake of copper and cadmium from factories discharge and observed acceptable efficiency of this biomass in the uptake of these metals.

In the last few decades, many reports have been published which illustrate the use of various biomasses in uptake of heavy metals from wastewaters. Irrespective of huge interest of workers in this method, the practical application of this process is still facing problems due to lack of a unified and systematic network for designing and development of process. Moreover, clogging of biomass, less mechanical strength, low particle size of biomasses used are obstacles in the large-scale application of biosorption. These problems can be overcome by immobilizing the biomass using polymeric beads which can increase the mechanical strength and particle size of adsorbent (Veglio and Beolchini, 1997) and also facilitate in binding with heavy metal ions without undergoing any reaction. Hence, the biomass should be immobilized using specific polymeric beads. But, the immobilization process of polymeric material must be cost effective.

4.18 Uptake of endocrine disrupting chemicals (EDC)

Endocrine disrupting chemicals (EDC) are novel water contaminants which can act like natural hormones and are now a day's reported in municipal discharge.Traditional wastewater treatment methods are unable to degrade these dangerous contaminants and these hazardous compounds entered into the food chain. These are non-biodegradable, highly toxic and highly persistent organic contaminants. These contaminants can imitate the natural hormone and affect the hormone systems of animal and humans and cause severe reproductive dysfunction, prostate and breast cancer (Ye et al., 2012).

The activated sludge is a process in which suspension of fine particles of microorganisms like bacteria, fungi, and protozoa are present in loose clumped masses (Rajasulochana and Preethy, 2016).Around 90% of waste and contaminated waters are successfully treated by using activated sludge derived materials in industrial and waste water treatment plants. This system has been extensively useful for removal of organic compounds found in contaminated waters. Several aerobic yeasts, bacteria and fungi and can degrade the compounds of carbon and hydrogen (hydrocarbons) to CO_2 and H_2O. Most of the pulp and paper industrial discharge is treated through anaerobic processes in contact reactors. Vidal and Diez (2005) have observed that sludge absorption, aeration volatilization, primary settling, and chemical precipitation degrade only a small part of EDCs and the maximum degradation of EDC is due to biodegradation.

Zhang and Zhou (2008) studied the uptake of six different estrogen compounds from municipal waste waters using plant material. Liu et al. (2009) compared the biodegradation and chemical oxidation methods for their role in uptake of EDC compounds. Gattullo et al. (2012) have used the variable concentrations of radish and ryegrass along with river natural organic matter and humic acid in HPLC to reduce nonylphenol in water. It was observed that both the plants are resistant to the nonylphenol and eliminate the nonylphenol (1 mg/l) at the time of germination. Gulnaz and Dincer (2009) have studied an algae and bacteria for their ability to remove the bisphenol and their intermediate products. Aeromonas (bacteria) and algaal culture were together used in this experiment and the yeast assay was carried out to study the endocrine disrupting action of bisphenol. It was observed that algae and bacteria together almost completely degraded the bisphenol and the product obtained after degradation also did not show any estrogenic activity. This method was also successfully used at industrial level. The experiment on comparative uptake of this chemical by bacteria and algae were also conducted and it was observed that the algae have higher efficiency for uptake of the organic and toxic chemicals. Zhou et al. (2014) used activated sludge along with the combination of four microalgae *Chlamydomonas reinhardtii*, *Chlorella pyrenoidosa*, *Scenedesmus obliquus*, and *Chlorella vulgaris* for uptake of metals, estrogenic and organic compounds from waste waters. This sludge derived integrated algal system work quite efficiently and successfully removed the entire organic and estrogenic compounds along with metals and various other contaminants. Microalgae *Scenedesmus* was observed to be the most efficient for complete uptake of estrogenic compounds. Hence, through algae-based remediation and activated sludge, the harmful EDC compounds can be removed cost-effectively.

4.19 Future prospects

Although huge efforts have been made to unravel the mechanism of adsorption in complex matrices but more comprehensive studies are still required. Many reports have been available regarding adsorption of water contaminants. But these studies

have been performed with high concentration of pollutants and the adsorption of emerging pollutants at low concentration is very limited.

The waste water treatment technique has its own limitations (technical and economic) in real-life situations. The adsorption process using hydrothermal carbonization method can be used as substitute to traditional pyrolysis. The adsorbent produced using hydrothermal carbonizations have more affinity towards pollutants to be adsorbed due to the presence of higher number of ligands on its surfaces. These functional groups are highly oxygenated and can also be activated by adding different templates for increasing their porosity which increases their adsorption capacities. However, they also require some specific reaction conditions such as pH, contact time and temperature. The work on HTCs is still in its infancy and requires more investigations for future applications. Similarly, the removal effeciency of organic compounds from water containing natural organic compounds using activated carbon is very low and can be improved for complete purification of waters. Hence, activated carbon must be modified to increase the complete adsorption of organic compounds. Moreover, the production cost of activated carbon needs to be reduced to make the whole process economically viable. Even though some attempts have been made to synthesize the modified value-added activated carbon from abundant and low-cost waste materials but more efforts are still required for the same.

The applications of agriculture by-products as adsorbent for elimination of lead, cadmium, and zinc are also very promising techniques. But the experimental conditions, adsorption capacities of different adsorbent, production of desired particle size, their recycling and washing are some of the limitation associated with low cost adsorbent. Moreover, the pretreatment of these adsorbent is required for increasing the functional groups and higher quantity of active sites for adsorption purposes.

Antibiotics in higher concentrations are highly toxic to marine life and for other terrestrial animals. The high amount of antibiotics and their derivatives are observed in wastewaters due to their release in municipal waste without proper treatment, hence, reducing the quality of usable waters (Kümmerer, 2001). These compound are cancer causing (Bendesky et al., 2002) and also slowly biodegradable (Al-Ahmad et al., 1999; Kümmerer et al., 2000). Different carbon materials like graphene oxide (Gao et al., 2012), $MnFe_2O_4$/activated carbon composites (Shao et al., 2012), and multiwalled carbon nanotubes (Zhang et al., 2011) have been used for uptake of antibiotics from water. However, only a few reports are available for removal of tetracycline using activated carbons. The adsorption capacity of the absorbents varies according to the type of antibiotics, concentration of natural organic matter and characteristics of the water. Hence, specific adsorbent are required to be developed for complete adsorption of antibiotics and other drugs from waste waters. Biosorption is a competitive technological solution for many problems associated with elimination of metal, metal ions and organic waste using traditional adsorbents (Wang and Chen, 2009). Biosorption process have several advantages like the use of biodegradable, cost effective and highly efficient adsorbent material for uptake of metal ions (Ahluwalia and Goyal 2007; Wang and Chen 2009). Irrespective of huge interest of

workers in this method, the practical application of this process is still facing problems due to lack of a unified and systematic network for designing and development of process. Moreover, clogging of biomass, less mechanical strength, low particle size of biomasses used are obstacles in the large-scale application of biosorption. These problems can be overcome by immobilizing the biomass using polymeric beads which can increase the mechanical strength and particle size of adsorbent (Veglio and Beolchini 1997) and also helps in binding with heavy metal ions to be absorbed without participating in the reaction. Hence, the biomass should be immobilized using specific polymeric beads. However, the immobilization process of polymeric material must be cost effective. Endocrine disrupting chemicals (EDC) are found in wastewater and are very difficult to be treated with conventional adsorbents. Vidal and Diez (2005) have observed that the degradation of EDC by sludge absorption, aerating volatilization, primary settling, and chemical precipitation is relatively very small and the maximum degradation of EDC is due to biodegradation. Hence, these compounds are required to be treated with specific attention. The nanomaterial based adsorbents are now attracting scientific community for their extensive use in adsorption process. The nanaomaterials can be used to increase the surface area of adsorbent to accommodate more pollutants particles in a smaller space. They can also be used to add specific functional groups on low-cost adsorbent and on activated carbon to adsorb heavy metals and other emerging contaminants effectively and efficiently with high accuracy. Therefore, it is suggested that more meticulous researches are required on the adsorption to achieve a clear understanding of the mechanism of adsorption of emerging pollutants and development of new adsorbents with specific adsorbing efficiency.

4.20 Conclusion

The present book chapter explained the removal of various emerging water pollutants added to water from anthropogenic and geogenic or natural processes, using adsorption regimes and includes the application of newly synthesized adsorbents for the elimination of these contaminants. The adsorbents like hydrothermal carbonization (HTC), hydrochars, low-cost adsorbents, activated carbons, and sludge derived materials have shown promising results as adsorbent and can be used for uptake and removal of various pollutants. The presence of different functional groups and reaction conditions (pH, temperature, and adsorption time) largely influence the removal of various contaminants via adsorption and determine the affinity between adsorbent and adsorbate. Although, some adsorbents are highly efficient in uptake of various types of contaminants/pollutants from aqueous solutions but meticulous and indepth researches are still required for the development of highly efficient and costeffective methods using green technologies for removal of emergent pollutants from waste waters and industrial effluents.

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CHAPTER

5 Performances of membrane bioreactor technology for treating domestic wastewater operated at different sludge retention time

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5.1 Introduction

5.1.1 Fundamentals of membrane bioreactors

Membrane bioreactor (MBR) is a modern technology for both domestic and industrial wastewater treatment. In this technology, the sludge could be separated effectively by membrane filtration, resulted in enhancing the quality of the treated water with free suspended solid (Visvanathan and Abeynayaka, 2012). Basically, MBR requires a small footprint. In addition, it could be operated at a long sludge retention time, resulted in a low sludge production (Lobos et al., 2006, Uan et al., 2008). In addition, membrane filtration could removal the pathogens from effluent (Hocaoglu et al., 2011). Since membrane can retain sludge in the bioreactor completely, the system can be operate at high sludge retention time (Martínez et al., 2020). This could help to enhance the degradation of pollutant constituents in the reactor.

It has been reported that the combination of membrane filtration and biological processes could provide an excellent suspended solids separation (Deng et al., 2020). Besides, membrane filtration could retain high sludge concentration in the reactor which could improve the wastewater treatment efficiency (Sun et al., 2020). It should be noted that literatures and the facts show that the MBR was applied successfully for treating municipal wastewater, domestic wastewater, and even high strength industrial wastewater treatment (Alizad Oghyanous et al., 2020). However, membrane fouling is big problem that affect the application of MBR in treating wastewater (Song et al., 2020). Therefore, significant works have been studied for controlling membrane fouling so far (Yu et al., 2018). During operation, membrane filtration technology could separate completely the sludge in the effluent (Hocaoglu et al., 2011). It should be noted that due to water scarcity, the development of MBR

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technology could provide an alternative method to produce high effluent quality, which could be reused in agriculture or in domestic purpose (Li et al., 2018).

5.1.2 Development of MBR studies

Membrane filtration, which combines with biological treatment is a good technology for treating wastewater. MBRs have several advantages over conventional biological processes (Melin et al., 2006). The common MBR configurations could be presented in Fig. 5.1A, B, and C.

So far, there has been an increase in MBR studies to identify the development of research directions in which treatment of municipal wastewater for the water reuse could be important (de Oliveira et al., 2018). Besides, studies on membrane fouling were done to overcome disadvantages of MBR operation (Sowmya et al., 2020).

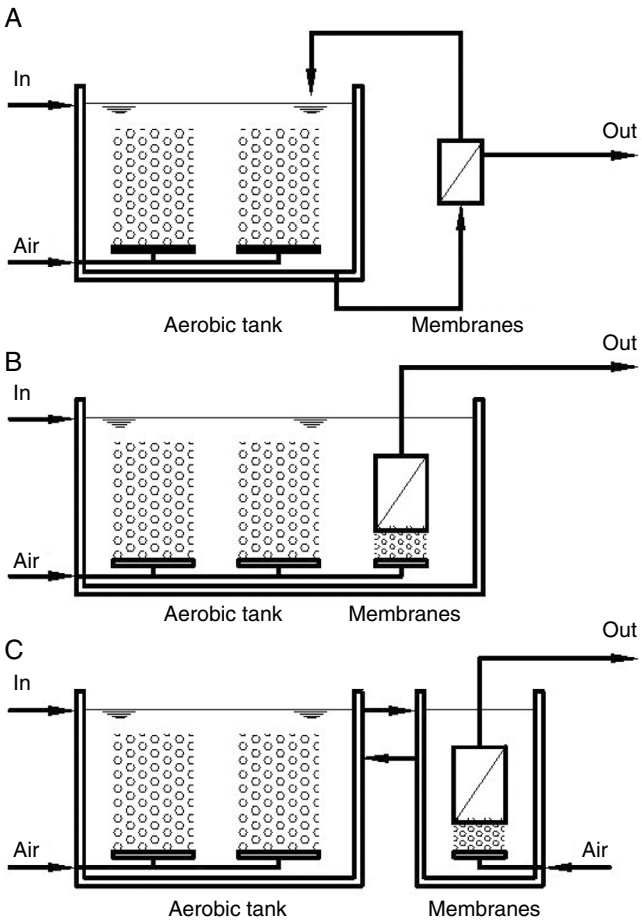

FIG. 5.1 Basic MBRs configurations.

MBR could be operated at high sludge retention time, resulted in low biomass production. Therefore, MBR technology could help to reduce the treatment and disposal cost of sludge wasted from the system (Sambusiti et al., 2020). In the conventional biological treatment system, operating at high sludge retention time could make a slow growth rates of microorganisms (Pahlavanzadeh et al., 2018). Besides, it could affect the microbial activity for the treatment efficiency and affect the system operation (Wu et al., 2020). Therefore, biomass retention becomes an important factor during operation in order to maintain a sufficient biomass or activated sludge within the bioreactor.

It is interesting that the MBRs could be operated independently in relation to the hydraulic retention time and sludge retention times. This could be helpful for operating the system at high organic loading rates (Fathali et al., 2019). Therefore, MBRs could be an attractive solution for treating both low strength municipal wastewater and high strength industrial wastewater to achieve the purposes of water reuse and less excess sludge production simultaneously. From the Fig. 5.1, it can be seen that the membrane could be worked by high pressure or by a vacuum pressure. As seen in the Fig. 5.1A, membranes are separated from the bioreactor and installed outside a bioreactor tank. This configuration was called as an external cross-flow MBR. In cross-flow MBR, a pump was used to push the effluent into the membrane model. A part of the permeate will pass through the membrane and retentate will be returned to the bioreactor. One of the advantages of the external cross-flow MBR systems is that the liquid cross-flow could help to reduce the cake layer on membrane surface, resulted in reduce membrane fouling (Lorhemen et al., 2019). In Fig. 5.1B and C, membranes are submerged inside a bioreactor tank or in a membrane tank. This is called as submerged membrane bioreactor configuration. In this configuration, a pump was used to create a vacuum pressure to withdraw the effluent from membrane.In addition, a gravity flow could also be applied to withdraw the permeate through the membrane. In this MBR systems, controlling the liquid velocity across the membrane surface is difficult (Mashayekhi et al., 2018). Therefore, cake layer can be minimized by aeration, which could create a strong bubble gas which could be passing the surface of membrane to reduce membrane fouling (Hawari et al., 2019).

5.1.3 Membrane fouling in MBR systems

Recently, membrane fouling in MBR systems has been still attracted in both research and development stage. Membrane fouling has been seen as a major challenge to the MBRs application (Zuthi et al., 2017). Therefore, development of different MBR configurations could be another driving force to study the strategy to control membrane fouling (Mahmoud and Liao, 2017). The air bubbling plays an important role to minimize the cake layer on membrane surface in MBR systems. In case of the membrane was submerged in a separate tank (Fig. 5.1C), it looks similarly to the external membrane. However, in this configuration, a pump is required to recycle the sludge to the bioreactor. Besides, the membrane in this system is also worked by a vacuum pressure condition, generated by a pump. This external membrane tank has been used

in several wastewater treatment plants in many countries (Zhang et al., 2019). One of the advantage of this configuration is that the fouled membranes could be cleaned easily, because membrane tanks could be worked separately. Membrane fouling is a big disadvantage resulted in high operational cost and replacement cost for application of MBR systems (Nie et al., 2017).Membrane fouling could be separated into reversible and irreversible fouling (Zhang et al., 2019). Reversible fouling could be removable by physical cleaning methods (Abdel-Karim et al., 2017). Irreversible fouling is difficult to remove by physical cleaning methods because it was caused by strong attachment of particles (Fortunato et al., 2019). So that it is generally only cleaned by chemical methods, using acid or alkaline solutions. Membrane fouling in the MBR systems was occurred due to two main reasons, i.e. cake layer formation by sludge and the precipitation of the inorganic compounds on the membrane surface (Di Trapani et al., 2019). Air bubbling in MBRs could be an effective way to minimize the membrane fouling.

5.1.4 Performances of MBRs at high biomass retention

Normally, MBR is operated with high mixed liquor suspended solids (MLSS) concentration (Germain and Stephenson, 2005). Because of high biomass retention, MBRs could be worked at high organic loading rates. High biomass retention capacity of the MBRs could provide a better performance because membrane could maintain higher biomass activity (Xu et al., 2019). It should be noted that a notably higher organic loading rates can be achieved in MBRs under aerobic conditions. It has been reported that in aerobic MBR with the open reactor, the ammonia removal could be improved at elevated temperatures when high aeration rates were applied. Application of MBRs enhance nutrient removal, resulted in low amounts of nitrogen and phosphorous in the effluent. High MLSS reduces bioreactor volume for the same organic loads that need to be treated (Schwarz et al., 2006). MBR operated at higher biomass concentrations could make an issue for pumping which increases membrane fouling. In addition, MBRs operated at higher biomass conditions could reduce specific biodegradation rate.

It should be noted that when the membrane fouling happened, the permeate flux of membrane will be declined. After that physical and chemical cleaning must be applied frequently to recover the flux (Tiwari et al., 2019). Besides, another strategy, i.e. as increasing the aeration rate, should be applied to avoid further fouling because fouling will deteriorate the membrane filtration. In the bioreactor, the membrane surface contact with the biological suspension or activated sludge, then the biosolid will be deposited onto membrane surface, resulted in reduce the pores of the membrane. In some cases, the combination of both activated sludge and inorganic precipitation could cause sudden drops in membrane permeability (Phuong et al., 2018). This is recorded by the sudden increasing of the transmembrane pressure. In addition, during operation, sludge recycled in the system by pumping can generate the mechanical sheer stress applied on the biomass. This could also be considered as one of the reason reducing the biomass size, resulted in increasing the membrane fouling in

MBRs. In addition, the cross flow velocity by aeration could affect the biomass, which may cause a reduction of the biomass size. The MLSS levels in the reactor is controlled by the sludge retention time (SRT). Thus, SRT is one of the operational factor affecting the treatment system performance strongly. As mentioned above, MBR system could be worked at long SRT. This could reduce sludge wasted from the MBR systems, resulted in saving the sludge disposal costs (Pollice et al., 2006). In recent years, many MBR systems have been operated MBR with long SRT. As a result, high sludge concentration in the system is an important factor to enhance the system treatment efficiency. However, more dead or inactive microorganisms could be accumulated in the MBR systems. Therefore, sludge activity could be reduced significantly when MBR operated at long SRT (Rosenberger et al., 2002, Zhang et al., 1997). Moreover, long SRT could result in poor thickening sludge that could affect the sludge dewatering (Schwarz et al., 2006).

5.1.5 Task and purpose of the study

Despite the previous studies, the relationship between SRT, MLSS, and the biomass properties in MBR have not been quantified systematically. Furthermore, the high sludge concentrations due to high sludge retention time in the MBRs could be a reason for increasing the sludge decay. Sludge decay could increase high extracellular polymeric substances concentration which strongly affect the membrane fouling. Therefore, it would be interesting and necessary to conduct an experiment for this lacking information. Selecting proper SRT could be helpful for designing and operating MBR systems. During operation of MBR systems, the high sludge concentration was normally maintained in the bioreactor, so that the small sludge particle size could be a potential issue for membrane fouling (Siddique et al., 2018). Therefore, the present study is aimed to identify the influences of SRT on the sludge properties (i.e. sludge bioactivities, sludge settling index, specific oxygen uptake rate, and sludge particle size distribution) in a small MBR system, operated at different SRTs. In addition, the treatment of organic compounds (i.e. COD) in the system was also examined. This work could provide a proper operational conditions which enhance the advantages of MBRs operated at a suitable SRT. This could help to adjust the existing challenges of current MBRs for future directions of design and operation.

5.2 Materials and methods

5.2.1 Experimental setup

A basic diagram of lab-scale MBR used in this work was presented in Fig. 5.2. The working volume of the bioreactor was 60 L (L × W × H = 450 × 150 × 900 mm).

In this study, five flat-sheet membranes were submerged inside the bioreactor. The membranes were made of polyvinyldene fluoride (PVDF, Hyosung Co., Ltd., Korea) with the pore size of 0.22 μm. Total filtration areas of the membranes were 0.5 m^2. Aeration was supplied from a network pipe located below the membrane

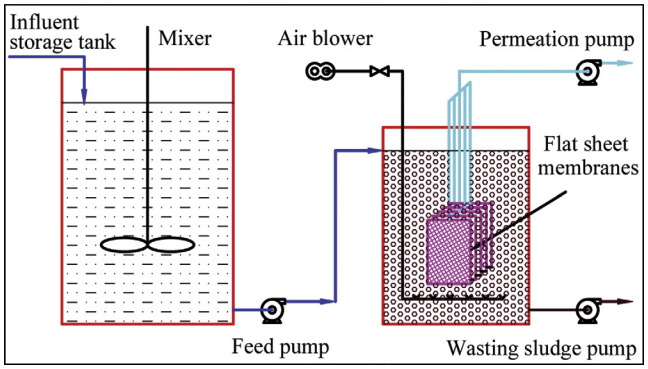

FIG. 5.2 MBR system used in this study.

sheets to provide oxygen for biotreatment and to avoid the deposition of sludge on the membrane surface. During operation, the permeate flow-rate was measured by a water flow-meter. Transmembrane pressure (TMP) was checked by a pressure gauge. In this study, domestic wastewater was stored in a feeding tank. Influent was pumped into the bioreactor depending the water level in the reactor. The hydraulic retention time (HRT) of wastewater was maintained at about 6 h. The effluent was filtered through membrane by a suction pump which was operated by a sequencing at on/off mode of 10/2 min. The permeation flux was maintained at 20 L/m^2.h.

5.2.2 Sludge retention time

The experiment was carried out with various SRTs which were changed from 10 to 60 days. During operation, SRT was controlled by discharging a certain sludge. The amount of sludge wasted was estimated proportional to the designed SRT. Basically, excess sludge was wasted daily from the drain of the MBR. In each operational condition, the sludge was discharged directly from the bioreactor. Bioactivities, settling characteristic, viscosity, particle size distribution, as well as microscopic observation of the activated sludge were monitored frequently to assess the influences of SRT on the sludge properties in the system.

5.2.3 Analysis methods

In this work, during operation the values of MLSS, MLVSS and SVI were measured based on Standard Methods (APHA 2005). MLSS andMLVSS were measured by using the methods 2540D and 2540E, respectively. COD was determined by the closed reflux, colorimetric method (Method 8000) and measured by a spectrophotometer (Hach DR/2500, Hach Co., USA). These parameters were analyzed two to three times per week. Bioactivities of the activated sludge were characterized by specific oxygen consumption rates (SOUR) which were weekly measured using a specific DO meter (YSI Model 5100, YSI Incorporated, USA). The settling characteristic of

sludge was weekly monitored by measurement of sludge settling index (SVI) according to the 2710 D method. Viscosity was weekly measured using a viscosity meter (Brookfield, Model LVDV-E, USA). Sludge particle size distribution was determined at the end of each experimental stage by a laser beam diffraction using a Mastersizer 2000 (Malvern Instruments Ltd., UK). Besides that, microscopic observation of sludge was measured by a Microscope SZX9 (Olympus Optical Co., Ltd., Japan).

5.3 Results and discussion

5.3.1 Effect of SRTs on sludge concentration in the system

As stated above, one of the advantages of the MBR is to maintain high MLSS (Germain and Stephenson, 2005). In this study, both MLSS and MLVSS concentrations, which were presented in Table 5.1, increased almost linearly with increasing SRT. In which, MLSS increased from about 4160 mg/L to about 14200 mg/L, and MLVSS increased from about 3450 mg/L to about 10800 mg/L for SRTs of 10 to 60 days, respectively. These could be easy to explained as long SRT could generate high sludge concentration in the MBR system. However, as showed in the figure, the ratio MLVSS/MLSS was decreased from 83% to about 76% when SRT was increased from 10 to 60 days. This is due to the inert substances accumulated in the MBR operated at long SRT.

The ratio of substrate/biomass (F/M) and the observed yield (Y_{obs}) were also estimated and presented in Table 5.1. As a result, the F/M ratio was varied from 0.13 to 0.35 kg COD/kg MLVSS.d. The obtained value was lower than that in the conventional activated sludge process (0.2 to 0.6 kg COD/kg MLVSS.d, (Tchobanoglous et al., 2003). Under low loading rate, the Y_{obs} were also very low and reduced from 0.25 to 0.10 kg MLVSS/kg COD along with SRT increasing from 10 to 60 days. It was reported that low ratio of F/M would be a factor limiting microorganism growth, and resulted in low sludge yield (Grady et al., 1999).

Table 5.1 Influence of SRT on sludge properties and operational conditions of MBR.

SRT, days	MLSS, mg/L	MLVSS, mg/L	MLVSS/ MLSS ratio, %	F/M, kg COD/kg MLVSS.d	Yobs, kg MLVSS/ kg COD	SVI, mL/g MLVSS	Viscosity, mPa.s	SOUR, mg O_2/g MLVSS.h
10	4160	3452	83	0.35	0.25	90	9.2	23.7
20	5879	4829	82	0.26	0.16	92	16.3	19.8
30	7974	6501	81	0.24	0.13	115	24.8	15.4
40	9597	7487	78	0.2	0.11	130	39.1	13.6
50	11649	9093	78	0.16	0.11	162	55.6	11.3
60	14208	10798	76	0.13	0.1	325	72.4	10.8

5.3.2 Effects of SRT on sludge bioactivity

SOUR could be a good indicator to evaluate the sludge bioactivity (Tchobanoglous et al., 2003). The observed SOUR of sludge in this MBR operated at SRT of 10 days was 23.7 mg O_2/g MLVSS.h, whereas it decreased to 10.8 mg O_2/g MLVSS.h at the SRT of 60 days (Table 5.1). The observations in this study showed that the SRT has affected the bioactivity of sludge obviously. A reduction of sludge bioactivity was corresponding to sludge yield. Membrane filtration was another factor which affects a reduction of SOUR. Membrane could retain most of the inert biomass in the system. Thus, they would be accumulated in the MBR system. Also, it could be confirmed that the SOUR reduced is correlated with ratio of F/M because low ration of F/M could result in low sludge yield.

5.3.3 Effect of SRT on SVI and viscosity

The effect of SRT on sludge volume index (SVI) and viscosity was presented in the Table 5.1. In fact, increasing the SRT resulted in higher MLSS which could help to increase the treatment performance at high volumetric loading rate. As showed in the figure, viscosity were increased gradually along with increasing SRT from 10 to 60 days, from 9.2 to 72.4 mPa.s, respectively. It should also be noted that that high viscosity could reduce oxygen transfer because air bubble rate to the surface of reactor was increased, resulted in reduction of contact time of oxygen and water (Massé et al., 2006). It can be seen in Table 5.1 that the SVI were increased only gradually along with SRT increased from 10 to 50 days, then it was increased suddenly when SRT was raised from 50 to 60 days. The increasing in SVI along with SRT is showing that sludge wasted from the MBR has a poor thickening properties. Actually, the poor settling would not affect the sludge separation in the MBR as the sedimentation process has been replaced by the membrane filtration process. However, poor settling sludge would have the negative impacts on the subsequent sludge disposal and management.

5.3.4 Effects of SRT on COD removal in the system

Table 5.2 shows the variation of the influent and efflent COD at different SRTs.

As seen from Table 5.2, low COD in the effluent was achieved when SRT was changed from 10 to 60 days. On the average, over 96% of the COD removal was obtained for all SRTs. COD concentrations in the effluent were ranging from 8 to 15 mg/L. Even, sometimes it was only about 3 mg/L. However, it should be noted that when MBR operated at SRT of 10 days, COD removal rate was slight low. In conclusions, the observations show that there was only a slight difference in the average COD removal efficiency for all studied SRTs. It should be also noted that for all SRTs operation, there were free particulate solids in the effluent. Therefore, the membrane filtration played an important role for removing suspended solids, resulted in improving the effluent quality. More assessment should be carried out to examine the nitrification and ammonia removal in the system.

Table 5.2 Influence of SRT on COD removal in the MBR system.

SRT, days	Range	Influent COD, mg/L	Effluent COD, mg/L	COD removal, %
10	min	248.0	7.0	88.6
	max	520.0	32.0	98.7
	average	358.8	15.2	95.3
20	min	342.0	6.0	96.7
	max	446.0	12.0	98.6
	average	379.5	8.7	97.7
30	min	362.0	4.0	97.5
	max	632.0	12.0	99.3
	average	504.7	7.7	98.4
40	min	360.0	5.0	96.2
	max	664.0	16.0	99.0
	average	471.5	9.5	98.0
50	min	342.0	5.0	97.3
	max	586.0	12.0	99.1
	average	428.2	8.2	98.0
60	min	380.0	2.0	96.9
	max	504.0	14.0	99.5
	average	445.0	7.3	98.3

5.4 Influence of SRT on sludge particle size distribution

In this study, the sludge particle size distributions of were measured frequently. The obtained results were presented in Table 5.3.

From the Table 5.3, it can be seen clearly that the sludge properties was changed due to the difference of the sludge flocs sizes. In addition, sludge particle sizes were affected strongly by the SRT. As showed in the Table 5.3, all sludge particle sizes were limited within 300 μm. The average sludge particle sizes at SRTs of 10, 20, 30, 40, 50, and 60 days were 131.1, 124.8, 83.2, 74.6, 47.1, and 24.9 μm, respectively. The result showed that the sludge particle sizes reduced with SRT increased. A wide range distribution of sludge particle sizes were observed. It was reported that small sludge particle sizes in the MBR could provide a good environment to improve the mass transfer of dissolved oxygen as well as soluble organic matter into the flocs, thus the system would enhance the organic removal rate (Germain and Stephenson, 2005). The sludge particle sizes observed in this study were a slightly larger than that in a recirculated MBR (Cao et al., 2005). The difference could be explained that a higher shear rate caused by the recycle pump in the recirculated MBR could expose

Table 5.3 Effects of SRTs on sludge particle size distribution.

	Particle volume percentage (%)					
Particle size (μm)	**SRT 60 days**	**SRT 50 days**	**SRT 40 days**	**SRT 30 days**	**SRT 20 days**	**SRT 10 days**
0	0.3128	0.5354	0.1032	0.2257	0.019	9.87E-04
5	0.9636	0.9221	0.1829	0.3511	0.0314	2.00E-03
10	2.3115	1.4922	0.3114	0.531	0.0507	3.96E-03
15	4.3185	2.2682	0.5094	0.7813	0.0802	7.60E-03
20	6.2834	3.2389	0.8004	1.118	0.1244	0.0142
25	7.12	4.3448	1.2085	1.5559	0.1891	0.0258
30	6.2834	5.4752	1.7531	2.1061	0.2815	0.0456
35	4.3185	6.4816	2.4435	2.7728	0.4106	0.0784
40	2.3115	7.2082	3.272	3.5504	0.5868	0.1311
45	0.9636	7.5306	4.2098	4.4217	0.8217	0.2131
50	0.3128	7.3907	5.2039	5.3558	1.1275	0.3371
55	0.0791	6.814	6.1806	6.3096	1.5158	0.5185
60	0.0156	5.9016	7.0528	7.2296	1.9965	0.7756
65	2.39E-03	4.8017	7.7323	8.0568	2.5768	1.1285
70	2.85E-04	3.6701	8.1451	8.7327	3.2583	1.597
75	2.65E-05	2.6352	8.2434	9.2059	4.037	2.198
80	1.92E-06	1.7776	8.0158	9.439	4.9007	2.9423
85	1.08E-07	1.1263	7.4889	9.4128	5.829	3.8309
90	4.76E-09	0.6705	6.7222	9.1296	6.7931	4.8511
95	1.63E-10	0.3749	5.7974	8.6122	7.7568	5.9748
100	4.34E-12	0.197	4.8038	7.9017	8.6782	7.1571
105	9.02E-14	0.0972	3.8245	7.0511	9.5129	8.3385
110	1.46E-15	0.0451	2.9254	6.1198	10.2172	9.4487
115	1.83E-17	0.0196	2.1499	5.1658	10.7521	10.4135
120	1.80E-19	8.03E-03	1.518	4.2412	11.0863	11.1623
125	1.37E-21	3.09E-03	1.0298	3.3867	11.2	11.6373
130	8.17E-24	1.11E-03	0.6713	2.6303	11.0863	11.8
135	3.78E-26	3.78E-04	0.4204	1.9868	10.7521	11.6373
140	1.36E-28	1.20E-04	0.2529	1.4597	10.2172	11.1623
145	3.83E-31	3.60E-05	0.1462	1.043	9.5129	10.4135
150	8.38E-34	1.01E-05	0.0812	0.7248	8.6782	9.4487
155	1.43E-36	2.68E-06	0.0433	0.4899	7.7568	8.3385
160	1.89E-39	6.64E-07	0.0222	0.3221	6.7931	7.1571

(continued)

Table 5.3 Effects of SRTs on sludge particle size distribution. *Continued*

Particle size (μm)	Particle volume percentage (%)					
	SRT 60 days	SRT 50 days	SRT 40 days	SRT 30 days	SRT 20 days	SRT 10 days
165	1.96E-42	1.55E-07	0.0109	0.2059	5.829	5.9748
170	1.57E-45	3.39E-08	5.18E-03	0.1281	4.9007	4.8511
175	9.87E-49	6.97E-09	2.36E-03	0.0775	4.037	3.8309
180	4.82E-52	1.35E-09	1.03E-03	0.0456	3.2583	2.9423
185	1.83E-55	2.45E-10	4.32E-04	0.0261	2.5768	2.198
190	5.42E-59	4.17E-11	1.74E-04	0.0145	1.9965	1.597
195	1.25E-62	6.69E-12	6.76E-05	7.85E-03	1.5158	1.1285
200	2.24E-66	1.01E-12	2.52E-05	4.13E-03	1.1275	0.7756
205	3.14E-70	1.42E-13	9.00E-06	2.12E-03	0.8217	0.5185
210	3.42E-74	1.89E-14	3.09E-06	1.05E-03	0.5868	0.3371
215	2.90E-78	2.36E-15	1.02E-06	5.10E-04	0.4106	0.2131
220	1.92E-82	2.76E-16	3.24E-07	2.40E-04	0.2815	0.1311
225	9.85E-87	3.04E-17	9.88E-08	1.10E-04	0.1891	0.0784
230	3.95E-91	3.15E-18	2.89E-08	4.91E-05	0.1244	0.0456
235	1.23E-95	3.06E-19	8.14E-09	2.13E-05	0.0802	0.0258
240	2.99E-100	2.79E-20	2.20E-09	8.97E-06	0.0507	0.0142
245	5.67E-105	2.39E-21	5.72E-10	3.68E-06	0.0314	7.60E-03
250	8.35E-110	1.93E-22	1.43E-10	1.47E-06	0.019	3.96E-03
255	9.58E-115	1.46E-23	3.42E-11	5.69E-07	0.0113	2.00E-03
260	8.57E-120	1.04E-24	7.88E-12	2.14E-07	6.59E-03	9.87E-04
265	5.97E-125	6.93E-26	1.74E-12	7.87E-08	3.76E-03	4.73E-04
270	3.23E-130	4.35E-27	3.71E-13	2.81E-08	2.10E-03	2.20E-04
275	1.37E-135	2.56E-28	7.58E-14	9.74E-09	1.15E-03	9.98E-05
280	4.49E-141	1.42E-29	1.49E-14	3.29E-09	6.17E-04	4.40E-05
285	1.15E-146	7.38E-31	2.81E-15	1.08E-09	3.25E-04	1.88E-05
290	2.30E-152	3.61E-32	5.09E-16	3.45E-10	1.67E-04	7.86E-06
295	3.57E-158	1.66E-33	8.86E-17	1.07E-10	8.44E-05	3.19E-06
300	4.31E-164	7.14E-35	1.48E-17	3.23E-11	4.17E-05	1.26E-06

sludge particle flocs. A microscopic evaluation of the sludge from MBR was carried out as well. Overall floc morphology of sludge at different SRTs were very different. Based on the observations in this study, it could be seen that the sludge particle sizes at different SRTs were almost larger than membrane pore sizes of about three times. Therefore, the small sludge particle size could not be a reason to contribute membrane fouling.

5.5 Conclusions

The effects of SRT on the treatment performance of lab-scale MBR treating domestic wastewater were examined under various SRT (varied from 10 to 60 days). Based on the observations, several conclusions could be withdrawn as follows. With increasing SRT from 10 to 60 days, the sludge concentrations in the MBR were increased from about 4160 mg/L to about 14200 mg/L. However, the ratio of volatile suspended solid to the total solid was decreased from 83% to about 76%. Under a low loading operation (F/M ratio varied from 0.13 to 0.35 kg COD/kg MLVSS.d), the Y_{obs} were decreased along with the SRT increased from 10 to 60 days. The SRT has affected bioactivity of sludge obviously. The measured SOUR of sludge at a SRT of 10 days was 23.7 mg O_2/g MLVSS.h, whereas it decreased to 10.8 mg O_2/g MLVSS.h at the SRT of 60 days. Viscosity were increased gradually along with SRT increased from 10 to 60 days, from 9.2 to 72.4 mPa.s, respectively. The SVI were increased only gradually along with SRT increased from 10 to 50 days, then it was increased suddenly when SRT was increased from 50 to 60 days. The average sludge particle sizes at SRTs of 10, 20, 30, 40, 50, and 60 days were 131.1, 124.8, 83.2, 74.6, 47.1, and 24.9 μm, respectively. Overall, the sludge particle sizes varied with SRT and floc morphology of sludge at different SRTs were very different. However, the COD removals was not significantly affected by the SRTs. Over 96% of the COD was removed for all studied SRTs. The effluent COD were ranging from 8 to 15 mg/L. Therefore, designing and operating MBR must be taken into account of the suitable SRT. The obtained results shown that in the SRT ranging from 10 days to 60 days, a higher SRT could provide a good bioflocculation of sludge. It also could give a lower membrane fouling rates.

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Abbreviations

SOUR	Specific Oxygen Uptake Rate
SVI	Sludge Volume Index
MBR	Membrane Bioreactor
MLVSS	Mixed Liquor Volatile Suspended Solids

MLSS	Mixed Liquor Suspended Solids
SRT	Sludge Retention Times
TMP	Transmembrane Pressure
HRT	Hydraulic Retention Time
F/M ratio	ratio of substrate/biomass

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CHAPTER

6 Advances in nanotechnologies of waste water treatment: strategies and emerging opportunities

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6.1 Introduction

With increase in population, in the last few decades, the demand of water supply for various purposes like drinking, irrigation, industries and other domestic works also increases. After utilizing, the water is often get contaminated with variety of different pollutants/contaminants. The contaminants such as organic (phenolic compounds, pharmaceuticals, pesticides, textile dyes), inorganic (heavy metals, mineral acids and inorganic salts), pathogenic bacteria, viruses, and other harmful chemicals are generally found in waster waters, affecting environment and health. Further, recycling and treatment of water for above mentioned purposes is a great challenge. Various physical (filtration, flocculation, and adsorption), chemical (oxidation) and biologicals methods (utilizing enzymes and microbes) are generally employed for the treatment of different grades of water. However, most of these technologies require considerable investments, cost and energy. Moreover, Cincinelli et al. (2015) also highlighted the inability of conventional/traditional technologies to remove various organic emerging contaminants. Therefore, safe and effective alternate technology which can treat wastewaters contaminated with wide variety of pollutants (even at low concentrations) is the need of the hour.

As per latest development, systems based on nanotechnology has showed potential to substitute traditional waste water technologies. Studies indicated that nanomaterial

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offers large surface area for high reactivity and further its size dependent properties makes it a good candidate to be used in waste water treatment systems (Bora and Dutta, 2014). Different nanomaterials have already been tested for the removal of heavy metals, microbial contaminants, pesticides, dyes, pharmaceutical and personal care products (Cincinelli et al., 2015; Berekaa et al., 2016; Jain et al., 2020). Nanomaterials, such as metal and metal oxide nanoparticles (Ag, Fe, Zn, TiO_2, ZnO, and iron oxides) (Lu et al., 2016), Nanoadsorbents (Polymeric resins, Activated aluminas and Zeolites) (Crini et al., 2019), Nanosorbents (Carbon-based, Captymer TM, Nanoclay, and Carbon-Iron) (Chorawala and Mehta, 2015), Nanomembranes (Nanofilteration) (Askari et al., 2015), Nanocatalyst (AgCCA, N-doped TiO_2, and ZrO_2) (Chorawala and Mehta, 2015) have showed great potential in literature reports. Further, with improved ability for detection and elimination of wide variety of contaminants, nanomaterials offers promising future alternate for wastewater treatment. However, most of the reported studies indicated the efficacy of nanomaterials/systems in small setups, therefore more concrete research to test the efficacies rigrously in natural field conditions is required. Further, long term studies to test the health and safety issues of these technolgies should also be addressed before commercialization and full scale applications. The present review summarizes the research in the field of safe and effective nanotechnolgy for waste water treatment.

6.2 Metallic nanoparticles

There are various methods of synthesizing metal nanoparticles, for example, physical methods (ultrasonication, ball milling and Photoirradiation etc.), chemical methods (coprecipitation sol-gel process and chemical reduction techniques), and biological methods (plants, bacteria, fungi and algae) (Iravani et al., 2018). These metal nanoparticles can be used to rapidly detect the low concentrations of pesticides in water. One such example is the use of Eu^{3+} ions combined with gold nanoparticles to detect organophosphorous compounds (Dasary et al., 2008). The fluorescence intensity of these molecules were found to increase when attached with gold nanoparticles. The fluorescence is quenched with addition of organophosphorus molecule because of liberation of the Eu^{3+} ions from the surface of the nanoparticles. DNA aptamer-based gold nanoparticle colorimetric assay was developed for detection of 6 organophosphorous pesticides (Bai et al., 2015). The aptamers were specific for the pesticides and this binding prevented the aptamers protecting the nanoparticles from aggregating in presence of salt. Gold nanoparticle solution turns from wine red to purple-blue colour in presence of salt and pesticides due to aggregation. However, aptamers need to be designed with increased binding affinity for more sensitive assays using this principle. Recent revisions to Maximum contamination limit (MCL) of heavy metals in drinking water, makes it essential to develop protocols for its detection even at ultralow concentrations. Use of nanoparticles based assays is based on the ability of nanoparticles to host a range of different ligands on its surface. An example is the use of DNA functionalized gold nanoparticles to detect Hg^{2+} ions

by Hg^{2+} promoted thymine base pairing (Lee et al., 2007). This approach has also been used to develop a chip-based scanometric device to detect low concentrations of mercuric ions using DNA functionalized gold nanoparticles (Lee & Mirkin, 2008). Another such example is the use of gold nanoparticles functionalized with a DNA strand that can undergo aggregation due to action of a DNAzyme in the presence of a substrate (Liu & Lu, 2003). The aggregation is inhibited in the presence of Pb^{2+} ion due to catalytic cleavage of the substrate. These methods can detect contamination greater than 100 ppb. Gold nanoparticles stabilized with polypeptide sequences have also been used to detect Pb^{2+} and Hg^{2+} contamination at the ppb level with differential color response (Slocik et al., 2008). The metal ions are specifically detected by the aromatic, hydroxyl and charged groups in the amino acids. Using this approach, even nanomolar concentrations of pollutant can be identified by Plasmon shifts of the absorption spectrum. In a similar approach, certain ligands are known that can complex with metal ions. This ligands when functionalized on surface of noble metal nanoparticles causes observable optical changes on complexing with metal ions even at concentrations at the ppm level.

Further, dyes are also the major pollutants in industrial effluents and are environmentally hazardous to the water bodies and living organisms (Safavi & Momeni, 2012). The complex structure of these dyes make them recalcitrant and resistant to degradation. Photocatalytic degradation with the help of nanoparticles can be an effective and environment friendly alternative. During photocatalytic degradation, nanoparticles get activated in the presence of ultraviolet/visual range radiation and create a redox environment (Beydoun et al., 1999). SnO_2 nanoparticles produced by ascorbic acid mediated synthesis were found to have photocatalytic activity in the degradation of methylene blue dye under UV irradiation (Tammina et al., 2018). MFe_2O_4 (M=Co, Ni, Cu, and Zn) nanoparticles synthesized by CTAB-mediated co-precipitation oxidation methods were found to be excellent photocatalyst for dye degradation (Gupta et al., 2020). The ferrite nanoparticles absorbed effectively in the UV-Vis-NIR region. The Ni ferrite nanoparticle showed the best rate for degradation of methylene blue dye. These particular nanoparticles showed 89%, 92%, 93%, and 78% decolorization of methylene blue, methyl orange, brilliant green and methyl red respectively. Recently, Jain et al. (2020) used aqueous leaf extract of *Carica papya* to produce silver nanoparticles (Pa-AgNPs), further these Pa-AgNPs have been observed to photocatalytically degrade Blue CP, Yellow 3RS, and their mixture in presence of sunlight. Table 6.1. Provides the list of various nanoparticles used for the degradation different contaminants generally found in wastewaters.

Metallic nanoparticles have also been reported for efficient antimicrobial activities (Garg et al., 2020). As per a recent report, silver nanoparticles prepared from *C. papaya* leaves (Pa-AgNPs) showed efficient antibacterial properties against *Escherichia coli* and *Staphylococcus aureus*, The Zone of inhibition of Pa-AgNPs highlighted the value of 14 mm and 15 mm for *S. aureus,* and *E. coli*, respectively (Jain et al., 2020). Similar antibacterial effects against gram positive and negative bacteria from biological synthesized AgNPs have been reported in literatures studies (Chauhan et al., 2016; Tyagi et al., 2019). It has been suggested that AgNPs can enter

Table 6.1 Various nanoparticles used for the removal of different contaminants.

Nanoparticles	Contaminant	Activity	References
Zinc-Nickel ferrite nanoparticles (Ni-$ZnFe_2O_4$)	Cr^{3+} ion	Photocatalytic removal of Chromium ions after 20 minutes of treatment. Increased removal was observed with increase in Zn in the nanoparticle composition	(Shukrullah et al., 2020)
Au and Pt nanoparticle decorated g-C_3N_4 heterostructure	Tetracycline Hydrochloride (TC-HCL)	Improved degradation efficiency as compared to g-C_3N_4 particles alone under visible light irradiation	(Xue et al., 2015)
Iron nanoparticles synthesized using green tea extracts	Anthraquinone and Azo dye mixtures	90% decolourisation within 20 minutes 0.53 ppm nanoparticle concentration at 70°C	(Truskewycz et al., 2016)
Gold and silver nanoparticles	Halocarbon pesticides	Complete mineralization of halocarbons in presence of alcohols to metal halides and amorphous carbon	(Nair & Thalappil, 2003)

bacterial cell by direct penetration or through porin proteins. Later, these AgNPs were observed to generate ROS (reactive oxygen species) which denature proteins and DNA, and cause bacterial cell death (Pareek et al., 2018). Further, various other metal and metal oxide nanoparticles such as Au, CuO, Fe_3O_4, ZnO, and TiO_2 have also been suggested for antimicrobial activities (Rafique et al., 2020; Tyagi et al., 2020; Kanagasubbulakshmi and Kadirvelu 2017; Singh et al., 2018; Bhau and Ghosh 2015; Santhoshkumar et al., 2014).

6.3 Nanoadsorbents

Adsorbents such as polymeric resins, activated aluminas, zeolites, etc. have been utilized for purification of wastewater. Despite their excellent performance, these are expensive for wastewater treatment (Crini et al., 2019).

Nanoadsorbents are prepared from organic or inorganic materials at nanoscale that have high adsorption properties. Due to their active surface, high porosity and miniscule size, they are capable of chelating contaminants of different molecular sizes, speciation, and hydrophobicity (Pacheco Sadott et al., 2006). Nano adsorbents function rapidly and have substantial pollutant-binding potential (Table 6.2). Additionally these nanoadsorbents can be regenerated chemically after they are exhausted (Yang & Xing, 2007).

Nanoadsorbents are a lucrative option for bioremediation of wastewater due to their unique chemical and physical properties that are attained due to the surface effects and volume effects (Khajeh et al., 2013). The large surface areas obtained

Table 6.2 Adsorption capacity of various nano adsorbents.

Nano adsorbent	Contaminants	Adsorption/Adsorption capacity/Removal %	Reference
Multiwalled carbon nanotubes	10 mg/L of Cu, Co, Cd, Zn, Mn, Pb	Cu(II)>Pb(II)>Co(II)> Zn(II)> Mn(II)	(Stafiej & Pyrzynska, 2007)
Graphene (GNS-B)	Phenanthrene	129.8 mg/g	(Apul et al., 2013)
Magnetic nano-particles coated zeolite	0.5 g/L As (III)	95.6%	(Attia et al., 2014)
Magnetic nano-adsorbent	2.5 g/L Zn (II)	95.0%	(Shirsath & Shirivastava, 2015)
Nanocrystalline titanium dioxide	0.2 g/L As (III)	>98%	(Pena et al., 2006)
Graphite oxide (GO)	methylene blue and malachite green	351 and 248 mg/g	(Bradder et al., 2011)

on decreasing the size of the large and bulk particles to nanoscale. This increase in surface area resulting from the fractionation and increase in number of smaller atoms under the symmetrical environment of local conditions and coordination number, leads to increase in free surface energy that ultimately increases the rate of chemical reaction (Khajeh et al., 2013). Additionally, nanoadsorbents have high adsorption capacity as the atoms on the surface are unsaturated, and thus can attract other ions such as trace metals (Cui et al., 2006) and organic compounds that are polar in nature (Wang, 2001).

The diverse properties of nanoadsorbents are also due to the volume effects which results in lower wavelength of the atoms that have higher frequency with higher particle energy. The volume effects also result in the phenomena of optical absorption spectra due to the blue shift of atoms. The superparamagnetic property is attained when the particle size is smaller when compared to the magnetic domain in a material. The volume effect further results in the improved catalytic properties that is due to the increase in average energy spacing as number of atoms are reduced in a free electron model (Wigginton et al., 2007).

The most extensively used nano adsorbents comprises of carbon-based nanomaterials such as activated carbon (AC), carbon nanotubes (CNTs), graphene etc. Metal or metal oxide-based nanomaterials, such as Fe_3O_4, MnO_2, ZnO, etc. Polymer-based nanomaterials such as Polypyrrole/Fe_3O_4 magnetic nanocomposite (Sadegh et al., 2017).

I. Carbon-based nanomaterials

Carbon nanoadsorbents have remarkable potential for heavy metal removal from contaminated wastewaters due to their exceptional surface area, reactivity, porosity and aspect ratio. Depending upon the architectures, carbon nanomaterials are zero-dimensional carbon nanospheres and carbon nanoparticles, one-dimensional

carbon nanofibers and carbon nanotubes (CNTs), two-dimensional carbon nanofabrics and graphene, and three-dimensional carbon nanofoams and carbon nanoclusters (Yu et al., 2018).

Carbon nanotubes (CNTs)**:** CNTs are nanoadsorbents that have high adsorption ability to remove heavy metals due to its exclusive electronic, structural, semiconductor, and optoelectronic as well as physical, chemical, and mechanical properties, they have been extensively used to remove heavy metals in wastewater treatment. CNTs occur as multiwalled (MWCNTs) and single-walled (SWCNTs) (Moradi et al., 2012).

II. Metal or metal oxide-based nanomaterials

Metal oxides at nanoscale have enhanced surface area and are excellent sorption for heavy metals. Examples include zinc, cerium, titanium oxides.

Iron oxide nanomaterials

Iron oxide nanoparticles for heavy metal remediation are quite desirable. The three phases of iron oxide are the magnetic phase viz. maghemite (γ-Fe_2O_4) and magnetite (Fe_3O_4) and nonmagnetic, hematite (α-Fe_2O_3). They can be created into different structural morphologies such as cauliflower-like structures, flowers, nanochains, nanorods, nanotubes, nanoparticles, etc. (Ray & Shipley, 2015).

III. Polymeric nanoparticles

Polymeric nanoparticles adsorbents are made up of polyacrylic ester matrix or polystyrene. These polymeric nanoparticles have physical properties such as adjustable surface chemistry and pore size distribution, large surface area, mechanical rigidity, and are regenerative (Pan et al., 2009).

6.4 Nanobiosorbents

The limitations with conventional biomass based biosorbents are that they are not durable and not mechanically stable and lack in selectivity as several functional groups are present on the biomass that lack specificity. The natural biomass gets rapidly saturated due to the sorption sites being occupied that require many cycles of desorption before another use (Mahamadi, 2019). Also these biosorbents are porous that limits their adsorption capacity and rate of adsorption as a result of intra-particle diffusion (Afkhami et al., 2010).Thus nanoadsorbents with exceptional physical and chemical properties and excellent adsorption capacity are explored.

Nanobiosorbents are materials that have structural components with dimension less than 100 nm. The nanobiosorbents utilised for decontamination of aquatic systems should have a high adsorption capacity especially for pollutants at lower concentrations (ppb). The contaminants should be easily desorbed and renewable. And it should be ecofriendly and economic and biomass based. The nanobiosorbents are classified according to their mode of synthesis viz. biosorbent immobilized on inorganic nanoparticles, nanobiosorbent modified by organic materials, magnetic modification of natural biosorbents, and modification of metal oxide by organic materials

(Krstić et al., 2018). In a study, Zhu et al., (2018) observed 94.7% removal of Cr (VI) from aqueous solution by utilizing green tea synthesized nano-zero-valent Fe/Cu composite. For the removal of Pb (II) nanocomposite obtained from chitosan highlighted the maximum adsorption capacity of 357 mg/g (Maity & Ray, 2018) and dithiocarbamated spororpollenin highlighted the maximum adsorption capacity of 95 mg/g (Ünlü & Ersoz, 2007).

6.5 Nanomembranes

Nanomembranes are well known for the treatment of wastewater contaminated with organic and/or inorganic pollutants (Karimi et al., 2016). Nanomembranes are made up of nanofiber, permeable in nature and less permeable to the targeted pollutants such as dyes, nitrate, heavy metals, phosphates, fluorides, etc. (Mahvi et al., 2011; Yousefi et al., 2016). Researcher utilized different type of materials for the manufacturing of nanomembranes to improve the overall removal efficiency along with the reduction in fouling and energy requirements (Saikia et al., 2019). The performance of nanomembranes during the treatment of wastewater depends on number of factors such as pore size of the nanomembranes, concentration of pollutants or contaminants in the wastewater, pressure applied during the treatment, etc. As compared to the other membrane dependent technology (microfiltration, ultrafiltration, and reverse osmosis) for the wastewater treatment, nanomembranes has upper hand as they remove the pollutant/contaminants from the wastewater even at low pressure. In addition to this, nanomembranes can easily reduce the microbial load of the wastewater along with the hardness. Additional characteristics of nanomembranes such as high rejection to divalent ions as compared to monovalent ions can make wastewater treatment process very selective for the particular solutes or pollutant present in the wastewater (Jagadevan et al., 2012). Further, it was observed that ionic state of the pollutant as well as of nanomembranes can play major role during the removal, due to electrostatic interaction (Shi et al., 2008). Table 6.3 indicates the different type of nanomembrane employed for the treatment of widepollutant.

Askari et al., (2016) investigated the dye removal efficacy of polyamide nanofilter membrane at various concentrations (60–180 mgL^{-1}) and pH (6-10). Maximum removal of up to 89% and 90% was obtained for disperse blue and reactive blue, respectively, at pH 10 and 800 KPa pressure. In another study, Rashidi et al., (2015) studied the removal efficiency of polyamide nanomembrane in term of different dyes (reactive blue 15, Reactive red 194, reactive yellow, reactive black and reactive orange 16). Up to 90% removal of dye was observed at 16 mgL^{-1} s during 60 min of operation. In addition to this, COD (chemical oxygen demand) of the wastewater (due to synthetic dyes) reduces to zero after nano-membrane treatment process. Amini et al., (2011) studied the dye removal efficiency of a nanomembranes developed using acrylic acid, polysulfone and PEG (Polyethylene glycol). Multiple dyes such as acid red 14, acid green 20, acid red 30, acid orange 7, acid red 81, acid red 30, etc. were used as a pollutant during the treatment process via nanomembrane. It was

Table 6.3 Different types of nanomembrane employed for the treatment of various pollutants.

Nanomembranes	Pollutant	Removal (%)	References
Hollow fiber nanofiltration (NF) membranes	Dimethyl phthalate (DMP), diethyl phthalate (DEP), dibutyl phthalate (DBP), di-n-octyl phthalate (DnOP) and diethylhexyl phthalate (DEHP)	DMP (82%), DEP (86%), DBP (91%), DnOP (95%) and DEHP (95%)	Wei et al., (2016)
Nanofiltration membrane (NE-90)	COD, BOD and TDS	COD (77%), BOD(74%) and TDS (86%)	Mozaffarikhah and Kargari, (2017)
Semi-aromatic polyamide membrane NF-270	Phenol	51%	Lempart et al., (2018)
Polyethylenimine cross-linked nanofiltration membranes	Enrofloxacin Cefadroxil	Enrofloxacin (85-93%) Cefadroxil (72%)	Zhao et al., (2018)
Polyethylene glycol based nanofiltration membrane	Tobramyci, clindamycin phosphate and cephalexin	Tobramyci (99%), clindamycin phosphate (94%) and cephalexin(93%)	Cheng et al., (2016)
Nanofiltration membranes NF 270 and Nanofiltration membranes NF 90	Norfloxacin	87-99%	De Souza et al., (2018)
Polyvinylidene fluoride nanofiltration membrane	Direct Red 28, Copper, Cadmium and Chromium	Direct Red 28 (65-94%), Copper (14%), Cadmium (44%) and Chromium (52%)	Zeng et al., (2016)
Polyethersulfone nanofiltration membrane	Direct red 16 and copper	Direct red 16 (995) and Copper (92%)	Abdi et al., (2018)
Polyacrylonitrile (PAN) thin-film composite nanofiltration membranes	Lead, Cadmium and Nickle	>93%	Jia et al., (2019)

observed that maximum removal of up to 86-99% was observed at a hydraulic permeability of 7.6 $Lm^{-2}h^{-1}bar$. Mahvi et al., (2011) examined the nitrate removal capacity of nanofilter membranes. Up to 80% removal of nitrate was observed during the treatment process. It was also concluded that, as the initial concentration of nitrate increases in the aqueous solution, the removal efficacy of the membrane decreases. Yousefi et al., (2016) employed nanofilters for the removal of multiple contaminants like phosphate, nitrate and fluoride from the groundwater. It was observed that, factors such as concentration of pollutant (phosphate, nitrate and fluoride) and flow rate of water through the membrane, affects the removal rate during the operation. Up to 98, 82 and 87% removal were observed for phosphate, fluoride and nitrate via nanofilter, respectively. H.R. Rashidi et al., (2012) examined nanomembrane (4040-TS80-TSF) process for the removal of dye from the textile wastewater. The nanomembrane was made up from polyamide and fibre glass. The dye removal experiment was performed at 56 bar and 25 °C with 110 cc/min flow rate for 45 min. It was observed that nanomembrane was able to remove up to 95-80% of dyes from the wastewater.

In another study, a nanomembrane was developed via electrospinning technology and examined for its ability to remove oil-grease, COD, BOD (Biological oxygen demand), turbidity and TSS (Total suspended solids) from the wastewater sample collected from Tabuk Sewage Treatment plant, Saudi Arab. The nanofibrous membrane developed by using Poly (vinylpyrrolidone) (PVP), N, N-Dimethylacetamide (DMAC) and Poly vinyl chloride (PVC). The developed nanomembrane was able to remove up to 100% oil-grease from the wastewater, followed by TSS (80%), BOD (71%), turbidity (64%) and COD (36%). In addition to this, the nanomembrane was also able to reduce the level of phosphate and ammonia from the wastewater. Zou et al., (2019) modified a commercially available nanofiltration membrane in term of negative charge density via poly(sodium 4-styrenesulfonate). The modified nanofiltration membrane was tested for the removal of nitrate from the ground water. It was observed that up to 88% removal was obtained from the ground water via modified nanofiltration membrane. Similarly, a poly(piperazineamide) modified nanofiltration membrane was employed for the treatment of atrazine (pesticide) from the aqueous solution. Up to 98% removal was observed for atrazine at concertation of 0.3 gL^{-1} (Karimi et al., 2016).

6.6 Nanocatalysts

Nanomaterials can act as catalyst for various reactions. Nanoparticles which possess catalytic properties includes, zero-valence metal, semiconductor materials and bimetallic nanoparticles, these catalytic nanoparticles can helps in removal of contaminants such as pesticides, herbicides, PCBs, azo dyes, etc. Various nanocatalysts like AgCCA, N-doped TiO_2, ZrO_2 can efficiently eliminate microbial contamination in water (Chorawala and Mehta 2015). Further, in the process of degradation of organic compounds, nanoparticles generates reactive species i.e., hydroxyl and superoxide radicles, which helps in oxidation of organic substances, further leading to their decomposition and mineralization.

6.6.1 Photocatalyst based advance oxidation process

There are several types of semiconductor photocatalyst, but TiO_2 and ZnO are observed to be more effective for the degradation of organic matter (Mills and Le Hunte., 1997). Band–gap energy of TiO_2 is 3.2ev and it uses UV radiation for excitation. When UV radiation falls on TiO_2 nanoparticle, than transition of electron from valance band to conduction band occurs which create hole in the valance band. Due to this, photocatalytic activity of electron in conduction band (e^-_{cb}) and hole in valence band (h^+_{vb}) are formed. Both electron (e^-) and hole can undergo oxidation and reduction in aqueous solution and produce free radicle which degrade organic matter (Carp et al., 2004). When water molecules contact with TiO_2, hole in valence band (h^+_{vb}) reacts with surface water to form $HO^{\cdot}$ free radicle and e^- in conduction band (e^-_{cb}) reacts with O_2 to produce superoxide free radicle ($O_2^{\cdot}$). Superoxide free radicle ($O_2^{\cdot}$) forms $HO^{\cdot}$ free radicle which undergo further reaction. $HO^{\cdot}$ free radicle degrade organic substances into intermediate product, than mineralized to CO_2, H_2O and inorganic ions (Konstantinou and Albanis., 2004; Akpan and Hameed., 2009; Zhang et al., 2010; Divyapriya et al., 2016).

6.7 Conclusions

With various limitations associated with traditional methods of wastewater treatment i.e., inability to properly degrade various emerging contaminants (especially pharmaceutical and personal care products), cost and energy intensiveness, etc, researchers have identified many substitutional technologies in this regard. Among various recognised technologies, nanotechnology has showed great potential to eliminate variety of organic and inorganic pollutants, pathogenic microorganisms in lab and small setups. Apart from size specific advantages offered by nanomaterials, it also acts as a ligand to get attach with many chemical groups, thereby provides efficient adsorption, selectivity, and reuse, making them as the best option for wastewaters contaminated with wide variety of pollutants. Recent reports suggested various strategies and advances in nanotechnological approach to treat wastewaters. Few nanotechnologies such as, nanosorbents, nanocatalysts, nanomembranes, metal and metal oxide nanoparticles showed promising results to remove pesticides, heavy metals, dyes, pathogenic microorganisms, pharmaceutical, and personal care products. Further, with increase in the use of nanomaterials in wastewater treatment, the toxicity concerns towards environment and health is also raising questions. Therefore, research to evaluate the long term effectiveness and toxicological effects of nanomaterials should be taken up seriously in order to move forward for their real applications in natural field conditions.

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CHAPTER

Water and Wastewater Treatment through Ozone-based technologies

7

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7.1 Introduction

Water is an incredibly valuable and abundant resource present on Earth's surface, it covers over 70% of the earth. It is found in three states, for instance, gas, liquid, and solid in nature. It is almost colorless with a minor hint of blue, odorless as well as a tasteless liquid at room temperature. A lot of substances dissolve in the water, it typically is known as a universal solvent. Water is a merely ordinary substance take place in nature in total three general phases of matter along with being crucial for every living organisms on Earth. It is a major component of the human body [Hossain, 2015]. The human body contains around 75% of water furthermore, and is necessary from the prolongation of life as well as body homeostasis. The brain, lungs, and blood of a human are made of 95%, 90% and 82% respectively. Water has various functions in the human body such as maintaining the body lubricant, regulation of temperature, removal of injurious toxins in addition to the transportation of nutrients to the entire body [Moustafa and Satesh, 2021]. In general, humans are liable for persuading water pollution [Owa, 2014]. The growth of the world's population and economy challenge the drinkable water supplies as well as ecosystem preservation, as manmade activities are the major stress on water systems. The rapid developing societies are consuming more and more water and enhancing pollution, ultimately responsible for freshwater resources stress [Wolf, 2019]. The demand and supplies of water are altering. Its future is uncertain but what is certain is that it will change. There are various factors such as enhancement of population, the huge quantity of water consumption per capita in growing various sectors such as household, urban as well as industrial water [Cosgrove and Loucks, 2015]. Population growth, the release of treated or untreated industrial, agricultural [Owa, 2014] fertilizer pesticide from agricultural runoff and municipal wastewater, are mainly polluting the water bodies. The major pollutants, micropollutants, and pathogens releases in water sources. Major pollutants comprise an overload of nutrients especially nitrogen and phosphorous cause eutrophication [Wolf, 2019] an extreme enhance in excessive aquatic algal gloom plus the growth of weed [Owa, 2014] and other plant growth which may

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reduce dissolved oxygen (DO) of water sources [Wolf, 2019]. It may cause a change in taste, odor in addition to sometimes color of water also. Household (sewage) wastewater is a waterborne waste of the public, the release of this untreated sewage in river is in huge quantity, ultimately it unhealthy for the river. Water pollution is responsible for the duel consequence of nature. It not only affects negatively to the livings organisms but also the environment. Water pollution has various damaging effects such as plants and animals nutrition, human health along with aquatic communities [Owa, 2014]. A sustainable, flexible, acceptable and climate independent drinking water supplies should be developed for reducing the effects of water pollution as well as benefited to the maximum population. There are various treatment technologies (primary, secondary and tertiary) presently available for solving and reducing the problem of water pollution and scarcity of water. The suspended solids removal and reduction of heavy metals, organic nitrogen phosphorus while not the micropollutants or pathogens adequately in the primary treatment of wastewater. Whereas around 85% of biochemical oxygen demand (BOD) and suspended solids are reduced in secondary biological treatments for instance membrane bioreactor (trickling filters) or activated sludge. A number of organic matters along with nutrients are digested and it reduces by microorganisms. The concentration of organisms like bacteria, viruses and protozoa can also be decreased by 3, 2.5, and 2 $\log_{10}$, correspondingly. Hence, further treatment of wastewater through conventional treatment for the adequate elimination of health target substances or microbes before releasing into the environment. A range of processes in advanced treatment technologies is using drinking water treatment plants. These encompass adsorption, media filtration, membrane filtration, oxidation as well as disinfection [World Health Organization (WHO) 2017]. The treatment of drinking water can comprise pre-treatment, coagulation, flocculation, filtration, sedimentation along with disinfection [Wolf, 2019]. Ozone is an emerging and attractive technology which developed and improved in current years for water treatment, thus enhancing its potential for thriving purposes. This book chapter is focused on water and wastewater treatment through ozone-based technologies.

The ozone-based technology or ozonation processes are very efficient in disinfecting plus organic pollutants degradation as of water. The use of ozonation process in wastewater treatment may slightly enhance in pH, chemical oxygen demand (COD) and fecal coliform reduction and increased in dissolve oxygen after treatment. Ozonation processes may substitute the conventional chlorination methods due to its nature (strong oxidizing) along with efficient disinfectant characteristics with no any side effects [Bhatta et al., 2015]. Ozone is a strong oxidizing agent and their oxidizing capacity is outstanding to nascent oxygen atoms as well as hydroxyl radicals. It reacts with the complex substances directly or indirectly and it breaks them into simpler molecules [Yasar et al., 2007]. The use of technologies in combinations of advanced oxidation processes (AOP) such as ozone (O_3), hydrogen peroxide (H_2O_2) and ultraviolet (UV) degrade the entire contaminants are receiving rising curiosity in current researches [da Silva et al., 2012]. The conventional treatment technologies are not suitable for the removal of pharmaceuticals from the surface as well as

drinking water. Ozonation and AOP are capable of degrading pharmaceutical chemicals present in water and wastewater [Ikehata et al., 2006]. Ozonation is a superior technology in compare to chlorination because; chlorine is required 30 mg/L for removing 90% of antibiotic-resistant bacteria (ARB) that is not viable while only 3 mg/L ozone required for 90% of ARB removal [Oh et al., 2014]. Ozone is used in the treatment of drinking water mainly for disinfection reason and for controlling color, odor and taste as well as it may improve the removal of iron and manganese also [Rahmana et al., 2010].

7.2 Global water scenario

As it is well known that, water is necessary for existence. It is essential for agriculture, cooking as well as washing. It is also crucial for ecosystems, comprising forests, marshland, and pastures [United Nations Children's Fund (UNICEF) 2017]. All country and its society are depending on the sustainable freshwater of adequate amount and qualities for their requirements; maintain economic growth and ecosystem on which the entire life depends [Watson, 2009]. Around 70% of the worldwide freshwater is employed in agriculture which involves crops irrigation and operations of livestock. Though, as per a study, several 4 billion people experiencing shortages of water presently for as a minimum one month of each year. Water crises are listed in the top threats on third place in terms of impact in a report known as Global Risks Report 2017 which published by the World Economic Forum. It is also reported in this report that water crises are an interconnected risk with the other sectors. At present, around 36 countries are facing an exceedingly great level of water stress. Below 2.5% of the globe's water supply may be categorized as freshwater. The distribution of worlds freshwater is shown in the Fig. 7.1 [United Nations Children's

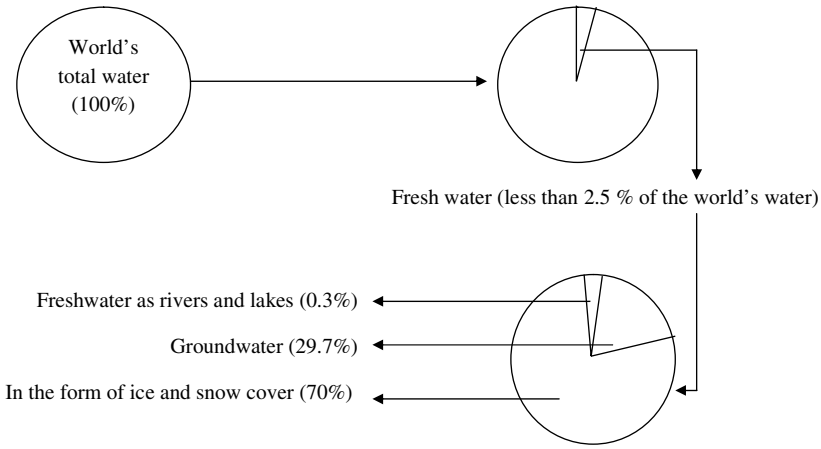

FIG. 7.1 World's freshwater distribution.

Fund (UNICEF) 2017]. The opinion that water is abundant, it takes place 70% of the earth, is not correct because only 2.5% of freshwater is of total water [Guppy and Anderson, 2017] whereas above two-thirds of the freshwater is ensnared in ice plus glaciers, leaving a minute portion presented to meet the water, hygiene along with sanitation requirements of the globe's population [United Nations Children's Fund (UNICEF) 2017]. This insufficient source of water will require to maintaining a projected population (9.7 billion) in 2050; along with, approximate 3.9 billion or more than 40% of the globe's population will exist in rigorously water-stressed river basins by that date [Guppy and Anderson, 2017]. The 60% of the accessible freshwater is present in just nine countries namely Brazil, China, Canada, Columbia, Indonesia, India, the Democratic Republic of Congo, Russia, and United States (U.S.). These nine countries show around 44% of the world's landmass as well as house to 35 % of the worldwide population. Numerous countries are by now under whether physical or economic stress of water [Baker et al., 2016]. An extreme exploit is also apparent, the worldwide population tripled during the 20th century, whereas the water use augmented six-fold. It is estimated that the demands of water are expected to increase by 400% from manufacturing, in addition to by 130% from domestic use between today and 2050 [Guppy and Anderson, 2017].

The water resources such as surface and groundwater have come under huge pressure all over the place because of diversions, pollution and withdrawals. It is reported in a study that, there are a number of global water challenges as: (i) above 2.8 billion of people will be existing in the either water-stressed or scarce area of the globe by the year 2025. (ii) Freshwater ecosystems, as well as environmental facilities as of watersheds and water resources, are gradually further at threat as of human pressures for instance dam diversions, industrial development and water withdrawals. (iii) Over 260 watersheds, having above 40 % of the global population, are combined by two or more than two countries (iv) 90 % of the total disaster associated casualty is related to water. (v) 95 % of the wastewater is released in the environment with no treatment all over the world. (vi) Around 2 million people, the immense majority children below five, pass on due to diarrhea every year; furthermore, around 90 % of diarrhea is accredited to dangerous drinking water, poor hygiene and insufficient sanitation [Watson, 2009]. Most of the countries are facing the problem of speedy deterioration of water resources because of increment in population and continuous decline of freshwater supply [Bhatta et al., 2015, Dinka, 2018]. The quality as well quantity of freshwater destructively is rising in developing countries due to continues urbanization and manmade activities also. Urbanization along with lack of appropriate sanitation is mainly responsible for the severe and crucial surface water pollution in the developing countries. A study demonstrated that the domestic, industrial moreover municipal wastewater is directly and indiscriminately released in the lakes and rivers and therefore it causes mainly water pollution in Nepal [Bhatta et al., 2015]. Some other important factors such as acidification, eutrophication, illegal waste release exercise, pathogens, salinization and sewage spills are also responsible for water pollution and shortage [Bwapwa, 2018]. South Africa obtained around 450 mm rainfall every year and is categorized as a country under water-stressed. The reachable

resources of freshwater may maintain only 80 million people. A number of African countries such as Congo, Ethiopia, and Papua New Guinea have surplus freshwater resources and still face water shortage issues because of economic reasons [Dinka, 2018]. There are mixtures of factors such as restricted and enormously polluted watercourses, short rainfall, population growth and high rates of evaporation, acidification, eutrophication, salinization, pathogens, and dumping of solid wastes in watercourses are the main reasons of worsening the water quality in South Africa and other countries also. In general, around 90 to 95% of sewage in addition to 70% of industrial wastewater is discharged in the surface waters consequently polluting available water [Bwapwa, 2018]. At present, around one-fifth of the global population or 1.2 billion people exist in physical water scarcity region, whereas one more about one-quarter of the world's population of around 1.6 billion people are facing economic water scarcity. It is projected in a study that around 800 million people will exist in countries or areas with a complete shortage of water and two-thirds of the globe's population might be under rigorous stress conditions of water by 2025 [OCHA, Policy Development and Studies Branch 2010]. Most countries in the Middle East experience water shortage, with water use, drastically exceeding entire supplies of renewable water. Many of the countries may not sustainably fulfil their present water demand. The water accessibility per person is likely to be slash in half by 2050 with present population growth as well as enhanced demand [United Nations Children's Fund (UNICEF) 2017]. OECD is projected that the OECD worldwide water requirement might enhance by 55%, set against obtainable resources that are limited still if it is renewable by 2050 [Mason et al., 2017]. Around 13.5 million Syrians had a requirement of humanitarian assistance while 6.3 million people were internally dislocated as of February 2017. Most people are lived in relocation camps or host communities in adjacent countries. While around 2.7 million existed in Turkey, 1 million are in Lebanon furthermore and further 660,000 are in Jordan as of mid-2016 [United Nations Children's Fund (UNICEF) 2017]. The twenty-five countries internationally with the slightest access to safe water (nineteen of them African) dominate the apex 50 countries with maximum mortality of child. The children (between 23% and 59%) of these countries undergo underdeveloped growth [OCHA, Policy Development and Studies Branch 2021]. Water scarcity is already causing problems in various countries and upsetting numerous sectors comprising farming and manufacturing. A zone influenced by drought with climate change which is responsible for the physical scarcity of water in each continent. The minimum water resources and population growth are the major reason for creating a situation of water shortage. Moreover, the countries where water tables are falling, for instance, Algeria, China, Egypt, Iran, India, Mexico, Pakistan and the United States. In Australia, water restrictions are presently in place in numerous area and cities of Australia in response to chronic scarcity ensuing due to drought. The geographical location of Yemen does not yield various freshwater sources. The Sanna is the capital of Yemen is expected to be the first main city at the global level which is experiencing complete water shortage. Libya is one more war-torn country coping with chief water-scarceness concern, the

shortage of water is not precedence due to the political commotion. Jordan is also a country which is located at the arid zone in the Middle East which is a threatened country with an elevated level of physical water shortage. The water resources in South African have inadequately been managing [Bwapwa, 2018].

7.3 Strategies for solving the water shortage issues

There are several significant options suggested in the study which may reduce the water scarcity problems faced by countries. These water management options are as follow: (i) development of more catchment areas, (ii) strict management policies/guidelines should be implemented, (iii) water limit throughout night hours as well as recycle-reuse plan, (iv) use of rainwater harvesting (v) seawater water utilization for toilet flush, (vi) water desalination, [Bwapwa, 2018], (vii) Separation of sources, (viii) to enhanced conservation of water as well as effectiveness, (ix) distributed management of stormwater that detains and utilizes rainfall (x) recovery and reuse of water (xi) water treatment, (xii) heat recovery, (xiii) management of organics for energy production, and (xiv) recovery of nutrients [Cosgrove and Loucks, 2015]. The proper implementation of water infrastructures maintenance, essential management approaches along with recent and competent remediation treatment technologies are required for solving the rising demand of clean water problem in various worldwide countries as well as especially water shortage countries [Bwapwa, 2018]. Ozone-based technologies are an emerging treatment technology for treating water and wastewater; it may not only solve the problem of water pollution but also the water scarcity problem of the world.

7.4 Why ozone-based technologies used for water and wastewater treatment?

Ozone is a bluish colored gas having boiling point (–111.9°C) while melting point (–192.5 °C), strongest oxidant [Rodriguez et al., 2008] having oxidation potentials of molecular O_3 is 2.07 V [Ikehata and Jodeiri, 2006], very reactive molecule [Gomes et al., 2019] as well as an outstanding disinfectant [Kritsevskaja, 2021]. It is seen by the microwave spectroscopy that the ozone molecule has an O-O (the distance of 127.2 pm) along with an angle of O-O-O is 116.78° [Rodriguez et al., 2008]. This gas has an odor generally explained as the odor of air later to a spring electrical thunderstorm. It is believed that the odor of ozone as like to smell of watermelons. Thus, it should be manufactured and employed at onsite. It is formed by transitory air or oxygen with the help of two electrodes having greater alternating potential difference [Tech Brief 1999]. Combination of O_3 plus oxygen (O_2) with over 20 per cent ozone turns into explosive. Ozone may be manufactured through a range of methods while in the present study a technique used known as dielectric barrier discharge. Dielectric barrier discharge has various uses, for instance, aerosol charging, biological

decontamination, control pollution through oxidation of volatile organic compound (VOC) or nitrogen monoxide, generation of UV or vacuum ultra-violet (VUV), production of ozone, processing of materials, surface modification, and electro filtration as well as treatment of potable and wastewater [Bhatta et al., 2015].

$$O_2(\text{Oxygen}) \rightarrow O^* + O^*$$

$$O^* + O_2(\text{Oxygen}) \rightarrow O_3(\text{Ozone})$$

Ozone is a strong oxidant which may be applied in potabilization of both the surface plus groundwater in addition to treating the wastewater also for removal of organic contaminants, inorganic ions and microbes. Ozone eliminates arsenic, iron and manganese from water through oxidation in the form of an insoluble material which further removed via filtration [Rodriguez et al., 2008]. Ozone may be applied as a coagulant, deodorizer, detoxifier, and disinfectant. Ozone may be reducing BOD, COD, and organic matter also [Shah et al., 2016]. Ozone is successfully used for the disinfection as well as the breakdown of dissolved organic contaminants. Ozonation also employed for the efficient removal of specific personal care products (PPCPs) [Paucar et al., 2019]. The rate of reaction of O_3 is fast, it generates some dangerous by-products (rotated and bromine may be produced while bromide is there, for instance in seawater), and creates dissolved oxygen (DO) as an end product of the reaction in freshwater. The dissolved ozone is efficient for removal color and turbidity, reduction of nitrite, control of algae, and enhanced microflocculation of small particles furthermore improved biological processing of dissolved organic particle. Usually, ozone is an efficient parasiticide, bactericide and virucide. [Sharrer and Summerfelt, 2007]. Sometimes ozone decay in water, particularly while H2O2, is there, to produce the hydroxyl radical, the strong oxidizer presented in the treatment of water. In case of aqueous solution ozone is decomposes by an intricate mechanism commenced through reaction by a hydroxide ion and further pursued by some radical oxidizing species (HO, HO_2 and HO_3) formation. O_3 in addition to HOx structure in liquid water remains indefinite [Rodriguez et al., 2008].

These days, ranges of disinfection methods using in water recovery are derived from those in the treatment of drinking water. The common methods incorporate chlorination, membrane filtration, ozonation and Ultra Violet (UV) irradiation etc. Amongst all these methods, ozonation treatment technology is gradually further employed in retrieved water disinfection. This ozonation process is capable to efficiently inactivate largely bacteria, virus, protozoon, spores and prion protein in water. It is also observed that ozonation generate a small number of disinfection by-products while it is used for disinfecting effluents produces form various processes of wastewater treatment. The doses of ozone are generally employed higher for disinfection in compare to doses required for color or odor reduction reclaimed water. Thus ozonation might eliminate chroma substances, odorants, pathogens as well as even several micropollutants at the same time [Xi et al., 2017]. Chlorine is also applied as a major disinfectant for treating water and wastewater treatment in almost water treatment plants all over the world. Though, it was recommended in a study

that while chlorine reacts with any type of organic matter exists in water ultimately produce by-products which comprise trihalomethanes (THMs) for instance chloroform. When these THMs go into the body it enhances the free radicals generation that is extremely carcinogenic in nature. Several types of cancers such as damages of kidney and liver, dysfunction of the immune system, hardening of the arteries, nervous system disorders as well as birth imperfection because of chlorine and THMs. Therefore, the United States has included ozone as a disinfectant in above 280 main water treatment plants. Ozone is powerful over two times than chlorine and performs 3000 times quicker in water treatment [Shah et al., 2016].

However, the molecular O_3 and hydroxyl (HO) radicals are engaged in ozone treatment of water as well as wastewater. The process of ozonation at higher pH (>8) is believed as an advanced oxidation process (AOP) due to increased formation of HO radicals in such circumstances. The oxidation potentials of molecular O_3 (2.07V) and HO radicals (2.80V) are representing that these are so many strong oxidants [Ikehata and Jodeiri, 2006]. Ozone has a unique characteristic i.e. the oxidizing capability to organic moreover inorganic molecules, because of that it is greatly useful in the treatment of wastewater. The oxidizing capacity of O_3 to oxidize different molecules makes it more useful for various applications such as potable water disinfection, odor removal in industries [Nilsson, 2015]. Ozone based technology or ozonation is employed for the treatment of effluent and ultimate release. When O_3 is applied for the final release of effluent, it is chiefly put in as an alternate to decolorization and/or chlorine disinfection [Loeb et al., 2012].

Various inorganic chemicals comprise arsenic, bromide ion, iron, iodide ion, manganese, nitrite, and romated reacts to oxidize [Kritsevskaja, 2021]. O_3 also reacts to the electronic rich moieties such as activated aromatics, thioethers, and tertiary amines. The formed HO radicals during self decomposition of ozone may react with the nonactivated aromatic compounds amides as well as alkenes also [Fornander, .2018]. A chemical reaction in which a substance discharges one or more than one electrons and turned into oxidized known as oxidation. As electrons may not subsist in its lonesome, they are accepting through a different molecule which turns into reduced. It is a great tendency of accepting electrons in O_3 from different other molecules as of it's inherited instability [Nilsson, 2015].

Ozone is not only used for the disinfection in water treatment but also in color, micro coagulation, odor, taste as well as different other water treatment application. O_3 devastated to the bacteria along with inactive viruses more quickly in comparison to any other chemical disinfectants [Kritsevskaja, 2021]. O_3 is a very reactive molecule having oxidation potential 2.07 V, furthermore, it has the ability to conduct to secondary oxidants (for instance HO radicals) by greater reactivity in several circumstances. It illustrates as a disinfectant agent and has potential to reacting with numerous cellular components for instance cell wall along with DNA structure. Ozonation having the capability to eliminate up 2 log units of cultivable fungi, intl1 genes and 16S rRNA while around 4 log units of enterococci, enterobacteria, and heterotrophs. Furthermore, the antibiotic resistance genes may be reduced under the detection limit [Gomes et al., 2019].

7.4.1 Advanced Oxidation Process (AOP)

The oxidizing agents (H_2O_2, ozone, and UV light) or unite of these oxidants in chemical methods which used for oxidizing organic substances called as advanced oxidation processes (AOP). A large number of factories employ this technique form reducing COD plus color [Abidin and Rahmat, 2010]. AOPs are used for the obliteration of target pollutants by using enormously reactive species. The produced radicals have greater oxidation potential in compare to O_3 and a rate of reaction is around a million times more, therefore bring about small contact time as well as footprint. AOP may also be used to accomplish full or incomplete oxidation of the contaminants in the treatment process. The ozone-AOP process is a very useful technique that applied in conditions where only ozone cannot attain full oxidation of wastewater substances. AOP may be successfully employed to enhance the reaction kinetics for removing even the very complex compounds [BOD and COD 2021]. AOP joint 2 of 3 processes: ozonation, hydrogen peroxide, or ultraviolet (UV) irradiation for getting synergistic oxidation results for obtained increased reductions of microbes or obliteration of dissolved organic carbon substances. The ozonation process followed by UV irradiation is applied to enhance the competence of microbial inactivation in drinking besides wastewater [Sharrer and Summerfelt, 2007]. The combination with other oxidation techniques, for instance, ultrasonic or UV irradiation techniques may also be of notice because of a good efficiency along with a lesser cost. The efficiency of ozone-based processes has been assessed in various industrial sectors for example electroplating, petroleum refineries/phenols, pulp and paper and textiles wastes under different scientific study and publications. The combined treatment technology of oxidation reduces the treatment timing besides enhancing the elimination effectiveness [Rodriguez et al., 2008]. Whereas grouping of ozonation with biological treatment appears to be a capable unit technique for eliminating BOD and COD of wastewater having dye and residual color [Abidin and Rahmat, 2010]. AOPs are a possible substitute method for decolorizing and as well as decreasing recalcitrant loads of wastewater from dyeing, finishing and textile effluents. The various AOPs, for instance, O_3, O_3/UV, O_3/H_2O_2, O_3/UV/H_2O_2, UV/H_2O_2, and Fe^{2+}/H_2O_2 are using for the degradation of organic pollutants (nonbiodegradable) in industrial effluents a smart option to conventional treatment techniques. It is also illustrated based on different studies that AOPs are efficiently removed color along with partly eliminate the organic substance of dyestuffs [Muhammad et al., 2008]. AOPs are also efficient treatment technique for treating persistent composite. The AOPs technique is a new but easily accepting and using in the treatment of wastewater containing dye mainly due to higher efficiency, cost-effective as well as effortlessness. This technique may AOPs can totally mineralize the dye chemicals. This process is based on the formation of more reactive radicals like $^{\bullet}OH$ in situ. These are nonselective oxidant molecules and it originates a series of reactions for devastating the organic substance in end products (inorganic) and/or, in most cases, into fewer damaging materials [Karami et al., 2016].

7.4.2 Benefits of ozone (O_3) based treatment

Generally, Chlorine is used as a major disinfectant for treating water at most of the water treatment plants across the globe. Though, current studies propose that, while chlorine reacts with whichever present organic substances in water, produce by-products comprise THMs for instance chloroform. On the entering of THMs in the body enhances the formation of free radicals that is extremely carcinogenic. As per U.S. Council of Environmental Quality, Cancer danger amongst persons consuming chlorinated water is as great as 93 % higher compared to persons whose water does not have chlorine. Therefore, the United States has included O_3 as a disinfectant in over 280 main water treatment plants. O_3 is above two times as potent as chlorine moreover performs faster 3000 times [Shah et al., 2016]. Ozone is employed like merely oxidant or in united with other oxidants or energy (AOPs) in treatment of ground, surface, or wastewater. The ozone-based treatment technologies have the general goal of optimizing the utilization of O_3 for getting better the disinfection or the present pollutants removal from the water [Rodriguez et al., 2008]. Ozone based water treatment has various advantages which summarized are as follow: (i) it has strong oxidizing power furthermore needs short reaction time, that makes possible the microbes (germs) comprising viruses, to be destroyed in a few seconds. (ii) this type of treatment supply oxygen to the water follow disinfecting [Tech Brief 1999] (iii) take away the color, odor [Shah et al., 2016] and taste also (iv) no need of chemicals (v) assists coagulation (vi) it oxidizes to manganese and iron (vii) It reacts with organic matter as well as eliminates the entire (viii) devastates and eliminates the algae [Tech Brief 1999]. (ix) It does not produce any odor [BOD and COD 2021] and or taste [Tech Brief 1999]. (x) It efficiently kills the bacteria (xi) oxidizes matters for instance iron as well as sulphur so that it may be sifted out of the solution. (xii) O_3 is an extremely reactive gas which may oxidise the bacteria [Shah et al., 2016] molds, organic substance furthermore other pollutants present in water. (xiii) O_3 changes reverse into the oxygen rapidly, furthermore leaves no trace one time it has been utilized [BOD and COD 2021] The probable benefits of employing O_3 together with biofiltration for wastewater treatment are as follow (i) reduction of COD with targeted or low dosages of O_3 as well as least operating expenditure. (ii) Operating costs are low because of the oxygen apply in the off-gas for tanks of activated sludge (iii) consumption of energy as well as oxygen because of multiline design of input system [Rau and Rosner 2004].

7.5 Worldwide status, history, and background of O_3 based technology for drinking water and wastewater treatment

The Carl Friedrich Schonbein was reported firstly about ozone and provided its name also in 1840 at the French academy of science. The name of ozone was derived from the Greek word ozein, “to smell,” its name is appropriate because the odor of ozone is greatly characteristic. It was discovered by J. L. Soret in 1865 and it also corroborated by him in the year 1867 that ozone is an allotrope of oxygen [Nilsson, 2015].

The full-scale application of O_3 for treatment of drinking water used first time in 1893 at Oudshoorn, Netherlands. Ozonation plants develop speedily all over Europe with widely held being situated in France furthermore numerous employing it as a major disinfectant. Ozone was identified for improving odor, taste, color removal and oxidized manganese and iron in a water source in the starting of 1900s. It was explored that influence of O_3 on coagulation in the 1960s while ozone improved the removal of particles. Ozone was applied for the control of disinfection byproduct trihalomethanes (THMs) and biological stabilization in the 1980s [Irabelli et al., 2008].

The initial trial of ozone use for the treatment of drinking water commenced in Japan with two cities in Northern Kyusyo in the near the beginning 1930s. While it uses were closed because of great humidity furthermore costly electricity. It was starting with the industrialization of Japan in the 1960s. There are more than 17000 treatment plants for water which producing treated water around 16 billion m^3. Presently, chlorination is a mandatory way of disinfection for the entire water. A feasible system for water treatment is offering in Japan nowadays as advanced water treatment methods, via O_3-GAC treatment (comprising membrane filtration). The percentage of treatment plants employing ozonation process is around two per cent among approximately eleven per cent of the overall water being treated through ozone A latest first installation as well as the practical purpose of O_3 for treatment of drinking water was Kanzaki treatment plant, Hyogo prefecture in the year 1973. Up to now, above 50 treatment plants for water have established ozonation as an advanced treatment method for elimination of color, taste, and odor along with manage THM formation. These treatment plants are functioning in an acceptable way. There was around 42000 lb/day (800 kg/h) capacity of ozone in the treatment of drinking water functioning in Japan from 2004. The total number of municipal wastewater treatment plants based on ozone treatment was only 3 in the year 1980 while it reaches more than 50 plants in the year 2010 in Japan [Loeb et al., 2012]. The Ozone first-time use for the treatment of drinking water for removal of taste, color, and odor in the USA in the starting of 1900s and developed gradually until speeding up began in the mid of 1980s. The largest potable water plant having 600 mgd~ 95000 m^3/h of the world go online in 1987 in Los Angeles with the established capacity to create 10000 lbs/day of O_3 from O_2 [Rice, 1999]. The installed capacity of ozone for treating drinking water goes over 525000 lb/day at the end of 2010 [Loeb et al., 2012]. The first application of O_3 commercially on a continual basis for the drinking water treatment in traced back to 1954 in Canada. It was an Otto Plate-type O_3 generators imported from France for disinfecting the drinking water [Larocque, 1999]. Ozone based treatment is an option for sewage treatment for removing micro contaminants. Ozone is an enormously reactive oxidant as well as thus an influential disinfectant also. It is using for drinking water disinfection in Europe since 1906 and it has been employed in several sewage treatment plants (STPs) also [Wang et al., 2018]. The growth of installations of ozone-based treatment technologies was slow until 1979, at what time the city of Montreal established 9600 lb per day O_3 capacity (182 kg/h). It was concluded by a committee in 2008 that the ozonation is the highly efficient oxidant for removing viruses, bacteria as well as injurious chemicals and was fewer damaging

to marine life. The acceptance gained for wastewater treatment through ozone in the United States in the 1970s and near the beginning of 1980s, when USEPA encouraged and provide construction funds up to 75% for the innovative and modern technologies for fresh wastewater treatment systems. There were forty-nine ozone-based wastewater systems set into service between 1975 and 2004, though merely seven systems of these are recognized to be presently functioning in 2007. The full-scale ozonation plants were constructing in the start of 1950s in Germany. Ozone is used for removing the undesired taste, odors and humic substances from municipal water that provides in Germany. There are above 100 water utilities employing ozone up to now. Ozone is using mainly for the treatment of water in Germany though is for swimming pool water treatment. There are 8 plants are upgraded for disinfection, and for removing odor, color, taste as well as micropollutants through ozonation in the Netherlands. Though the main goal was accomplished, regrowth causes five companies for discontinuing ozonation once more or to put back ozonation with the use of activated carbon. As well above twenty groundwater and riverbank filtration plants are set up UV apparatus for post disinfection. France is assumed as the cradle of ozonation by analysis of water disinfection starting in 1886. Although, more than 700 ozonation plants in France were in functioning by 1990, as mainly for drinking water. The initial key function of O_3 for drinking water in France as well the planet was in Nice in the year 1906. While ozone (22500 m^3/day) was used for disinfecting the slow sand filtered water as of the Vesubie River. The firstly O_3 based treated water was delivered in 1909 to Paris. Paris has 12 water plants having more than 500 kg/h of whole ozone capacity. O_3 is the option and prefer for disinfection of drinking water in France with almost chief cities exercising such treatment [Loeb et al., 2012].

7.6 Use of ozone-based technology for disinfection

Several fungi play a role in causing diseases in human beings. While, numerous other organisms may cause food alteration, altering them inappropriate for intake for instance as molds, among others. The ozone treatment applied on the different dose, temperature, pH and contact time for the different fungus such as *Aspergillus flavus, Candida aspergillus, Candida albicans, Clostridium chauvoei, Candida parapsilosis, Clostridium tetani* and *Tricophyton verrucosum.* The 1.5 and 60 mg/L dose of O_3 may reduce the *Candida albicans* (99%) and *Aspergillus flavus* (78%) respectively [Rojas-Valencia, 2011]. Though most used disinfection system is chlorination, it has few disadvantages like huge quantity/doses needed along with the chance of unsafe by-products formation also. Presently special attention is given on ozone and photo-based technologies for disinfection to obtained treated water having good quality. Ozone is capable to inactivate an extensive variety of pathogens for example bacteria, comprising its spores, protozoa, viruses as well as prion protein. The O_3 is highly competent in compare to chlorine about disinfection, comprising smaller reaction times with no microbial regrowth. While residual O_3 is decayed rapidly into O_2 and therefore does not comprise any trouble. Virus and bacteria are

greatly vulnerable to O_3 oxidation compare to protozoa, as a lesser quantity of ozone is needed for removing virus along with bacteria. Therefore, O_3 is an attractive disinfectant for inactivation of virus and bacteria both. There are some microorganisms such as bacteria (*E. coli*), virus (Adenovirus, Coxsackievirus, and Echovirus) and protozoa (*C. parvum, G. muris,and G. lamblia*) which may be removed via O_3 treatment technology [Gomes et al., 2019]. A study was conducted for inactivating the waterborne pathogens such as *E. coli, Shigella* sp., *Salmonella* sp. as well as *Vibrio cholerae* in synthetic water in addition to secondary municipal wastewater through the solar as well as UV titanium dioxide photocatalytic ozonation. It was observed that the Photocatalytic ozonation efficiently inactivated the bacteria and also constructive synergistic relations, bringing about synergy indices of equal to 1.86 representing a performance very much greater in comparison to photocatalysis and ozonation separately [Mecha et al., 2017]. The other microorganisms that can be removed by the ozone-based treatment technology which is summarized in Table 7.1.

The ozone decomposes into the water as hydrogen peroxy (HO_2) and OH radicals having the enormous oxidizing capacity and create a significant role in disinfection. It is usually assumed that due to protoplasmic oxidation, bacteria are smashed resultant degeneration of cell wall (cell lysis). There are certain parameters such as contact time, the vulnerability of target organisms, as well as O_3 concentration which decide the efficiency of disinfection. It is demonstrated in a study that the design of O_3 as a primary treatment must be on the basis of simple criteria incorporating demands of O_3, O_3 residual along with lowest contact time for achieving necessary cyst as well as viral inactivation needs [Shah et al., 2016]. Ozone should be produced on-site and the stream of gas is employed to the water flow by suitable liquid/gas contacting circumstances. It is considered that for accomplishing the great disinfection using O_3 because it obliterates the important components of microbes by oxidation reactions. O_3 is a strong oxidant that uses as a disinfectant, which may cause and disturb the bacterial cell membrane functioning, enzyme and inside cell interactions also. Though, the common result of the disinfectants on bacteria along with other organisms is well known, while not the accurate mechanisms firmly established. In the case of viral disinfection, ozone is considered for achieving viral disinfection by the oxidative attack on the coating of protective protein, likely interactions with deoxyribonucleic acid or ribonucleic acid can be a factor also. The main objective of ozonation at various water treatment plants is to obtained disinfection log-inactivation credit for different organisms such as cryptosporidium, giardia and viruses at levels of regulated or higher than regulated. The 1-log inactivation value is equal to 90% inactivation, similarly, 2 log is 99%, as well as 3 log, is equal to 99.9% etc. In general, the term log inactivation or removal in its place of per cent removal is applied in regulations for simplicity in reporting of disinfection [Kritsevskaja, 2021]. An internal disinfection process needed in a recirculating aquaculture system for controlling pathogens population growth in addition to heterotrophic bacteria. Application of ozone alone and followed by ozone with UV irradiation was applied for evaluating the efficiency of both in terms of heterotrophic and total coliform bacteria reduction into a reuse system of water. It was observed in the study when only ozone employs

Table 7.1 Microbial disinfection/inactivation through ozone.

S. No.	Ozone based Treatment for water/wastewater	Dose of O_3	Organisms reduction / inactivation	Microbial reduction / inactivation	References
Bacteria					
1.	Ozone	Ct of 0.12–0.50 mg/L min	*A. salmonicida, Pseudomonas fluorescens, Aeromonas liquifaciens,* and *Yersinia ruckerii,*	99.9%	[Sharrer and Summerfelt, 2007]
2.	Ozone	5.0, 8.0 and 10.0mg O_3/L	Total coliform	2.00 to 4.06 log(10)	[Da Silva et al., 2010]
			Escherichia coli	2.41 to 4.65 log(10)	
3.	Ozone	0.6 to 1 O_3 (mg/L)	*E. coli*	99.99 %	[Rojas-Valencia, 2011]
		1.97 O_3 (mg/L) for 10 min	*Staphylococcus aureus*	99%	
		0.48 to 0.84 O_3 (mg/L)	*Vibrio cholerae*	95%	
		2.6 O_3 (mg/L)	*Salmonella typhimurium*	89%	
4.	Hydro-optic disinfection (HOD) and Ozone treatments	-	Heterotrophic bacteria	50 to 100%	[Cobcroft and Battaglene, 2013]
			Vibrio sp.	100%	
5	Ozone	0.5 gO_3/g dissolved organic carbon (DOC)	Autochthonous bacteria	99%	[Lee et al., 2016]
6.	Ozone	6.0×10^{-3} (mgO_3 min/L)	*E. coli*	2 log inactivation	[Rojas-Valencia, 2011]
7.	$O_3 + H_2O_2$	1.6 7 (mg/L) + 1.7 (mg/L) for 10min	Total Coliform	3 to 3.12 Inactivation (log_{10})	[da Silva et al., 2012]
			E. coli	3.06 to 3.23 Inactivation (log_{10})	

Table 7.1 Microbial disinfection/inactivation through ozone. *Continued*

S. No.	Ozone based Treatment for water/wastewater	Dose of O_3	Organisms reduction / inactivation	Microbial reduction / inactivation	References
Viruses					
8.	Ozone	(Ct) of 0.005– 0.010 mg/L min.	IPNV (infectious pancreatic necrosis virus) and IHNV (infectious hematopoietic necrosis virus)	-	[Sharrer and Summerfelt, 2007]
9.	Ozone	4 to 8.5 O_3 (mg/L)	Polio II	99 %	[Rojas-Valencia, 2011]
10.	Ozone	1.9×10^{-3}(mgO_3 min/L)	*Echovirus*	2 log inactivation	[Gomes et al., 2019]
		4.1×10^{-3} (mgO_3 min/L)	*Adenovirus*		
		8.0×10^{-3} (mgO_3 min/L)	*Coxsackievirus*		
Algae					
11.	Ozone	3 mg/L for 5 min	Algae	76 %	[Hajiali and Pirumyan, 2018]
Fungi					
12.	Ozone	1.5 O_3 (mg/L) for 10 min	*Candida albicans*	99%	[Rojas-Valencia, 2011]
		60 O_3 (mg/L) for 4 min	*Aspergillus flavus*	78 %	
		0.8 to 2.0 (mg/L) for 180min	*Clostridium chauvoei*	4 log	
Protozoa					
13.	Ozone	3.08 (mgO_3 min/L)	*C. parvum*	2 log inactivation	[Gomes et al., 2019]
		0.24 (mgO_3 min/L)	*G. muris*		
		0.65 (mgO_3 min/L)	*G. lamblia*		
14.	Ozone	10 O_3 (mg/L)	*Giardia lamblia*	99.9 %	[Rojas-Valencia, 2011]

at dosages that ranged from 0.10 – 3.65 min mg/L, the reduction in counts of total heterotrophic bacteria and total coliform bacteria were 1.1 to 1.6 LOG10 and 1.9 to 3.1 LOG10 respectively. The effective inactivation of bacteria shown at least O_3 ct dosage (0.1 mg/L O_3 after a contact time of 1 min) while uppermost ct dosage of O_3 (0.2 mg/L O_3 after a contact time of 16.6 min). Therefore, merge O_3 dosages (0.1 to 0.2 min mg/L) with a UV irradiation of around 50 mJ/cm^2 would constantly decrease bacterial counts near the zero. The obtained results show that combining ozonation and UV irradiation may disinfect successfully to the recirculating water before it goes backs to the tank of fish culture [Sharrer and Summerfelt, 2007]. There are some factors which considered to decide the treatment for disinfection are (i) water quality (category and quantity microbes) (ii) toxicity of disinfectant (iii) Quality of drinking water treatment plants (DWTPs) and wastewater treatment plants (WWTPs) (iv) effluent final features (v) formation of disinfection by-products (vi) expenses. Some other factors are also play a crucial role in affecting the disinfection efficiency such as ions of ferrous and manganese, organic, nitrites and sulphides substances that decrease the quantity of oxidizing disinfectants with the resulting microbes inactivation reduction [Collivignarelli et al., 2018].

Ozonation process of treatment for an anaerobic effluent is efficient for the inactivation of E. coli and total coliform. A study concluded that the O_3 dosages employed 6.8 to 9.0 mg/L for different samples and achieved result bacterial standards set up by WHO Guidelines of < 1000 *E. coli* / 100 mL. A minute variation was obtained in COD values [da Silva et al., 2012]. Ozone is being used for disinfection of drinking water as well as chemical oxidation for more than a century. It is well known that ozone is efficiently used for inactivating the protozoans, bacteria, comprising chlorine-resistant pathogens for example Legionella, Giardia cysts as well as *Cryptosporidium parvum* oocysts [Wolf, 2019]. It is reported that all viruses are reduced with the help of conventional sewage treatment. A further quantity of some viruses has reduced to undetectable levels through ozonation. Thus ozonation is a promising technique for decreasing the transmission of numerous human pathogenic viruses. Ozone has the efficient disinfecting ability for parasites furthermore bacteria in clean water and also reduce the number of enteric bacteriophages along with viruses. The step involved in ozonation lifting pumps, generator units where ozone production, injection of O_3 through static mixers, contact tanks furthermore last contact filters [Larocque, 1999]. The action mechanisms are reported for advanced and natural processes. Advanced technologies are fascinating even though it is in the research state, whereas conventional technologies are using mainly. It is a tendency to practice of chlorine-based disinfectant, despite in several forms might cause disinfection by-products formation particularly in Italy. The disinfection treatments are categorized into three (advanced, conventional and natural treatment) categories in this study. The use of chlorine dioxide (ClO_2), chlorine, O_3, per acetic acid and UV radiation for disinfection is considered under the conventional treatment technologies. The advanced treatment technologies are grouping of O_3 and UV radiation, O_3 and H_2O_2, UV radiation with titanium dioxide, H_2O_2 and UV radiation, membranes technologies. While the natural disinfection treatment technologies comprise percolation/

infiltration in soil, slow sand filtration, wastewater stabilization ponds as well as constructed wetlands. The Recreational Water Quality Criteria (RWQC) and Environmental Protection Agency (EPA) suggest that the employ of bacterial organisms such as *E. coli* and *Enterococci* as the indicator for freshwater Currently for wastewater the standards in effect in Italy *E. coli* considered as the solitary indicator of fecal pollution [Collivignarelli et al., 2018]. The main target is to attained characteristics of reclaimed water that is suitable for future use as well as is defensive of man and environment health [U.S. Environmental Protection Agency (USEPA) 2012]. O_3 is much more efficient in comparison to chlorine, ClO_2 or monochloramine against the rotaviruses. Furthermore, there are definite pathogens for instance Mycobacterium fortuitum are further resistant to O_3 than other organisms like *E. coli,* poliovirus type 1 or *Salmonella typhimurium*. O_3 is also fairly efficient against oocysts and protozoan cysts as well as against Bacillus subtilis spores [Bitton, 2014]. As we know that ozone is used in the treatment of drinking water. Ozone is applied for disinfection of drinking water, it not only disinfect the drinking water but also odor and taste control as well as remove the color, manganese and iron. Pre-coagulation ozonation process may also efficiently decrease doses of coagulant through getting better destabilization of particles as well as aggregation, reduce the THMs forerunner along with improving turbidity of filtered and settled water also. It was also illustrating in their study that the AOP such as Ozone/Hydrogen peroxide would improve the processes of water treatment as well as the quality of finished water [Rahmana et al., 2010].

7.6.1 Mechanisms of Inactivation by Ozone

Ozone play important role in inactivating the microorganisms through the production of hydroxyl (OH) as well as superoxide (O_2^-) free radicals. Ozone influences the enzymatic activities, DNA and permeability of cells of the bacteria where residues such as guanine or thymine emerge to be the largely vulnerable targets. Ozone injured to the nucleic acid core or protein coat in case of viruses while in case of rotaviruses both [Bitton, 2014].

7.7 Treatment of municipal and industrial wastewater through Ozone-based technology

A huge quantity of various prescription and non-prescription drugs of diverse categories is eating all over the globe yearly. These pharmaceutical complexes comprise analgesics, antidepressants, antipyretics, antibiotics, regulators of blood lipid, agents of chemotherapy along with contraceptive drugs. After the management, these complexes are digested partly and excrete through the faeces plus urine, furthermore consequently go into the STPs for the treatment of these compounds as well as various other inorganic and organic components in the wastewater. Though, it has been revealed that these several pharmaceutical complexes are not entirely separated in the sewage treatment plants [Ikehata et al., 2006]. There are as a minimum of

80 personal care products (PPCPs) such as antibiotics, antiepileptics, antidepressants etc have been recognized in discharge through STPs moreover surface waters worldwide. It was observed in a study that the filters effluents show obviously that the complexes removal was more while pre-coagulation ozonation was put into practice than the processes of conventional treatment while O_3 was not employed. Different scientific groups reports show to worry about that the traces of drugs which might formulate their way into tap water. Studies point out that O_3 and activated carbon are capable treatment technologies for removing pesticides along with pharmaceuticals traces also [Jasim et al., 2006]. O_3 reduces the color and COD of wastewater while enhancing pH to some extent. Though there was no major alter observed in total dissolved solids (TDS) and electrical conductivity [Bhatta et al., 2015]. Ozone has a range of applications for municipal wastewater treatment plants (Fig. 7.2) comprise conditioning of sludge, secondary effluent disinfection, control of odor and primary effluent peroxidation. Besides disinfection, O_3 decrease color furthermore enhances levels of DO [Loeb et al., 2012].

A full-scale experience of sludge reduction through the short contact time ozonation into a WWTP chiefly fed on textile wastewater. The performance of WWTP more than a 3-year functioning data series was studied furthermore compared by a 2 year functioning with ozonation of sludge. Full-scale ozonation of sludge was used to a portion of 20% of the recycle sludge run at WWTP primarily textile effluents treatment. It improves the notable enhancement in settle ability of sludge, which consecutively endorsed plant operators to retain a good quantity of mixed-liquor suspended solids (MLSS) in the biological reactors by in that order high sludge retention time (SRT). The surplus sludge generation was decreased by 17% later one year of testing time. Though, present oxygen which was passed through ozonated flow in the aeration tank amazingly decreased the concurrent nitrification-denitrification reactions that generally take place in the aerobic biological reactor which set up prior to the ozonation process. Thus the removal efficiency of nitrogen and phosphorus dropped from 58 to 46% and 70% to 28% respectively, as a result of decreased biosynthesis [Gardoni et al., 2011]. A study was conducted for illuminating the efficiency in dyeing wastewater treatment from a treatment plant and used three processes of treatment raw wastewater-coagulation-biological treatment (RCB), raw wastewater-pre ozonation-biological treatment (ROB) and raw wastewater-biological treatment-post-ozonation (RBO). The removal of DOC through the biological treatment of RW obtained 200 mg/L that was obviously greater than that of 12 mg/L through ozonation. In contrast, only 108 mg/L of DOC elimination was noticed with biological treatment in RW later ozonation. It was observed that reduce in dissolved organic carbon (DOC) and BOD_5 in the subsequent order RCB ≥ RBO > ROB and ROB ≥ RCB > RBO respectively. Whereas color also removed efficiently via ozonation for both RW and RW subsequent to biological treatment and reduction of color in the following order: RBO > ROB ≥ RCB [Takahashi and Kumagai, 2008]. There are various methods for instance adsorption, biological treatment, coagulation, electrochemical oxidation, flocculation that is feasible and use in removal of dye from industrial wastewater. Hence, the conventional methods, for

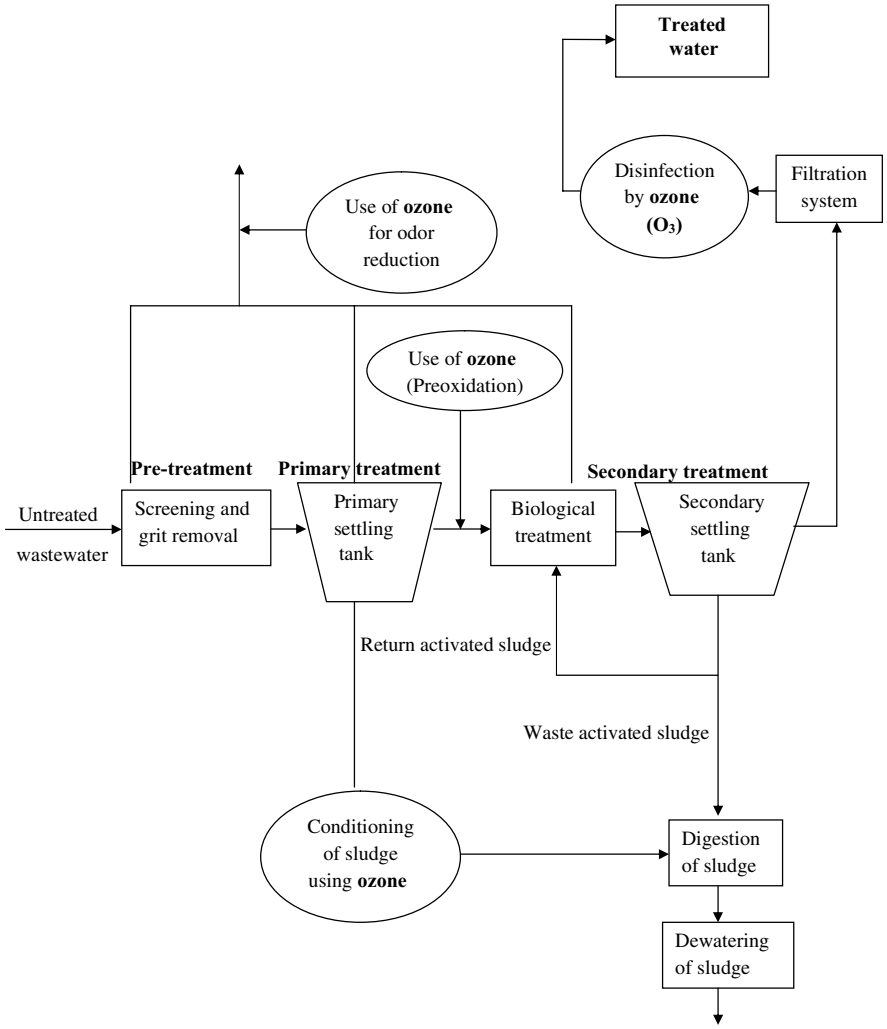

FIG. 7.2 Municipal wastewater treatment trough ozone-based technology.

instance, biological, chemical and physical processes or use its collection of every is incompetent for the removal of dye [Karami et al., 2016]. Whereas ozonation is the method of treatment which offer excellent result in degradation of dyes as well as eradicates any trouble to a large extent. The AOPs which may generate oxidizing OH radicals have been recognized as a competent method for dyes degradation [Iranifam et al., 2011]. AOPs are an alternative technique to reduce and decolorize recalcitrant loads of wastewater from textile industries. In case of AOPs hydroxyl

(OH) radicals are produced in water, these radicals are extremely reactive as well as nonselective oxidants which may oxidize the organic complexes Oxidation with O_3 is recognized to be an influential technique to decolorize the reactive dyes through obliterates the chromophoric system [Sharma et al., 2013]. The textile industries use a huge amount of water as well as wastewater generation also from various steps in dyeing and finishing processes. The wastewater generated from dyeing and printing units having rich in color, reactive dyes along with chemicals residues, for instance, complex components, numerous aerosols, a huge concentration of COD and BOD in addition to a large amount of hard to degrade substances [Wang et al., 2011]. The wastewater generated from dye sector can cause an environmental problem for instance eutrophication in getting water bodies and environmental concern regarding the likely carcinogenicity as well as the toxicity of several organic dyes. Dyes are not only responsible for reducing the penetration of light and photosynthetic activity but also diminish the DO level of those water bodies. There are a number of treatment methods are applied such as physical, chemical and biological for treating dye holding wastewater. Among these, all treatment methods activated sludge, adsorption and flocculation treatment technology are commonly used in Indonesia. Biological methods of treatment are regularly employing for treating textile effluents. Though, microbial-based methods of treatment are not able to remove color quickly. The present organics in textile wastewater treated biologically be required to be achieved through definite techniques that improve the biological degradability of organics for instance ozonation [Suryawan et al., 2017]. There are various research performed for assessing the ozonation performance in grouping with the biological process of treatment for decreasing the dye in wastewater. It was reported that the AOPs such as the mixture of O_3/H_2O_2, UV/Hydrogen peroxide and UV/O_3 increased the rate of degradation of 1, 3, 5-trinitrotriazacyclohexane (RDX) because of enhanced the formation OH radical [Abidin and Rahmat, 2010]. It was explored that the consequence of pre ozonation and following biological treatment method on reducing in DOC along with color for dyeing wastewater. It was observed and reported that removal of color up to 88.6 % furthermore concentration of DOC steadily reduced due to ozonation. Following biological treatment process was eliminated DOC drastically [Takahashi et al., 2007]. It was compared in a study that treatment of raw as well as the effluent of biotreated (upflow anaerobic sludge blanket, UASB) textile dye bath through ozonation and AOPs [Muhammad et al., 2008].

Removal of pharmaceuticals takes place through O_3 either by direct oxidation with O_3 or by indirect reaction with OH radicals. The broad variety of rate constants for diverse pharmaceuticals builds it complex to forecast the removal of pharmaceuticals at various doses of O_3 [Fornander, .2018]. It was also examined in one more study that the efficiency of ozone-based processes of advanced oxidation for eliminating the pharmaceuticals as of water and wastewater. The finding shows that ozonation methods of treatment are more efficient in comparison to other conventional oxidation methods (ClO_2 and Cl_2) in removing pharmaceuticals along with dropping toxicity of water or wastewater effluent [Almomani et al., 2016]. There are various types of PPCPs are being consumed in huge amount in present societies

furthermore the practices of PPCPs will probably carry on intensifying in upcoming time also. The influence of ozone dose along with reaction time on treatment process of Ozone/UV65W was looked into for PPCPs elimination in the secondary effluent of WWTP. The observed result shows that Ozone/UV65W treatment has the potential for eliminating a large variety of PPCPs as of the secondary waste matter of the WWTP [Paucar et al., 2019].

7.8 Removal of physical pollutants (odor and taste) through Ozone-based technologies

O_3 is an efficient oxidizer of color because of complexes of dissolved organic as well as unlike chlorine will not produce chlorinated organic compounds. It was also reported in this study that the 1 mg O_3/liter be able to eliminate 10 color units and has revealed that around 1 mg O_3/mg dye is needed for obtaining 95% of color removal, though this ratio fluctuates with dye type. The ratio enhanced to approx 1.5 for removal of 100%. The production of odor and taste in drinking water may have numerous causes. The odor and taste producing composites may take place in raw water; however, it may be formed also for the period of water treatment. The employ of O_3 as an oxidant may reduce these problems. Wet chemical scrubbing employing O_3 is an excellent solution for controlling odor within circumstances where there is great intensity odor, more air volumes or inadequate space to site an odor management system. O_3 is very effective for the oxidation of unsaturated composites. In the case of oxidation of pesticides, the combination of O_3 with H_2O_2 (AOP technology) is more efficient in comparison to O_3 alone. 2-methylisoborneol (MIB), as well as Geosmin, is instances of resistant odorous complexes generated by algae have a minute odor moreover taste threshold and frequently occur in water. However, O_3 is still extremely effective in removing particular these compounds. The combination of peroxidation and filtration methods appears to be a highly efficient way of removing the odor and taste constituents [Shah et al., 2016]. Ozone may employ for control of odor and taste in addition to for oxidation of inorganic pollutants also [Wolf, 2019]. In the case of drinking, water ozone is used mainly for disinfection point of view as well as odor and taste control. Besides it ozonation may get better removal of iron and manganese and color also [Rahmana et al., 2010].

7.9 Removal of various chemical pollutants (COD, BOD and coloring agents) from wastewater through Ozone-based technologies

The use of O_3 has been broadening for treating wastewater, while its major function is to contribute to the reduction of micropollutants in the effluent of secondary wastewater as well as the lessening of their load from the water environment. Ultimately, O_3 is flattering an important part of numerous potable reuse trains, while it may be

employed for pre-oxidation of organic matter of effluent, reduction of micropollutants furthermore disinfection [Gerrity et al., 2013]. As per ESCO International study, the rate of COD removal for industrial wastewater is greater than 95% if employing oxidants such as ozone doses. It is also accounted that the primary control parameters for the elimination of BOD along with COD by O_3 based AOP are quantity/dose, pH and contact time. As the oxidants (O_3) dose is augmented, carbon, C-C single bonds are assault furthermore broken resultant in the reduction of BOD, COD and TOC [Shah et al., 2016]. The quality of COD, as well as color removal of RR120 azo dye through preozonation subsequent with CMAS treatment, were assessed for use in the effluent treatment of industrial azo dye. The pH reduction points out that the acidic byproducts formation. Results indicate that the biological treatment is more competent at mineralizing the byproducts of the ozonation, however fewer proficient at the color drop in comparison to the ozonation method itself. In addition, the ozonation and the mechanism of biological treatment at lower O_3 doses concurrently play a role in the removal of COD. Though, it was considerably contributed through direct oxidation at the maximum dose of O_3. Ozonation of dyes generally produces small organics particle which generates a residual COD. Hence, these formed COD may further be degrading through biological treatment. Therefore, it is suggested that ozonation should be employed at medium O_3 doses since a pre-treatment for joint ozonation biological treatment for elimination of azo dye [[65]Abidin et al., 2016]. Ozonation is capable for decolorizing of Remazol Brilliant Blue, Reactive Green 19, Reactive Red 120 and Reactive Black 5 even though a minor dose of ozone (0.3 mg O_3. mg dye^{-1}). Contrarily, it was observed the considerable reduced in the quantity of COD in a huge variety of O_3 doses (1.2 mg O_3. mg dye^{-1}) [Abidin and Rahmat, 2010]. In another study, these compounds such as Reactive Green 19, Reactive Red 120, Reactive Black 5 and Remazol Brilliant Blue were chosen among azo dyes because of its more solubility in the water environment. COD elimination was contributed at the same time through ozonation as well as biological treatment at lesser doses of O_3 [Abidin and Ridwan, 2011]. The total oxidation of azo dye was the main reason for the greater removal of COD at high O_3 dose. It was also observed that the biodegradable portion of COD might be additional oxidized as well entirely eliminated through ozonation. Another emerging method is known as AOPs used for oxidizing organic substances through oxidizing agents, for instance, O_3, UV light, H_2O_2 or grouping of these oxidants. Almost industries are using this process for removing color and COD. However, it may not gratify the environmental release criterion through itself unaccompanied along with relatively high cost also. The grouping of ozonation, as well as biological treatment, appears to be proficient unit methods for removing residual BOD, COD and color containing dye wastewater [Abidin and Rahmat, 2010]. The growing of textile industries in Bandung, Indonesia is one of the fast-growing industries. It releases a huge quantity of exceedingly colored wastewater because of the great quantity of use of water in addition to the employ of dyes also during the manufacturing process. There is a big problem of color removal in processing textile wastewater through the treatment of conventional biological process because of its ineffectiveness. An additional treatment required for color removal as

post-treatment for releasing treated wastewater. Ozonation is a well-known process for efficiently removing textile color [Wantoputri et al., 2019]. Ozonation applied for COD and color removal of raw furthermore anaerobically treated UASB joint industrial (primarily textile) wastewater in a lab-scale bubble column reactor. It was obtained that the most favourable process conditions for biotreated effluent the pH and temperature 8 and 25°C respectively consequence in the removal of color and COD 100% and 96% respectively for ten min ozonation. The best result demonstrated with the use of ozonation for post-treatment of anaerobically treated effluent for the elimination of color and COD than the pretreatment of joint industrial effluent of the similar nature. Though, the effectiveness of ozonation method was greater than before at high pH. The best results for raw as well as biotreated wastewater was noticed on pH of 9 and 8 correspondingly. Whereas temperature illustrated a bad effect on the elimination efficiency while temperature enhances (> 30°C) resulted in incessant reduce degradation of COD and color [Yasar et al., 2007]. The ozonation relevance is enhanced in current years, these treatments have some major disadvantage being associated with the formation of by-products, which may have toxic along with carcinogenic features and thus should be studied further. The joint treatment of ozonation as well as following biological degradation through a biofilm, for decreasing the COD and color was examined in the present study. The obtained results show that the ozonation of Remazol Black B dye at pH (3 to 11) was efficient, partly oxidizing and effluent decolorizing entirely, even at comparatively more quantity of dye (500 mg/L) [de Souza et al., 2010]. In almost cases concentration of COD is always greater in comparison to BOD in wastewater process as not the complete organic substances are biodegradable. Several industrial effluents for instance dairy, pulp and paper, breweries, iron and steel and mining also generates wastewater during process having high COD >1000 ppm. The organic COD of wastewater may be categorized into two biodegradable and non-biodegradable (Fig. 7.3). O_3-AOP is advantageous in circumstances where O_3 may not attain full oxidation composites present in wastewater. AOP applied in these cases and boost the reaction kinetics to eliminate even the more complex materials. The Fig. 7.3 shows the summary of different types of complexes along with how it may be treated with O_3 [U.S. Environmental Protection Agency (USEPA) 2021].

It was studied by other researchers that the oxidation method of industrial wastewater treatment moreover the influence of these systems on the elimination of color as well as algae are talked about in details. O_3 is very unstable furthermore must be produced on the site. The oxidation potential (2.07 V) of O_3 is higher in comparison to chlorine (1.36 V) or hypochlous acid (1.49 V), in addition to, hence it produces superior and proficient consequence in the removal of color and algae than the other substitutes in definite wastewater treatment methods [Hajiali and Pirumyan, 2018]. There are several ozone-based treatment processes is also applied by different researches in their studies for removal of various pollutants such as BOD, COD and color etc from wastewater are listed in Table 7.2. There is a study involved a comparative analysis of the effectiveness of numerous O_3-and/or UV-based methods such as O_3, UV/H_2O_2, O_3/Hydrogen peroxide, UV/Ozone along with UV/H_2O_2/Ozone

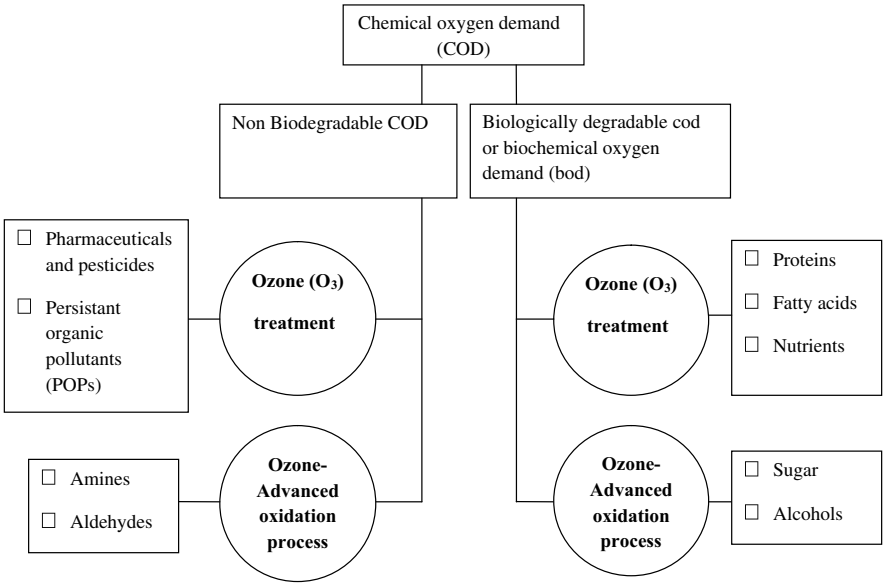

FIG. 7.3 Removal of various pollutants through ozone-based technologies.

for phenol reduction as a model hazardous contaminant in wastewater. The most excellent experimental circumstances regarding chosen different process parameters, the dosage of H_2O_2 as well as initial pH were found out for the entire applied AOPs. A variety of AOPs was assessed based on its eco-effectiveness, a decrease of TOC, decompose of phenol as well as their cost-effective. It was also recognized that the removal of total phenol may be accomplished through regulating the H_2O_2 dosage furthermore pH. In general, the total quantity of mineralization depended on these parameters such as amount and kind of oxidants and/or type of UV light process in addition to their considered processes parameters also. The UV/H_2O_2/O_3 process was achieved maximum total mineralization amount (TOC, 58.0%) elimination. UV/H_2O_2/O_3 was revealed more appropriate process from both eco as well as cost-effectiveness points of view [Kusic et al., 2006].

7.10 Factors affecting the Ozonation process

Various researchers have studied about the factors affecting the efficiency of the ozonation process. The decay rate of O_3 is influenced by several factors, for instance, initial concentration of O_3, dosing methods of O_3, pH, pipe and temperature *etc* [Yannan et al., 2013]. The performance of ozonation processes is affected by factors such as temperature and pH. The O_3 takes place in molecular O_3 at acidic conditions (lower pH) furthermore its breakdown into extremely reactive species

Table 7.2 Removal of various types of pollutants through ozone-based treatment technologies.

S. No.	Treatment methods used	Types of waste treated	Removal of Pollutants and their percentage (%)	Time consumed (minute)	References
1.	$UV/H_2O_2/O_3$ process	organic pollutants (phenols) containing wastewater	TOC (58.0%)	-	[Kusic et al., 2006]
2.	Ozonation of anaerobic bioprocess effluent	Raw and anaerobically treated up-flow anaerobic sludge blanket (UASB) combined industrial (mainly textile) effluent	100% color and 96% COD	10 min	[Yasar et al., 2007]
3.	Ozonation	Upflow anaerobic sludge blanket (UASB) treated effluent	COD (75%), color (95%) and BOD (85%)	25 min	[Muhammad et al., 2008]
4.	$UV/H_2O_2/O_3$	Petroleum wastewater	Phenols (100%),	-	[Rodriguez et al., 2008]
	$TiO_2/UV/O_3$-BAC	Textiles wastewater	Coloring substances (90%) Dyes, TOC (50%)	-	
	Ozone (O_3)	Agriculture wastewater	Pesticides (Complete)	-	
5.	Ozonation	Raw dye bath effluent	Color (58%)	-	[Muhammad et al., 2008]
6.	Combined ozonation and biological treatment	Hydrolyzed textile azo dye-containing effluent	Color (96%), COD	-	[de Souza et al., 2010]
7.	Ozonation	Azo Dye Industrial Effluent	Color (almost Complete), COD	-	[Abidin and Rahmat, 2010]
8.	Ozone	Anaerobic sanitary wastewater effluent	COD (37.6% to 48.8%)	5 to 15 min	[Da Silva et al., 2010]
9.	Ozone + hydrogen peroxide	Anoxic sanitary wastewater treated	COD (7.50 to 9.40%)	10m & 20m	[da Silva et al., 2012]

(continued)

Table 7.2 Removal of various types of pollutants through ozone-based treatment technologies. *Continued*

S. No.	Treatment methods used	Types of waste treated	Removal of Pollutants and their percentage (%)	Time consumed (minute)	References
10.	Ozone based technology	Industrial wastewater	COD (95%), BOD and TOC	-	[Shah et al., 2016]
11.	Ozone	fulvic and humic substances	Complete color removal	-	
12.	Ultrasonic powers (US)/ O_3/H2O_2 system	Azo dye, reactive red 198 from aqueous solutions	Color (100) and COD (69%) removal of RR198	40 min	[Karami et al., 2016]
13.	Ozonation		Toxicity (66%)	-	[Almomani et al., 2016]
14.	GAC and ozone treatment	effluents from sewage treatment plants	87-95% of the total concentrations of active pharmaceutical ingredients	-	[Beijer et al., 2017]
15.	Ozone treatment	Textile wastewater treatment containing reactive black-5	Color (96.9 %)	5 hours	[Suryawan et al., 2017]
		Industrial wastewater	COD (77.5%)	2 hours	
16.	Ozone		color	-	[Hajiali and Pirumyan, 2018]
17.	Ozone and hydrogen peroxide	Endek wastewater treatment	Color (90%) COD (22%)	60m	[Suryawan et al., 2017]
18.	Ozonation	Artificial treated textile wastewater	Color (100%)	10m	[Wantoputri et al., 2019]

such as $HO_2^{\bullet}$, $HO^{\bullet}$ and $HO_3^{\bullet}$ happen in an alkaline condition. Among all these species, $HO^{\bullet}$ is a very significant oxidant as its rate of attack is 106-109 times quicker compared to the reaction rate of molecular O_3 [Yasar et al., 2007]. The ratio among O_3 as well as OH radicals is pretentious with pH into wastewater. The increment in pH value enhances the amount of OH radicals. In addition, an enhanced pH affects the certain functional group's reactivity of the pharmaceuticals. For example, with increase the pH amines turn into further reactive, it is because of enhanced electronegativity. The best pH of the rate of reaction monitored at pH, 8, in deionized water by means of added scavengers [Fornander, .2018]. pH may be a significant parameter in O_3 disinfection. It cannot be right away clear as the properties of disinfection at a specified concentration of O_3 solution are not thought to fluctuate considerably through pH, as a minimum pH of 9. Alternatively, it is significant to know that the specific needed O_3 dosage to accomplish a goal disinfecting amount for O_3 will fluctuate as decay rates of O_3 enhance by pH particularly over pH of 8. Disinfection might still be attained under elevated pH circumstances as the action of O_3 is comparatively fast [Kritsevskaja, 2021]. It was observed in another study that the elimination of COD percentage during ozonation process reduced as of 48 % to 39 % while pH was enhanced as of 6 to 7 moreover after that rose to 57 % as the pH of 8. The COD elimination percentage was persisted approximately unaffected at the pH more than 8. The dye degradation along with COD elimination at pH, 6 is associated to direct oxidation of O_3 by molecules of dye that is the main pathway reaction into acidic condition. By pH increment, the COD removal was also enhanced. It is also reported that the reactive radical formation rose because of speeding up O_3 decomposition rate [Karami et al., 2016]. It was observed that ozonation effects take place perhaps because of slight alter in pH as well as the concentration of carbonate not due to any direct reaction of O_3 itself. Ozonation effects are significantly affected through parameters of raw water quality, for instance, natural organic matter (NOM), pH, category and quantity, hardness along with coagulation conditions (a type of coagulant, quantity) as well might even influence systems damagingly [Rahmana et al., 2010]. It is obvious that other factors have an effect on the reaction mechanism furthermore rates as found through different studies. The efficiency of O_3 to oxidize the inorganic plus organic complexes is a role of pH and temperature of the water. There are numerous variables, for example, BOD, COD, heavy metals, pH, TSS, the temperature of the water so on that require being considered in the use of wastewater. O_3 at low (less than 7) pH react mainly as the O_3 molecule through selective as well as for a moment comparatively slow reactions. Ozone decomposes speedily into OH free radicals at high (more than 8) pH and which react extremely fast. Various composites which are oxidized gradually will oxidize quickly while pH is attuned to the alkaline side. The most appropriate pH was 8 to 10 obtained for the oxidation of organic particles [Hajiali and Pirumyan, 2018]. The inactivation of the virus through O_3 considering parameters of pH and temperature. The MS2 inactivation was examined more than pH (6.5 to 8.5) as well as in the range of temperature (2 to 22°C), approximately treatment qualities of water and wastewater. With the increment in both the pH and

temperature speeded up the inactivation, while the effects were slight [Wolf, 2019]. It was illustrated that the decolorization of direct dyestuff wastewaters was notable in the pH of 12 (basic condition). A great number of bubbles was produced on an elevated airflow rate of O_3. Hence O_3 treatment is excellent for dyestuff wastewater in decolorization [Turhan and Turgut, 2009].

Temperature also influences the efficiency of ozone treatment. The effect of temperature on ozonation is a net consequence of two concurrent outcomes for example rates constant increment in a reaction as well as the changes in O_3 solubility by temperature. The solubility of O_3 decreases with rising in temperature, thus the quantity of O_3 obtainable reduces for the reactions that can consequence in a complete decrease in degradation. The distinction in solubility slows down reactions among O_3 plus organics. The efficiency of O_3 enhances as the rate of reaction increases with enhance in temperature (between 5 to 20°C), whereas solubility is not greatly affected. Though, the COD elimination is not influenced considerably up to 40°C because of compensation of boost in the rate of reaction by means of reducing in O_3 solubility. Conversely, a declining trend comes into view beyond 50°C as reduce in solubility conquers enhance in rate of reaction [Yasar et al., 2007].

There are numerous catalysts employed jointly with O_3, for example, electrocoagulation, H_2O_2, semi-precious as well as precious metals and ultrasonic agitation. Although, usually and well recognized used the ultraviolet rays at the 254 nm of wavelength. Finally, it was found that the various complexes which neither O_3 nor UV independently may eliminate, though UV and O_3 jointly may be eliminated as well as the elimination rate is enormously fast, for a moment in as minute as two seconds [Hajiali and Pirumyan, 2018]. It is well known that the dissolved effluent organic matter (dEfOM), suspended solids as well as microbiota complexity into the wastewater might be the main parameters illuminating the difference of effectiveness of ozonation treatment. As expected, the effectiveness of the ozonation process was extremely O_3 dose, in addition, to contact time-dependent [Iakovides et al., 2019]. Ozonation processes may be affected via organic carbon that may work as a scavenger or promoter or both. Though, the huge quantity of organic carbon is generally related by reduced rates of oxidation. COD and DOC are generally employed for characterizing the organic carbon throughout the oxidation. The COD reduced when oxidation of organic complexes takes place, though, the composite is normally not mineralized thus capitulating no or small DOC reduction. Turbidity is also a very important parameter. It is measuring the cloudiness in a fluid due to suspended particles. Cloudy effluent having elevated turbidity might point out the problem in the process of treatment plus poor control of the process. The ozonation might be affected in two modes through inorganic salts: by the rate of mass transfer or by performing as a scavenger or promoter. Salts may decline the coalescence of bubbles through raising the ionic strength into wastewater, therefore enhancing the bubble's surface area furthermore raise the rate of mass transfer. Nitrite reacts quickly with O_3 furthermore may consume a major quantity of O_3. Nitrate product form when oxidation of nitrite takes place [Fornander, .2018].

7.11 Conclusion and Future prospects

Water is an incredibly valuable supply and rich compound that without it, a man may not exist for some days on earth. Water plays several considerable utilities in our body. All living organisms like humans, plants and animals are made of main water. It is typically recognized as a universal solvent. The major use of water is in houses, agriculture and various industries. The foremost causes of water pollution are population growth, fast industrialization and urbanisation; apply science and technology in addition to modern practices of farming. There are many of the conventional treatment techniques for instance activated sludge, adsorption and chemical coagulation are available for the treatment of wastewater are applied for removal of pollutants, even if there are several limitations, chiefly high cost of operation. Whereas currently, many disinfection methods are using in water recovery which derived from those in the treatment of drinking water. The widespread methods comprise chlorination, membrane filtration, ozonation and Ultra Violet (UV) irradiation *etc.* In the midst of all treatment methods, ozone-based technology is steadily further employed in retrieved water disinfection. Ozone is a strong oxidant that utilizes for potabilization of ground or surface water as well as in the treatment of wastewater for getting rid of organic pollutants, inorganic ions furthermore microbes also. It is applying as disinfectant, taste and odor remover. Ozone based treatment is removing bacteria, protozoa and viruses very efficiently. The oxidizing agents such as H_2O_2, O_3 and UV light or joint of these oxidants within chemical methods are used for oxidizing organic substances named as Advanced Oxidation Processes (AOP). AOPs are using in the industrial sector in COD and color removal. The main reason of using this technology because it has many qualities such as strong oxidizing power, needs short reaction time, quick disinfection, oxygen supply to the water follow disinfection, color and odor removal, chemicals not required, oxidises to manganese and iron, reduce BOD and COD, no odor produce etc. There is further need to research in this field for more improving these technologies.

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CHAPTER

8

Constructed wetland: a promising technology for the treatment of hazardous textile dyes and effluent

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8.1 Introduction

Globalization and industrialization have made a huge impact on the textile industry in the recent years. Textile industry contributes majorly to the global economy employing large number of workers throughout the world. Since textile industries are labor-intensive, many developing countries invest their human resource in it (Keane and te Velde, 2008). The Indian dye industry has grown by huge percentage in the past decade, making India the second largest producer of dyes in Asia, after China (Singh et al, 2017). India alone contributes to 6.6% of the dye production worldwide (Shenai, 1995).

Beside several benefits, textile industry contributes to a large percentage of pollution. The dyes produced and utilized by the textile industry require large quantities of water during different processes. After the dying processes, the wastewater containing synthetic dyes is released directly into the water bodies causing harm to the aquatic flora and fauna (Robinson et al., 2001; Ghaly et al., 2014; Rai et al., 2005). Textile wastewater heavily pollutes common ground water and soil.

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With the exponentially increasing population and urbanization, there will be an increase in the global water demand in the future. Agriculture accounts for majority of water demand followed by industries leading to only a small proportion left for domestic use and drinking purpose (Mekonnen and Hoekstra, 2018). The major challenge posed by textile industry is the discharge of large amount of untreated wastewater which is produced during the preprocessing steps of textiles and fibers (Watharkar et al, 2015). This discharge has detrimental effects on human health, animals, and environment. Recalcitrant dyes present in the textile effluent are carcinogenic and mutagenic (Watharkar et al, 2015). The textile wastewater contains high concentration of dyes with complex chemical structures along with other toxic chemicals, humectants, salts, oxidants, surfactants, acids, bases etc. The textile wastewater is characterized by high physicochemical parameters like biological oxygen demand (BOD), total Organic carbon (TOC), total suspended solids (TSS), chemical oxygen demand (COD), and high concentration of organic halogens as well as inorganic substances such as chlorides, sulphates, nitrites, metals, and sulfides (Venceslau et al., 1994); due to all these factors treatment of textile effluent is very difficult (Pandey et al., 2007).

Numerous treatment strategies have been adopted to treat textile wastewater. Physical methods like adsorption, membrane filtration offer advantage since they are cost-effective and easily operated. Adsorption is one of the popular methods but is only capable of removing dyes and not degrading it (Robinson et al., 2001). Chemical methods like oxidation and flocculation are also used but are expensive and are not widely used due to requirement of large quantity of chemicals, energy, and further may form harmful substances. Moreover, these methods are very expensive, it becomes unaffordable for small scale industries (Khandare et al., 2013b).

Recently, considerable attention has been focused on phytoremediation as a bioremediation approach of dye degradation. The exploitation of plants either alone or augmented with bacteria, fungi and/or yeast have known to be successful in degrading textile dyes. Moreover, as compared to physical and chemical strategies, phytoremediation is evidenced to be cost-effective, and ecofriendly. Phytoremediation offers multiple advantages of being solar energy dependent and a carbon neutral process of degrading textile dyes, heavy metals, landfill leachates, polyaromatic hydrocarbons, petroleum, and other contaminants (Dietz and Schnoor, 2008; Pilon-Smits, 2005). This capability of degradation can be fully owed to the fact that plants have the ability to extract contaminants like dyes (Govindwar and Kagalkar, 2010) and ultimately degrade into non-toxic metabolites. Plants possessing deep, fibrous roots are preferred for phytoremediation of textile effluents. Additionally, plants are habitats to a wide range of microorganisms which assist in degradation of contaminants through multiple enzymatic pathways (Khandare et al, 2011; 2013b; Rane et al, 2014).

In recent decades, successful phytoremediation experiments are being implemented at lab and pilot scale. For this purpose, constructed wetlands (CW) are being used for the large amount of textile effluent treatment. CWs are treatment plants designed, constructed and operated in controlled conditions and offers use of either known plant-microbial consortium or plant with activities of some unknown

microbes (Haberl et al, 2003). This method provides multiple advantages like low cost, environmentally friendly, easy operation, high efficiency and minimum production of physical and chemical sludge (Bulc and Ojstršek, 2008). The presence of detoxifying and decolorizing enzymes like laccase, lipase, oxidoreductase, and lignin-modifying enzymes in microbes help in degrading the textile dyes and contaminants (Ajao et al, 2017; Singh et al, 2016; Costa et al, 2018; Roy et al, 2018; Zabłocka-Godlewska et al, 2018).

Present chapter discusses different types of commonly used dyes, their harmful effects to the environs including human health. Further efforts have been taken to overview CWs and current research status of textile effluent treatment using CWs.

8.2 Classification of dyes

Dyes can be defined as organic substances with complex structure having ability to absorb light from the visible spectrum to produce color (Rehman et al., 2020). Structure of dyes can be divided into three parts: the chromophore, auxochrome, and the matrix (Laurent et al, 2010). The chromophore is the active site of the dye which locates the atoms involved in the absorption of light from the visible spectra while the auxochrome fixes the dye and is also involved in the modification of the color property of dye. The chromophore group of dye is capable of dyeing only in presence of auxochrome molecules (Benaissa, 2012). The third part of the dye is the matrix (Laurent et al, 2010).

Table 8.1 summarizes different types of dyes, its feature and various applications. Dyes used for industrial purposes can be classified into acid, basic, reactive, direct, disperse, vat, sulphur, metal complex, mordant, and azoic dyes. Due to the presence of certain functional groups like carboxylic acid, amine and azo group, textile dyes cannot be easily treated with traditional treatment systems (Temesgen et al, 2018). Synthetic dyes are used by the industry since they are inexpensive and have strong fixating property (Burkinshaw and Gotsopoulos, 1996). Table 8.2

8.3 Impact of dye toxicity on environment

Despite textile industry offering employment to a large number of workers around the world, it also contributes to large percentage of pollution globally (Desore and Narula, 2018; Bhatia, 2017). The various processes such as bleaching, dyeing and washing involved in the textile industry use a massive quantity of portable and drinking water (Hossain et al, 2018). The textile and clothing industry poses many detrimental effects on the environment and living beings (Muthu, 2017). The textile industry causes air pollution by releasing particulate matter, oxides of nitrogen, Sulphur, and organic compounds and dust (Bhatia, 2017). The most harmful emission of textile industries is the release of untreated textile sludge into normal water reservoir (Bhatia, 2017), which contains 80% of the net discharge. The textile effluents pose

Table 8.1 Types of dyes, features, and various applications.

Sr. no.	Category of Dye	Features	Application	Reference
1.	Acid	1. High affinity towards basic molecules of fibers. 2. High solubility	Used in textile, pharmaceutical, printing, leather, dye paper industries. Applied mostly on nylon, cotton and wool	Wu et al, 2020; Miladinova et al, 2016
2.	Reactive	1. High wet fastness and available in various types 2. Reactive groups bind to the fibers 3. Forms covalent bond with sulfhydryl or amine group present in textile fibers 4. Good light fastness 5. Better dyeing processing results	Widely applied for cellulosic fibers and sometimes silk and wool fibers dyeing	Zhang et al., 2005; Benkhaya et al, 2016; Benkhaya and ElHarfi, 2017; Hassan et al, 2009; Mortazavi-Derazkola et al, 2017; Gürses et al, 2016; Shankarling et al, 2017
3.	Azoic	1. Around 60-70% of the textile dyes are azo dyes. 2. Non-biodegradable 3. Insoluble in water	Textile, food, paper, leather, cosmetic and printing industry.	Ferreira et al, 2004; Raman and Kanmani, 2016; Hassan and Carr, 2018
4.	Mordant	1. Form complex with TiO_2 surface 2. Have low affinity for certain textile fibers	Used for dying of silk, wool, and leather	Millington et al, 2007; Nikfar and Jaberidoost, 2014
5.	Direct	1. Have strong affinity for cellulose fibers	Popularly used to colour paper related materials	Jalandoni- Buan et al, 2010
6.	Basic	1. Will either be positively charge or may have a delocalized charge on dye cation. 2. Have poor migration properties 3. Water-soluble and produce colored cation in solution	Usually used for acrylic paper and nylon and polyester substrates	Hunger, 2003; Silkstone, 1982; Broadbent, 2001

Table 8.1 Types of dyes, features, and various applications. *Continued*

Sr. no.	Category of Dye	Features	Application	Reference
7.	Vat	1. Better color fastness 2. Excellent light and wet fastness property 3. Soluble in hot water	Used for cellulosic fibers	Khatri et al, 2017; Burkinshaw, 1995; Burkinshaw and Son, 2010; Hihara et al, 2002
8.	Metal complex dye	1. These are acid dyes having chelating sites to be able to combine with metal atoms. 2. Produce faster shades on selective textile substrates.	Applied in textile industries on wool, silk and nylon	Chakraborty, 2010
9.	Sulphur	1. High molecular weight 2. Good light fastness 3. Not chlorine resistant	Commonly used to dye cellulose fibers	Houssem and Oussama, 2014; Burkinshaw and Salihu, 2017; Tahir et al, 2016
10.	Disperse	1. These are mostly based on azo structures. 2. Either Insoluble or slightly soluble in water 3. Non-ionic and non-biodegradable 4. Have remarkable leveling properties with good constancy at high temperature dyeing processes	Mostly used on polyester but also used for nylon, cellulose acetate and acrylic fibers	Fang et al, 2020; Shamey, 2009; Clark, 2011; Saquib and Muneer, 2003; Jamil et al, 2020

Table 8.2 Overview of studies on constructed wetlands system for textile dye/effluent treatment.

Sr no	Sample	Dye	Vegetation	Microbe	ADMI* or Color removal (%)	COD** removal (%)	BOD# removal (%)	HRT##	Reference
1.	Synthetic wastewater	-	Cocoyam and cattail	-	72.16 in Cattail unit; 77.13 in cocoyam unit	68.24 in Cattail unit; 72.45 in cocoyam unit	-	1.21 Days	Mbuligwe, 2005
2.	Synthetic wastewater	Acid Orange 7 (AO7)	*Phragmites sp.*	-	99	93	-	-	Davies et al, 2006
3.	Wastewater collected from a local dyeing firm	-	Phragmites australis	-	90	84	66	2 Days	Parac-Osterman et al, 2007; Bulc and Ojstršek, 2008
4.	Synthetic wastewater	Acid Orange 7 (AO7) 50 mg/L	*Phragmites australis*	-	98	86	-	3 Days	Ong et al, 2010
5.	Textile effluent	Direct Red 5B	*Portulaca grandiflora*	*Pseudomonas putida*	98	59	38	40h	Khandare et al, 2013a
6.	Wastewater collected from a local textile industry	-	*Phragmites australis, Dracaena sanderiana* and *Asplenium platyneuron*	-	61-79 in HF wetland; 37-61 in VF wetland	58-64 in HF wetland; 29-80 in VF reactor	52-54 in HF wetland; 78-89% in VF reactor	0.2-1.8 days in VF; 0.7-7.1 days in HF	Saeed and Sun, 2013
7.	Textile wastewater	Acid Yellow 2G (250mg/L)	*Canna indica and Typha angustifolia*	-	89.06 for *C. indica*; 93.58% for *T. angustifolia*	61.10% for *C. indica*; 64.85% for *T. angustifolia*	-	3.75 days	Yalcuk and Dogdu, 2014
8.	Textile dye water collected from local textile industry	-	*Typha domingensis*	Endophytic bacteria *Microbacterium arborescens* and *Bacillus pumilus*		79	77	72h	Shehzadi et al, 2014

Table 8.2 Overview of studies on constructed wetlands system for textile dye/effluent treatment. *Continued*

Sr no	Sample	Dye	Vegetation	Microbe	ADMI* or Color removal (%)	COD** removal (%)	BOD# removal (%)	HRT##	Reference
9.	Primary-treated domestic wastewater	Acid Orange 7 (AO7) 300mg/L	*Typha latifolia*	-	100	-	-	5 days	Tee et al, 2015
10.	Textile wastewater	-	*Alternanthera philoxeroides*	-	84	65	60	72h	Rane et al., 2015
11.	Textile effluent	-	*Pogonatherum crinitum*	Immobilized *Bacillus pumilus*	93	78	70	12 days	Watharkara et al, 2015
12.	Synthetic wastewater	Basic Red 46 and Acidic Blue 113 (215mg/L) Congo Red	*Phragmites australis*	-	For BR46, 94 and 89 For AB113, 71 and 50 (for 48h and 96h)	For BR46, 82 and 74 For AB113, 73 and 52 (For 48h and 96h)	-	48h and 96h	Hussein and Scholz, 2017
13.	Textile effluent		*Typha angustifolia and Paspalum scrobiculatum consortium*	-	76 (Decolorisation efficiency of 94%)	70	75	96h	Chandanshive et al, 2017
14.	Textile effluent	Methyl Orange	*Fimbristylis dichotoma and Ammannia baccifera*	-	79	72	77	60h	Kadam et al, 2018
15.	Textile wastewater	-	*Bracharia mutica*	Microbacterium arborescens, Bacillus endophyticus, Bacillus pumilus and Pantoea sp.	74	81	72	72h	Hussain et al, 2018
16.	Wastewater collected from Mahesh dye processors	-	*Vetiveria zizanioides and Ipomoea aquatica*	-	76	79	84	5 days	Chandanshive et al, 2020

serious implications on the environment since it constitutes non-biodegradable textile dyes pollutant (Orts et al, 2018).

Dyes used by the industry are highly soluble in water which makes it challenging to completely eliminate by traditional methods (Hassan and Carr, 2018). Dyes impart color due to the presence of chromophoric molecules (Shamey and Zhao, 2014) which causes detriment to the water bodies by a significant change in pH levels and higher BOD, COD, TSS, and TOC. The accumulation dyes in water bodies generates foul odors, bacterial proliferation, awful taste and unusual coloration (Zhang et al, 2012; Khattab et al, 2018; De Lima, 2007; Carneiro, 2010). It reduces light diffusion into the water affecting the photosynthetic activities of aquatic plants and oxygen level in water bodies (Hassan and Carr, 2018). Certain azo dyes have low affinity towards fibers and are washed down into the textile wastewaters which is then used for agricultural purposes in developing countries (Adegoke and Bello, 2015) causing a negative impact on soil fertility and plant growth (Adegoke and Bello, 2015).

8.4 Impact of dye toxicity on living beings

Textile dyes are lethal, carcinogenic, and mutagenic (Khatri et al, 2018), persist in the environment for longer time and enter the food chains and gets concentrated through biomagnification as it reaches higher trophic levels (Sandhya, 2010) various diseases and disorders in humans and other animals (Khan and Malik, 2018). The ability of the dyes to be non-biodegradable in traditional treatment systems is accountable for accumulation in the soil and sediments through public water transport system (Vikrant et al, 2018).

The textile factories uses numerous synthetic dyes, some of them having a half-life of 2-13 years (Copaciu et al, 2013) and exhibiting heavy metals like nickel, copper, cobalt, and chromium in their composition (Christie, 2001). Heavy metal ions are absorbed by gills of fishes leading to accumulation in the certain organs (Vargas et al, 2009). Metals like chromium extend significant damage to plant growth along with reduced photosynthetic efficiency and CO2 absorption (Copaciu et al, 2013). Synthetic dyes, upon ingestion, are responsible for the occurrence of many disorders such as dermatitis and central nervous system related disorders (Khan and Malik, 2018). Certain disorders occur due to exchange of certain enzymatic cofactors leading to inactivation of enzyme activity (Copaciu et al, 2013).

Inhalation and oral ingestion of dust can cause irritation in the eyes as well as skin. Workers handling reactive dyes might suffer from dermatitis, rhinitis or asthma, allergic conjunctivitis, (Hunger, 2003). Textile dyes are also responsible for causing genetic abnormalities which is a major threat to human health (Thakur, 2006; Christie, 2007). Some textile dyes are capable of causing mutations in the genome. For example, Azure-B has ability to intercalate between the strands of DNA and RNA (Christie, 2007; Haq and Raj, 2018; Khan and Kumar, 2016). *In vitro* studies shows that, it inhibits activities of monoamine oxidase, an important enzyme of the neural system (Factor and Weiner, 2007; Petzer et al, 2012). It also causes inhibition of

glutathione reductase (Paul and Kumar, 2013), which is having role in cellular redox homeostasis. Another dye, disperse red 1, being used in the textile industry is also reported for mutagenic property (Chequer et al, 2009). It exerts chromosomal aberrations (Duarte and Rai, 2016) and develops DNA adducts (Chequer et al, 2011) leading to cancers (Hsu and Stedeford, 2010). A similar mutagenic activity is exhibited by Disperse Orange 1(Chequer et al, 2009) causing DNA impairment in the form of base pair substitutions and frameshift mutations (Ferraz et al, 2011).

Azo dyes are widely used in the textile industry because of cost-effectiveness and strong fixating property. Majority of the azo dyes used are resistant to degradation due to complex chemical structure. In addition, these dyes pollute the groundwater and produces aromatic amines upon the action of gut microbiome or enzymes resulting in cancer (Piatkowska et al, 2018; Christie, 2007). The azo reductase enzyme present in humans is responsible for reduction of azo compounds into aromatic amine compounds responsible for adverse health effects (Jen-Kun and Yan-Hwa, 1973). There are certain azo dyes which impart carcinogenicity without being reduced into metabolites. Some of the dyes include Aniline Yellow (4-Aminoazobenzene) which causes hepato-carcinogenicity, solvent yellow (o-Aminoazotoluene) is responsible for producing tumors of urinary bladder, gall bladder, and liver. para red (Paranitraniline) and methyl yellow also possess strong genotoxic carcinogenicity.

Dyes containing anthraquinone group shows detrimental effects to human health. The amino group of anthraquinones is responsible for anemia, uterine dystrophy, ataxia, uremia, chronic hepatitis and glomerulonephritis (Sendelbach, 1989). Another category of dyes, sulphur dyes are resistant to degradation because of their complex structure (He et al, 2004), making treatment more challenging (Fewson, 1988). Textile effluents release harmful gases like hydrogen sulfide (H_2S) during treatment procedures. Presence of H_2S can cause skin irritation and is toxic even in lower concentrations (Doujaiji and Al-Tawfiq, 2010). It also produces a foul odor in water bodies upon discharge (Bai, Y., and Bai, Q., 2019).

8.5 Dye remediation strategies

Different methods of dye removal are in practice at the research and industrial level. All the methods have their own merits and demerits. None of the technology has proven fully successful. However, biodegradation of dye is effective method, because it directly degrades complex structure of dye into partially or nontoxic metabolites. Here, different dye remediation strategies have been discussed briefly:

8.5.1 Physical methods

Physical methods are one of preferred methods due to multiple advantages like easy operation, high efficiency, lack of requirement for reagents (Singh and Arora, 2011). These methods are capable of removing dyes in the range of 86.8-99% with adsorption technique showing maximum efficiency (Katheresan et al, 2018). Some other

physical processes used for the removal of dyes include membrane filtration and ion exchange method. The major drawback of physical method is, it won't degrade dyes and can only separate them from wastewater.

8.5.2 Chemical methods

Number of chemical pollutant removal methods are being studied and applied for dye remediation. Advanced Oxidation Processes (AOPs) involves the production of hydroxy radicals which are capable of removing contaminants from water at high concentrations. Among the chemical methods, technologies like ozonation, photo-Fenton, Fenton, ultrasound, photo-catalysis, electrochemical oxidation use hydroxy radicals as potential oxidizing agent (Stefan, 2017). Other chemical processes used for dye detoxification include coagulation-flocculation which involves the aggregation of solid contaminants in water (Butani and Mane, 2017; Ahmad et al, 2015). Recently, new environment friendly AOP based on electrochemical technology has been employed for treating wastewater which offers slightly more advantages than conventional chemical methods. However, as earlier discussed in introduction, chemical method involves the use of chemicals and reagents in dye removal and are energy-intensive, costly requiring substantial amount of chemicals (Dos Santos et al, 2007; Crini, 2006). In addition, production of secondary pollutants creates an obstacle in further treatment and proper disposal (Katheresan et al, 2018).

8.5.3 Biological methods

Among the three methods, biological method (Bioremediation) is considered to be effective, environmentally friendly, less energy consuming and inexpensive. In addition, it requires fewer reagents, produces minimum sludge and causes enhanced mineralization of dyes. The dye removal in this method works either by adsorption on the microorganism biomass or degradation of dyes by microbes (Popli and Patel, 2015). The presence of cell wall components in microorganisms constitute charged functional groups which attract the dye molecules particularly azo dye (Jafari, 2014) for further catabolism.

Bioremediation involves the use of plants (Phytoremediation) and microbes like bacteria, fungi, algae and yeast out of which bacteria-assisted degradation shows the maximum effectiveness in dye removal (Das et al, 2016). Phytoremediation is one of the most studied bioremediation strategies due to its several advantages like ecofriendly, low cost, optimum efficiency, ability to degrade diverse types of dye, forms consortium with soil bacteria for enhanced degradation and can be applied to develop technology at industrial site. Several enzymes are playing crucial role in the phytodegradation of dyes into non-toxic metabolites (Kabra et al., 2013; Khandare et al., 2011, 2013a, b, 2014). Bacteria have advantages like easy culturing and faster growth as compared to other microbes and are therefore useful for azo dyes degradation (Yang et al, 2014). Bacteria degrade dye efficiently using different enzymatic pathways and converts toxic dye into partially or nontoxic metabolites.

Algal-assisted biodegradation (Phycoremediation) uses algae for degradation of dyes in textile effluent. Algal biomasses exhibit high absorption capacity and surface area for efficient removal of contaminants from wastewater (Gupta et al, 2014). During dye metabolism, algae produce CO_2 and H_2O as byproducts (Alvarez et al, 2015). Degradation of dye molecules using fungi is also used which is through catalytic action of extra- and intracellular enzymes like Lignin peroxidase (LiP), manganese peroxidase (MnP) and laccase which help in detoxification of toxic dyes (Yahiaoui et al, 2014; Naraian et al, 2018).Yeast is also considered suitable because of its characteristic property of rapid growth, absorbing high dye concentrations and ability to survive in adverse conditions (Khan et al, 2013; Jafari et al, 2014; Šafaříková et al, 2005). Currently, hybrid treatments are also employed in which two or more microorganisms are combined to get maximum efficiency in removal of dyes within a shorter period (Lee et al, 2012).

According to a recent research, enzymes are considered to have maximum efficiency in removing dye molecules (Katheresan et al, 2018). However, their use is limited due to high cost and several barriers for large scale operation including inactivation of enzymes due to highly polluted wastewater (Hochstrat et al, 2015). Industrial and partially purified enzymes serve as better alternatives to pure enzymes because of their cost-effectiveness, high efficiency, and reliability (Nguyen et al, 2016). Enzymes like laccases and azoreductases have the capacity to breakdown azo dyes at lab scale (Rodriguez et al, 1999; Reyes et al, 1999).

8.6 Constructed wetlands: a step towards technology transfer

Constructed wetlands can be defined as treatment plants designed and manufactured by utilizing the natural resources in controlled conditions for the treatment of diverse types of wastewater. It is environmentally friendly and cost-effective, hence, considered as a suitable alternative to the traditional wastewater treatment systems (Vymazal, 2011). The basic design of this system involves the use of porous materials like gravel or soil sown with macrophytes like *Typha, Schoenoplectus, Phragmites* and *Cyperus*. The wastewater seeps down through the layer of gravel increasing the contact with the rhizomes and roots of plants. The macrophytes help in the uptake of toxic compounds from effluent as well as help in aerobic degradation of organic matter. However, increased levels of pollutants in the effluent can alter the plant's remediation efficacy (Kabra et al, 2013; Khandare et al, 2013b). Hence, plants can be used along with endophytic bacteria for the symbiotic relationship with plants and offers multiple advantages (Soleimani et al, 2010; Yousaf et al, 2011). Initially, it protects plants from detrimental effects of contaminants in the textile effluent and enhances stress tolerance of plants. Bacteria colonize the internal tissues of the plants, acquire nutrients and residence, and in return reduce toxicity and evapotranspiration of contaminants (Weyens et al. 2009; Khan et al. 2013). The pollutant degrading activity of endophytic bacteria makes them suitable candidates for dye degradation. In addition,

it promotes plant growth, fixes nitrogen, enhances siderophore production and helps in phosphorus solubilization (Arshad et al. 2007; Glick, 2010).

8.7 Classification of constructed wetlands

Constructed wetlands can be categorized into two main types depending upon the presence or lack of water on the surface (Free water surface or subsurface flow) or direction of flow (vertical or horizontal).

1. Constructed wetlands with surface flow (CWSF)

These are large canals or basins constructed with an appropriate medium like soil for growing plants along with water which usually flows at a shallow depth in the CW system. In this system, water is directed through an inlet which flows through the entire wetland system to one or more outlets. Factors like low flow rate, shallow water depth along with plants regulating the water flow ensure plug-flow conditions (Bendoricchio et al, 2000). CWSF can be classified depending on different kinds of vegetation like free floating, Floating leaved, emergent and submerged.

Free water surface wetland systems (FWS) act as land-intensive biological treatment units. The wastewater containing dissolved chemicals and contaminants enter through the inlet and get distributed over a large area. Suspended solids in the wastewater settle down beyond the inlet while the soluble organic matter, measured as BOD, is removed by the wetland vegetation along with microbial growth. The vegetation enhances the process of sedimentation and filtration by preventing the re-suspension of particulates from the surface. The major source of oxygen supply is done by periphyton and algae by diffusion between air and water and by means of photosynthetic processes of plants in the water basin (Kadlec et al, 2000). The aerobic zones present in the sediments as well as at surrounding area are involved in oxidation of ammonia by nitrifying bacteria. Anoxic zones are involved in the conversion of nitrate into nitrous oxide free nitrogen or n by denitrifying bacteria. Phosphorus is removed via different mechanisms like adsorption, absorption, complexation and precipitation but rate of phosphorus removal is quite slow. In FWS treatment systems, suspended microbial growth assists in the removal of dissolved solids which are decomposed aerobically in the water channel and anaerobically near the bottom region.

FWS constructed wetlands are being used in the various types of wastewater like domestic, municipal, mine drainage, agricultural, highway, landfill leachate, urban, and airport.

2. Constructed wetland with subsurface flow

Constructed wetlands with subsurface flow can be with horizontal or vertical flow.

Horizontal Subsurface Flow Constructed wetland (HSSF CWs)

This type of wetland system comprises of a rectangular plot implanted with vegetation and covered with an impermeable membrane. The wastewater used in this system is mechanically pretreated to avoid clogging of filtration beds and successive

surface flow. The wastewater entering from the inlet passes through the filtration material in an almost horizontal path to reach the outlet. The media encounters a system of aerobic, anaerobic and anoxic regions during its passage.

Since there is limited supply of dissolved oxygen in filtration beds, there is prevalence of anoxic and anaerobic conditions in HSSF CWs. There are few zones involved in aerobic degradation mainly near the roots and rhizomes which are responsible for the release of oxygen into the substrate (Brix, 1987). Suspended solids are removed either by sedimentation or filtration in HSSF CWs. Aerobic and anaerobic zones are involved in the degradation of organic matter. Nitrogen is removed by nitrification/denitrification while phosphorus is removed by adsorption and precipitation. Denitrification occurs in anoxic/anaerobic regions but is limited due to inadequate supply of nitrate since a major part of nitrogen in the wastewater is in the form of ammonia. HSSF CWs are mostly employed for the treatment of civic and domestic wastewaters. However, it has also been reported for the treatment of wastewater originating from industrial and agricultural practices.

Vertical Subsurface Flow Constructed Wetland (VSSF CWs)

A vertical subsurface flow CW is built by planting a layer of macrophytes on a flat surface containing material like coarse sand or gravel. Initially, VSSF CWs did not get enough popularity because of its high maintenance and operational costs. However, its ability to remove larger concentration of ammonia as compared to HSSF CWs lead to its revival. The wastewater is fed into the system periodically which over the sand surface and then slowly seeps down into the bottom side drainage network. The surface bed is allowed to drain completely permitting the air to fill-up the interstices in the bed. This periodic feeding helps in the proper supply of oxygen due to regular emptying of beds which therefore helps in nitrification (Cooper, 1999).

Macrophytes perform an important role in VSSF CWs by providing strength and stability to the surface. The plant roots influence the hydraulic conductivity of the filter. Insulation of the bed is provided by the aboveground biomass while the belowground parts help in the attachment of bacteria. This system helps in the removal of organic substances, ammonia and TSS from the wastewater. VF CWs are employed in treatment of municipal and domestic wastewater, landfill leachate, airport runoff, textile and chemical wastewater.

3. Hybrid Flow Constructed Wetland (HF WC)

It is an amalgamation of horizontal and vertical flow wetlands provides advantages by increasing the efficiency of treatment (Cooper, 1999). It is also known as Krefeld system, the Max Planck Institute Process (MPIP) or Seidel system (Seidel, 1965). In this system, vertical flow (VF) beds are arranged followed by several horizontal flow beds in series. The macrophytes used in VF CW are frequently *Phragmites australis* while HF CW beds are planted with growing macrophytes like Sparganium, Iris, Schoenoplectus (Scirpus), Typha, Carex and Acorus (Vyamazal, 2013). Since Vertical Flow systems possess a larger oxygen transport capacity, it provides favorable conditions for nitrification while the process of denitrification of nitrate occurs in the HF CW. Hybrid CW are used mainly for the treatment of municipal and domestic wastewater (Vyamazal, 2011).

8.8 Recent developments in textile wastewater treatments using constructed wetlands

After successful phyto-remediation of dye or dye effluent, next step towards technology development is constructed wetland-based system for large amount of dye or effluent remediation. Consortium of different potential plants in a reactor gives better idea about dyes and plant behavior towards degradation.

Mbuligwe S. E. (2005) performed an experiment using engineered wetland systems of dimensions 2850 × 600 × 600 mm (length x width x height). The wetland was used for treating synthetic wastewater and was operated for hydraulic retention time (HRT) of 1.21 days. In this study, two different types of vegetation (Cocoyam and Cattail) were used to test their efficiency in dye removal. The results showed a significant decrease in the color concentration by 72.16% and 77.13% for cattail unit and cocoyam unit respectively. Further substantial decrease in COD level by 68.24% and 72.45% and sulphate levels by 52.99% and 58.53% for cattail unit and cocoyam unit was reported respectively indicating potential of both plants in dye remediation. Davies et al. (2006) studied vertical-flow wetlands planted with *Phragmites* sp. to degrade Acid Orange 7 (AO7) found in the wastewater. There was 99% and 93% removal of color and COD respectively. Ong S.-A et al. (2010) conducted experiment using two different up flow constructed wetland (UPCW) (aerated and non-aerated) for treatment of Acid orange 7 (AO7) dye water at 50 mg/L concentration. The non-aerated wetland was containing *Phragmites australis* and *Zizania latifolia* while the aerated wetland had planted with *P. australis* alone. Both wetlands were built with dimensions of 18 cm diameter and 70 cm height. 5mm glass beads were filled to a depth of 6cm of the wetland reactor for uniform distribution of influent. A layer of gravel was filled above the glass beads for proper growth of emergent plants and biofilm. Aeration was provided at a depth of 30 cm from surface through two porous chargers in aerated wetlands. Wastewater used in this experiment was prepared in laboratory and consisted of following constituents (in mg/L): C6H5COONa (107.1), CH3COONa (204.9), NH4NO3 (176.1), NaCl (7.0), MgCl26H2O (3.4), CaCl22H2O (4.0), and K2HPO43H2O (36.7) giving CODCr 326 mg/L, T-N 62 mg/L, and T-P 5.0 mg/L. The concentration of Azo dye was 50mg/L and 7.7 pH was recorded at the inlet. There was a considerable removal percentage of COD, A07, T-N, T-P, NH4-N, and NO3-N up to 86, 98, 67, 25, 96 and 86% respectively in aerated wetland while the removal efficiency was 82, 96, 64, 28, 92 and 100% respectively in non-aerated wetlands at HRT of 3 days. Furthermore, increased AO7 dye concentration led to a drastic decrease in the removal efficiency due to inactivation of enzyme activities produced by plant systems.

Another study was performed using a double-stage vertical and horizontal flow CWs in Slovenia at a dyeing firm to treat textile wastewater collected from a local dyeing firm. The wetland was lined with sand and gravel respectively, planted with *Phragmites australis* and operated for 2 days. The removal percentage of BOD, COD, TOC, TSS Total nitrogen, organic nitrogen, ammonia, sulphates, surfactants, and ADMI color was recorded to be 66, 84, 89, 93, 52, 87, 33, 88, 80, and 90% respectively (Parac-Osterman et al, 2007; Bulc and Ojstršek, 2008).

A lab scale phytoreactor planted with *Portulaca grandiflora* augmented with *Pseudomonas putida* used for treating textile effluent containing Direct Red 5B was found to decrease the color, BOD, COD, TOC, TDS, turbidity and TSS by 98, 38, 59, 37, 71, 41, and 60%, respectively (Khandare et al, 2013a). One more pilot scale study conducted in 2013 (Saeed T. and Sun G. 2013) employed combined horizontal and vertical constructed wetlands for the treatment of textile industry wastewater in Dhaka, Bangladesh. The dimensions of the HFCW were 1.01 × 0.45 × 0.7m (Length × Breadth × Height) while those of VFCW were of 1.5m height and 0.15m diameter. The supporting media was organic sugarcane bagasse and Sylhet sand with differing depth in both the wetlands. The plants used in VF were *Phragmites australis* and *Dracaena sanderiana* while HF wetland was planted with *P. australis*, *D. sanderiana* and *Asplenium platyneuron*. A decolorizing efficiency within a range of 61-79% was observed in HF wetland while 37-61% removal efficiency observed in VF wetland. BOD and COD elimination was in the range of 29-80% and 78-89%, respectively in VF wetland while in HF reactors it was 58-64% and 52-54%, respectively. The average inorganic nitrogen reduction was higher in VF reactor (52-66%) when compared to the HF reactor (3-42%).

Yalcuk A. and Dogdu G. (2014) carried out VFCW for the treatment of Acid Yellow 2G E107 dye containing wastewater. The system constituted three vertical wetland filters occupied with sand, fine gravel and zeolite. *Canna indica L.* and *Typha angustifolia L* were planted in the wetland. This system was operated for a period of 90 days showing a considerable decrease in color concentration by 61% and 46% for *C. indica* and *T. angustifolia*, respectively and a Phosphate percentage removal of 87% and 88%, respectively. Shehzadi M. et al. (2014) conducted a study while exploiting plant-microbe relationship in vertical constructed wetland to treat textile dye water. The textile wastewater was used from textile industries situated in Khurianwal, Pakistan. The plant used was *Typha domingensis* in combination with endophytic bacteria *Microbacterium arborescens* and *Bacillus pumilus*. The experiment was completed in 72 hours with a significant decrease in the physicochemical parameters. There was a reduction in BOD, COD, TSS and TDS up to 77, 79, 27 and 59% respectively. The significant decrease in the physicochemical parameters can be attributed to 1-aminocyclopropane-1-carboxylic acid deaminase activity in *T. domingensis*.

The treatment of wastewater containing Acid Orange 7 (AO7) spiked with a concentration of 300 mg/L was studied using a different plant, *Typha latifolia* in HSCW. The wetland had dimensions 2 × 0.5 × 0.8 m (Length × Breadth × Height). Supporting media was consisting fiber glass with raw rice husk and pea gravel in a ratio of 2:1. Different HRT was maintained to check the efficiency of dye removal and found 100%, 83% and 69% dye removal at 5, 3 and 2 days of HRT respectively. Notably, the wetland consisted of a combination of aerobic, anaerobic and anoxic regions which assisted in complete mineralization of AO7 dye (Tee et al., 2015). Another pilot scale study performed by Rane et al. (2015) used phytoreactor planted with *Alternanthera philoxeroides* for the synthetic textile wastewater treatment comprising a mixture of dyes (Navy Blue HE2R, Scarlet RR, Rubin GFL, Disperse Yellow

4G, Green HE4B, Brown 2GR and Reactive Orange HER). The phytoreactor was constructed (1.2 × 0.61 × 0.61) with an inlet 0.45m above the ground. *A. philoxeroids* are shown to successfully degrade textile effluent and found to decrease ADMI color value, COD and BOD by 84%, 65% and 60%, respectively in the period of 72h. Watharkar et al. (2015) performed a study which involved the construction of hydroponic reactors using plastic crates of dimensions 46.6 × 29.4 × 18.3 cm for treatment of textile effluent. The reactor was planted with *Pogonatherum crinitum* augmented with immobilized *Bacillus pumilus*. A considerable detoxification was recorded after 12 days. In this study, ADMI color value, COD, BOD, TSS, TDS, and turbidity of the textile effluent reduced by 93%, 78%, 70%, 70%, 13% and 90%, respectively. An increase in oxido-reductive enzyme activity including tyrosinase (647%), riboflavin reductase (4005%), laccase (197%), veratryl alcohol oxidase (99%), lignin peroxidase (71%), DCIP reductase (147%) was observed in *P. crinitum* indicating role of these enzymes in the catabolism of dyes.

Hussein and Scholz (2017) used vertical flow CW plant for the treatment of synthetic wastewater comprising Basic red 46 and Acidic Blue 113 dyes. There was a 50% and 94% reduction in COD levels within HRT of 48h and 96h, respectively. The average dye concentration at the inlet was 215 mg/L. For AB113, the percentage removal of color and COD was recorded to be 71% and 73% and 50% and 52% for 48h and 96h, respectively. For BR46, the percentage removal of color and COD were recorded to be 94% and 82% and 89% and 74%, respectively. Chandanshive et al. (2017) performed an *in-situ* experiment for textile effluent treatment containing Congo Red dye using aquatic macrophytes *Typha angustifolia* and *Paspalum scrobiculatum*. The wetland was constructed of dimensions 91.4 × 1.2 × 0.6 m. There was reduction in COD, BOD, TDS, and TSS (70, 75, 57, and 47 % respectively). ADMI color value was significantly decreased by 76% in within 96h. Further, study reported reduction in the heavy metal concentration by 28-77%. Increase in oxido-reductive enzyme activity of like vertatryl alcohol oxidase, laccase, lignin peroxidase and azo reductase in the root tissues of *P. scrobiculatum* and *T. angustifolia* have been evidenced.

Recently, an *in-situ* experiment performed by Kadam S.K. et al. (2018) used floating phyto-beds co-planted with (*Ammannia baccifera* and *Fimbristylis dichotoma*) for the Methyl Orange dye treatment from textile effluent. The wetland was constructed using cement tank having 2.7 × 1.5 × 1.2m dimensions with floating phyto-beds. These phyto-beds were built using PVC pipes, aluminum metal wire gauze and PVC plastic sheet of dimensions 2.1 × 1.2 m. This study was done at the Common effluent treatment plant, MIDC, Kagal, Maharashtra, India for duration of 60h. There was a significant reduction in ADMI color value, BOD, COD, TSS and TDS by 79%, 77%, 72%, 56% and 66%, respectively. Furthermore, induction in the activities of enzymes such as riboflavin reductase, NADH-DCIP reductase, laccase, lignin peroxidase, azo reductase and tyrosinase by 206.87%, 145.03%, 189.00%, 28.45%, 86.44%, and 9.51% respectively was reported in the plants under study. Hussain et al. (2018) conducted an experiment using textile wastewater from textile industry situated in Faisalabad, Pakistan. A pilot scale VFCW (1.21 × 1.21 × 1.21m)

having volume of 1000L was designed. The VFCW was layered with plastic sheets at a height of 6 inches from the bottom followed by 50cm of coarse gravel, 30 cm of fine gravel layer and then finally 15 cm of washed river sand to support plant growth. The vegetation used was *Bracharia mutica* considering its ability to degrade pollutants and hygienize water (Ashraf et al., 2018; Fatima et al., 2016) augmented with *Bacillus endophyticus*, *Bacillus pumilus*, *Bacillus sp. Microbacterium arborescens* and *Pantoea* sp. The experiment was completed within 72 hours. There was a significant decrease in the physicochemical parameters and ADMI color value of the wastewater with 74, 81 and 72 reduction in color, COD and BOD levels, respectively. Furthermore, there was an increase in the DO levels of the water up to 188%. Along with physicochemical parameters, there is a significant removal of heavy metals like Fe (89%), Ni (88%), Cr (97%), and Cd (72%).

A very recent pilot scale study performed by Chandanshive et al. (2020) used the similar concept of floating phyto-beds for the textile wastewater detoxification comprising synthetic mixture of dyes in a metal tank (1.2 × 0.61 × 0.61m). The textile wastewater was collected from textile industry situated in Ichalkaranji, Maharashtra, India and floating phyto-bed for study was implanted with *Vetiveria zizanioides* and *Ipomoea aquatica*. There was a significant reduction in dye concentration and physicochemical parameters like ADMI color value, BOD, COD, TDS and TSS by 74, 81, 74, 47 and 66% respectively after a period of 72h in the phytobed planted with *Vetiveria zizanioides*. Phytobeds containing *V. zizanioides* and *Ipomoea aquatica* consortium showed degradation of textile wastewater containing synthetic dyes mixture and lowered ADMI, BOD, COD, TSS and TDS by 76, 84, 79, 51 and 83 % within 5 days. Induction in enzyme activities such as lignin peroxidase, laccase, veratryl alcohol oxidase, and azo reductase was observed in the plant root tissues signifying their importance in the catabolism of dyes. Fig. 8.1

8.9 Conclusion and future prospective

Textile industry releases large quantities of toxic contaminants and recalcitrant dyes which cause harmful effect on the ecosystem and health of human beings. Therefore, treatment of textile effluent is very crucial factor before releasing into the environment. Phytoremediation using constructed wetlands is an innovative approach which is recently being studied by scientific community around the world. It provides practical approach to work on pilot scale using real textile effluent under controlled or normal environmental conditions. This method proves to be cost-effective, ecofriendly and an efficient alternative to conventional methods. It exploits the decontaminating and decolorizing efficiency of plants coupled with microorganisms. However, most of the treatment reactors have remained only at laboratory scales and require implementation on large scale. More efforts need to be taken at original site of dye contamination for on filed application. Constructed wetlands using consortium of plant-plant and plant-microbe may prove ecofriendly, and less expensive technology for the efficient treatment of concentrated textile effluent in future.

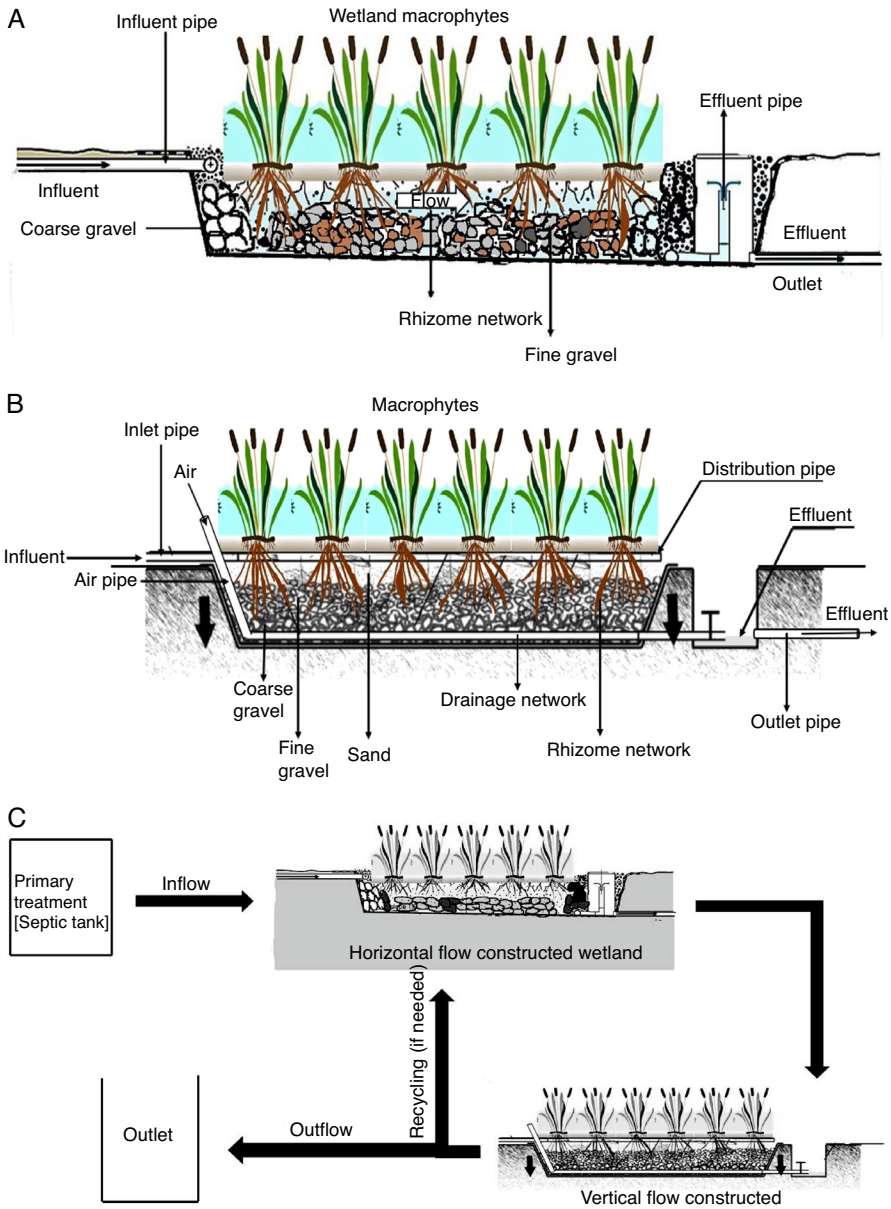

FIG. 8.1 Schematic diagram of A: horizontal, B: vertical, and C: hybrid constructed wetland system.

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CHAPTER

9

Biogenic nanomaterials: Synthesis, characteristics, and recent trends in combating hazardous pollutants (An arising scientific horizon)

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9.1 Introduction

As a result of the tremendous increase in worldwide population, some natural resources have started to suffer from deficiency. In addition, the enormous development in several industries resulted in water pollution/contamination. Water pollution is a huge problem that threatens living communities worldwide. Owing to industrialization and urbanization, water resources have been polluted with several contaminants/pollutants. Henceforth, this problem has started to be of great concern since the past few decades. The World Health Organization (WHO) estimated that within two upcoming decades, nearly one billion people in the world will suffer from difficulties in finding safe and clean water due to the deficiency of enough water resources and water contamination. As a result, the development of advanced technologies for treatment of wastewater and supply of potable water from water bodies is urgently required. To this end, nano-based technologies can be effectively used for the treatment of polluted water to obtain clean and safe drinking water. Different effluents are discharged in water resources including; chemical, physical, biological, and radiological matters. Physical contaminants are any sediments or organic materials that remain suspended in rivers, lakes, and streams. Physical contaminants significantly affect the physical appearance of water. Whereas, chemical contaminants may be in the form of either elements or compounds. In this context, the chemical contaminants may be naturally occurring or as a result of human activities. Chemical contaminants involve; salts, toxins, heavy metals, pesticides, and organic and inorganic dyes, pharmaceutical residues, and so on. Meanwhile, the biological contaminants include contamination of water resources with parasites and pathogenic microorganisms such as bacteria, fungi, protozoa, and viruses Eventually, radiological contaminants involve

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the chemical elements which have unbalanced number of protons and neutrons. These elements usually result in the formation of unstable atoms. These unstable elements emit ionized radiation. Examples of radiological contaminants include uranium, cesium, and plutonium.

Dyes are coloring agents that are applied in several industries such as textile, food, cosmetics, plastic, paint, ink, printing, pharmaceutical, photographic, and paper industries (Chequer et al., 2013). Dyes are mainly classified into two basic categories referred to as ionic and non-ionic dyes (Ghodke et al., 2018). Ionic dyes are in turn categorized into two main groups, namely cationic and anionic dyes. Cationic dyes bear positive charge while anionic dyes carry negative charge. Cationic dyes involve all the basic dyes; whilst acid, reactive and direct dyes come under the class of anionic dyes. Generally, the origin of dyes may be either natural or synthetic. Fig. 9.1 illustrates some examples of the natural and synthetic dyes. Natural dyes were usually fabricated and derived from different plant parts such as leaves, roots,

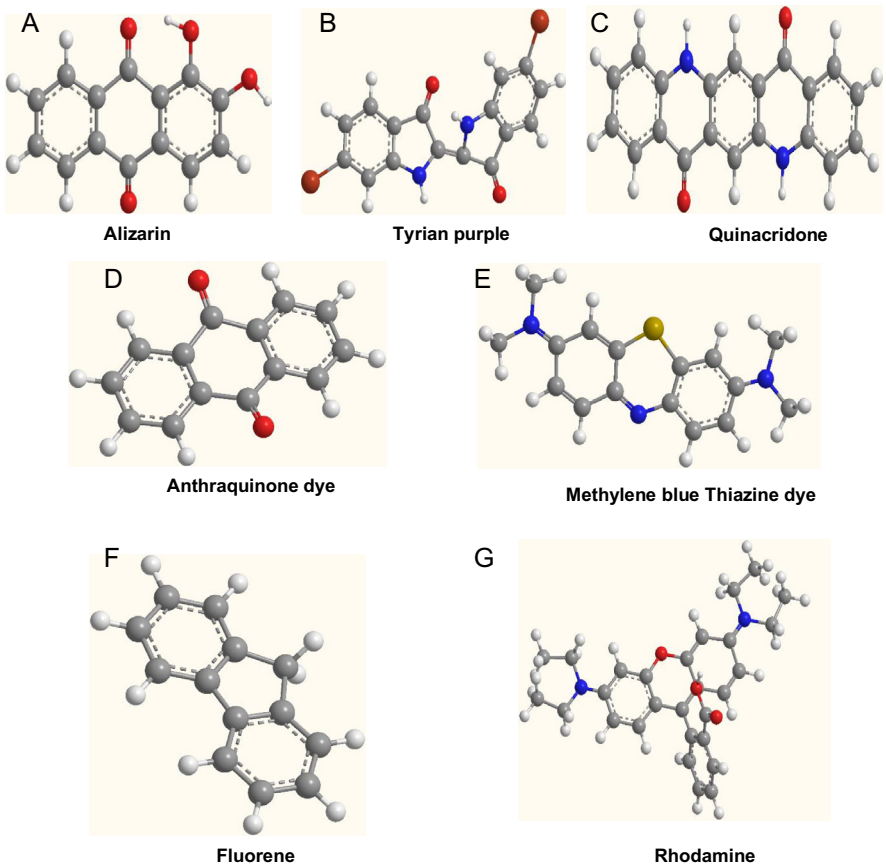

FIG. 9.1 Representative list of some natural (A-C) and synthetic (D-G) dyes.

stem, bark, wood, and lichens. However, the manufacturing of synthetic dyes began in 1856. Abel (2012) demonstrated that the first man made synthetic dye was created by William Henry Perkin in 1856, which was named "mauveine" (i.e., an organic aniline dye). Natural dyestuffs are never exactly the same in intensity and hue. Whilst, synthetic dyes can be produced consistently (Ziarani et al., 2018). Synthetic dyes are chemically manufactured from petroleum byproducts, chemicals, and earth minerals. Since the manufacturing of mauveine, thousands of synthetic dyes have been introduced. Dyes are organic compounds that contain three significant molecules, involving chromophore, auochrome, and - matrix (Benkhaya et al., 2020). Chromophore is the active site of dyes. It contains several functional groups mainly; nitro (—NO_2), nitroso (—N=O), azo (—N=N—), carbonyl (—C=O), thiocarbonyl (—C=S), and alkenes (—C=C—) groups. Chromophores possess dyeing potential only by the addition of other groups of atoms referred to as "auochrome". These auochromic groups are responsible for dye coloration and fixation. They are either acidic (COOH, SO_3, and OH) or basic (NH_2, NHR, and NR_2). Whereas, the matrix contains the rest of the atoms. Even though dyes are extremely beneficial, they pose severe negative impacts when they are accumulated in water systems. This is mainly endorsed to dye structural composition and origin. Yuan et al. (2020) reported that nearly 50% of the used dyes are not fixed in textile fibers and are released in liquid phases, hence exemplify a persistent pollutant in water systems. Dye wastewater contains waste byproducts, which are one of the most toxic effluents. They are carcinogenic to humans, causing dysfunction to central nervous system (CNS), kidney, brain, liver, reproductive systems and pose threats to the surrounding environments,and aquatic fauna. Another important issue is that dye polluted water systems restrict the penetration of sunlight, which affects the underneath aquatic fauna. Another negative impact from the long persistence of dyes in water bodies is the high chemical oxidation demand and appearance of fouling odor.

The discharge of heavy metals in water bodies directly or indirectly from process industries is one of the biggest issues that have attracted attention in the past few decades. Industries like tanneries, pesticides, paper, and mining are mainly responsible for the discharge of heavy metals (Fu and Wang, 2011). Generally, heavy metals are non-biodegradable and have a great tendency to accumulate in living organisms. Additionally, heavy metals are characterized by their persistent nature and stability. However, these features cause further complications during treatment processes. Ghodke et al. (2018) reported that even when heavy metals are present in trace amounts, they can be toxic and carcinogenic, which poses a severe health problem to humans and aquatic organisms. Exceeding the allowed concentrations of heavy metals causes a negative impact on human physiology (Kumar et al., 2014). For instance, the intake of lead through drinking water causes anemia, cancer, mental disability, renal diseases, and damages in the CNS. Whereas, exceeding the allowed limits of chromium results in skin problems and lung cancer in humans. Additionally, cadmium has been found to have a higher bioaccumulation tendency with long half-life in human bodies (Al-Khaldi et al., 2015). Despite the importance of zinc as one of the essential elements in human body, excess quantities of zinc proved to be harmful.

It causes vomiting, anemia, skin irritation, stomach nausea, and cramps. Bioaccumulation of mercury endorses severe health effects as it is a non-biodegradable element (Al-Khaldi et al., 2015). Long-term exposure of mercury causes impairment in kidney, and respiratory and nervous systems' functions.

Phenolic compounds are among the most common effluents particularly in process industries such as petroleum, rubber, disinfectant, pharmaceutical, pigments, agrochemicals, gasoline, coloring, plastics, coal conversion, and petrochemical industries (Butun et al., 2017). For instance, wastewater generated from oil industries contain high concentrations of several phenolic compounds. When these effluents are released into the surrounding environment, they accumulate in surface and ground water bodies, causing a major environmental concern. Even at low concentrations, phenolic compounds have been found to be extremely notorious and carcinogenic to humans and living organisms (Sonawane et al., 2008). Harmful effects such as damages to the liver, lungs, kidneys, and vesicular systems take place by the continuous exposure to toxic phenolic compounds. It is important to mention that the basic structural composition of phenol is likely the same as that of insecticides and herbicides, which are known to be non-biodegradable. Detecting the presence of phenol and its related compounds occurs via the alterations in taste and odor. Several worldwide organizations like the European Union and the US Environmental Protection Agencies have set phenol as one of the most toxic pollutants to humankind. It has been listed among the highest 114 threatening organic compounds (Feng et al., 2013). It should be noted that chlorination of water contaminated with phenolic compounds leads to the formation of deleterious polychlorinated phenols, which are extremely hazardous.

Modern medical science has witnessed a major jumping over the last few years, particularly with the synthesis of a wide range of therapeutic compounds. Several biomedications are increasingly manufactured based upon the growing market demands worldwide. These biomedications include hormones, antidepressants, antibiotics, antipyretics, analgesic, anti-inflammatory drugs, and chemotherapy products (Joung et al., 2014). Kyzas et al. (2015) introduced a study, which showed that approximately 80% of cosmetic and pharmaceutical products generate traces of organic pollutants, which are then dumped in wastewater streams of the United States. Several disciplines are the prime reasons behind the release of pharmaceutical contaminants such as hospital, municipal, and animal wastes, as well as research activities. In 2006, Gross and coworkers demonstrated that the discharge of estrogens (i.e., therapeutic hormones that are significantly used for birth control) in water resources poses damaging effects on the reproductive system of aquatic animals (Gross-Sorokin et al., 2006). Generally, massive quantities of sulfonamides are manufactured as human therapy and for livestock production. Contamination of water with sulfonamides results in severe chronic effects (Ji et al., 2009). According to Zhang et al. (2014), pharmaceuticals and personal care products (PPCPs) have resulted in the emergence of extensive non-stop discharge in different aquatic sources. These contaminants pollute the environment through several routes including; the direct discharge from either hospitals and pharmaceutical industries, domestic sewage, and effluents from

water treatment plants (Yang et al., 2017). Unfortunately, severe environmental risks occur because pharmaceutical agents are persistent in nature and they may result in creation of antimicrobial resistance. Besides, they accumulate in food chains through plants, fish, aquatic organisms, and drinking water. Yang et al. (2017) demonstrated that certain limits have been set to restrict the release of PPCPs in aquatic sources. These limits are in a very low range from ng l^{-1} to μg l^{-1}. Antibiotics are considered one of the most widely used pharmaceutical medications. The excessive release of antibiotics in the environment leads to accumulation of their residues in aquatic sources. Furthermore, their persistent presence leads to development of antibiotic resistance in microorganisms (Majumdar et al., 2020).

Different conventional technologies have been employed for water treatment. However, they are extremely costly and time and energy consuming. Nanotechnology is one of the most advanced scientific disciplines in modern materials science (Sajjad et al., 2018). Nanotechnology has witnessed enormous progress since the past few years. Nanomaterials are characterized by their amended properties, involving size, surface area, distribution, and structure (Mirzaei and Darroudi, 2017). The diverse and extensive applications of nanoparticles (NPs) are attributed to their extraordinary characteristics, which are more advantageous than their bulk correspondents (Alsaba et al., 2020). Although, chemical and physical techniques generate well-defined NPs with the desired size and shape, they require high production costs and high energy requirements. Besides, they release intermediates, which are detrimental to living organisms and to the surrounding environment (Suresh et al., 2018). These disadvantages restricted their application particularly in the biomedical fields. Henceforth, in order to address the increasing demands for environmentally-friendly NPs, researchers have utilized biological sources as reliable, non-hazardous and eco-friendly alternatives for the fabrication of biologically driven NPs (El-Gendy and Omran, 2019). This chapter emphasizes the usage of different biological entities for the fabrication of different nanomaterials. Additionally, a significant highlight upon the lacuna of synthesis mechanisms and the agents behind the bioreduction, stabilization, and capping processes are thoroughly introduced. This chapter also addresses the recent milestones of using biologically synthesized nanomaterials in removing toxic pollutants such as heavy metals, dyes, phenolic compounds, etc.

9.2 History of nanotechnology and conventional synthetic routes of nanomaterials

In 1959, the physicist Richard Feynman, a Nobel Prize laureate, presented a lecture entitled "There's Plenty of Room at the Bottom" during the meeting of American Physical Society held at Caltech. In this lecture, Feynman introduced the idea of matter manipulation at the atomic levels. His ideas proved to be totally correct later on. He has been designated as the father of modern nanotechnology (Gahlawat and Choudhury, 2019). Then 15 years after the valuable lecture of Feynman, the Japanese Professor Norio Taniguchi was the first to introduce the term "nanotechnology".

At that time, nanotechnology was used to describe semiconductor processes, which occurred on the nanometer scale. Professor Taniguchi supported the idea that nanotechnology is closely related to processing, separation, integration, and deformation of materials by one atom or one molecule. Afterwards, the golden era of nanotechnology started in 1980s by the discovery of fullerenes by Kroto, Smalley, and Curl. Later on, Eric Drexler, Professor at the Massachusetts Institute of Technology (MIT) used the creative ideas of Feynman and Taniguchi and wrote his book, which was entitled "Engines of Creation: The Coming Era of Nanotechnology" in 1986. Drexler's vision of nanotechnology focused mainly upon "molecular nanotechnology". Additionally, the science of nanotechnology was further developed when Iijima, another Japanese scientist, managed to synthesize carbon nanotubes (CNTs). The beginning of the 21st century witnessed a great interest in nanoscience and nanotechnology. In the United States, President Bill Clinton started to advocate high funding for research in this emerging technology and the decision was released during his speech at Caltech on January 21, 2000. After three years, President George W. Bush approved the law concerned with 21st Century Nanotechnology Research and Development Act.

Nanomaterials typically describe "materials with particle sizes of one billionth of a meter" (nm = 10^{-9} m). Synthesis of NPs takes place through two main routes, namely "top-down" and "bottom-up" approaches. In top-down approach, NPs are fabricated via the disintegration of bulk materials into fine small reduced particles (Ahmed et al., 2016). This approach can be attained via physical and chemical methodologies such as lithographic (Biswas et al., 2012), mechanical (e.g., millingor grinding) (An et al., 2018), sputtering (Ting et al., 2017), chemical etching (Hou et al., 2019), thermal evaporation (Tao et al. 2018), pulsed-laser ablation (Chang et al., 2013), and photo-reduction techniques (Bukka et al., 2019). Yet, these approaches have major drawbacks like surface structure imperfections, high energy consumption, and environmental and health risks. Whilst, in the bottom-up approach, NPs are synthesized via the self-assembly of atoms into nuclei and then to the nanoscale particles. The bottom-up strategy involves microemulsion (Rojas et al., 2005), radiation- induced (Mittal et al., 2013), co-precipitation (Han et al. 2015), chemical vapor deposition (CVD) (Fang et al., 2017), sol-gel technique (Abdullah and Kamarudin, 2017), pyrolysis (Karim et al., 2017), hydrothermal (Liu et al., 2017), solvothermal (Yu et al., 2017), wet chemical methods (e.g. chemical oxidation/ reduction of metal ions) (Yahya et al., 2019), and electrodeposition methods (Abdullah et al., 2019). Basically, these chemical methodologies depend upon the usage of potentially hazardous and lethal solvents. Besides they require high cost investments, high energy consumption, long reaction periods, and pose toxicity to humans and environments because of the release of the non-ecofriendly intermediates (Nadaroglu et al., 2017). These disadvantages hinder their large-scale production. Most chemical synthesis techniques use lethal reductants like sodium borohydride ($NaBH_4$), sodium citrate, ethylene glycol, and hydrazine (Ishak et al., 2019). However, poor control over particle size and particle size distribution occurr and thus additional stabilizers or capping agents such as ascorbic acid, polymers [e.g. polyethylene glycol, poly (vinyl

alcohol), polyvinyl pyrrolidone (PVP)], ligands (e.g. octadecyl amine, and pyridine), dendrimers, surfactants [e.g., cetyl trimethylammonium bromide (CTAB), and sodium dodecyl sulfate], phospholipids, and gemini surfactants are required to avoid aggregation of NPs (Ishak et al., 2019).

9.3 Nanobiotechnology: An arising scientific horizon

Biological synthesis of NPs is a green synthetic approach which follows the bottom-up strategy in which metal atoms are assembled altogether to produce clusters and finally NPs. Nanobiotechnology is the interface between biotechnology and nanotechnology. In other words, nanobiotechnology/bionanotechnology/nanobiology represents the interaction between nanotechnology and life sciences. Nanobiotechnology is a relatively arising field of science, which provides nanostructures with specific biological and physicochemical features to facilitate their application in biomedical and agricultural disciplines in particular. Moreover, nanobiotechnology successfully managed to address several challenges associated with water remediation, food preservation, and biodiversity problems. Advancements in nanotechnology have led to diverse applications in biomedical sciences.

Microorganisms have evolved as very promising biological entities for the biological fabrication of nanomaterials (Omran et al., 2019; Grasso et al., 2020). Microbial nanotechnology is an eco-friendly and a green approach that depends on using microorganisms such as bacteria, actinomycetes, yeast, fungi, micro algae, and viruses for NP production. Microorganisms are so far the most diverse and significant living creatures in the whole world, mainly due to their enriched genetic diversity. A huge number of bacterial, fungal, and micro algal species were screened through various attempts for the synthesis of NPs. Microbial synthesis of NPs possesses diverse advantages including (Malik et al., 2014):

a. It is a cost-effective and less cumbersome, less time consuming, less complicated, and most importantly non-hazardous as no toxic intermediates or byproducts are released.
b. Additionally, with continuous interest and attempts, it has also been realized that some of the intended applications of NPs are feasible only through their specific biological mode of synthesis such as medical applications.
c. Another interesting aspect of microbiologically manufactured NPs is its provision with high yields in a definite time span.
d. An additional advantage of the microbial synthesis of NPs is the fact that it is a bottom-up approach. This methodology includes far less energy requirements, less wastage of inputs, and more practical control of constituent ingredients.
e. Microbially synthesized NPs also possess enhanced stability, biocompatibility, and reduced toxicity mainly due to the biological coating with biogenic surfactants or capping agents

Exploring the natural secrets for the synthesis of NPs by microbes is increasingly attractive. The interactions between metals and microbes are exploited for

multiple biological applications such as bioleaching, bioremediation, biocorrosion, and biomineralization. The microbial synthesis of NPs has emerged as a promising field of research interconnecting biotechnology and nanotechnology. The mechanism of NP- microbial synthesis includes enzymatic reduction of metal ions, sorption on the cell wall, and subsequent chelation with extracellular peptides and polysaccharides (Deshmukh et al., 2016).

Bacteria were the first microorganisms to be investigated in early studies for the synthesis of metal and metal oxide NPs due to the relative easiness of cultivation and manipulation. Biosynthesis of NPs by bacteria takes place as a defense mechanism (resistance mechanism) towards the toxic effects of metals. The resistance caused by the metal ions on the bacterial cell in the environment is responsible for synthesis of the metal NPs (Saklani and Suman, 2012). As the cell wall being negatively charged, it interacts electrostatically with the positively charged metal ions. Enzymes present within cell wall are chiefly responsible for the bioreduction of metal ions to NPs. Actinomycetes are microorganisms which share important characteristics of fungi and bacteria and are able to produce secondary metabolites (Manimaran and Kannabiran, 2017). Actinomycetes develop numerous special adaptations to survive in extreme habitats. Among these mechanisms; enzyme transduction, metabolism regulation, maintenance of membrane structure and function Synthesis of NPs using fungi is referred to as "myconanotechnology". Due to their monodispersity, today fungi are the most common nano-bio-factories (Omran et al., 2019). Fungi are more advantageous compared to other microorganisms in many aspects (Zomorodian et al., 2016):

a. Fungal mycelia have the potential to resist agitation, flow pressure, and many other conditions in bioreactors when compared with bacteria. They are easy to handle and grow. They have very high wall binding capacity. Fungal mycelia can be easily handled in downstream processing.
b. Out of microbes, fungi are the most effective candidates for the synthesis of metal and metal oxide NPs in a large-scale production. Compared with bacteria, fungi can be used as sources for the production of large amounts of NPs. This is due to the fact that fungi secrete higher amounts of proteins, which are directly translated to higher productivity of enzymes, leading to high yields of NPs.
c. Mycosynthesis of NPs is a straightforward route for attaining easy and stable biologically-driven NPs. Most fungi contain important metabolites and biomolecules with high bioaccumulation capacity and simple downstream processing as they are easy to culture for effective and low-cost production of NPs. Moreover, compared with bacteria, fungi are highly tolerant for metal uptake. (Alghuthaymi et al., 2015) explained three possible mechanisms which might be involved in the mycosynthesis of metal and metal oxide NPs. These include nitrate reductase action; electron shuttle quinones, or both together.

Using plants for the fabrication of NPs is designated as "phytonanotechnology". Phytonanotechnology has drawn extensive attention of many researchers because of

their rapid, economical, and eco-friendly synthesis steps. NP fabrication is carried out in one-pot reaction (Yasmin et al., 2020). Additionally, extracts of several plant parts such as leaves, seeds, stems, roots, and fruit peels have been extensively investigated for the synthesis of NPs (Chandra et al., 2020). It has been proposed that proteins, amino acids, vitamins as well as secondary metabolites such as flavonoids, alkaloids, polyphenols, terpenoids, heterocyclic compounds, and polysaccharides have significant role in metal salt reduction and in capping and stabilization of the synthesized NPs (Ebrahimbabaie et al., 2020). Recently, phytonanotechnology has provided new avenues for the synthesis of NPs because of its eco-friendliness, simplicity, rapidity, stability, cost-effectiveness, scalability, and biocompatibility. Besides, the capability to be medically applied as water is the sole used solvent. In food and juice processing industries, massive amounts of wastes are yielded during processing phases that separate edible parts from the non-edible ones (Omran et al., 2017). Additionally, large amounts of agro-industrial wastes are generated annually, such as sugarcane bagasse, wheat bran, rice bran, and corn cob. It is estimated that 60 million tons of solid waste is generated every year in Egypt (Omran et al., 2017). Solid waste management (SWM) is defined as the process of collection and treatment of all solid wastes. This process includes several techniques such as recycling, upcycling, and disposal. It is a critical public issue, which affects both the environment and human health. Waste management is not limited to the collection of wastes and their disposal; but also involves collection, transportation, sorting, and recycling/upcycling of wastes. SWM is highly affected by people's culture and their awareness level. Legislation and environmental concerns of organic solid waste management are severely increasing. The discarded fruit peels such as lemon, pomegranate, mandarin, orange, egg and shrimp shells as well as the organic fraction of municipal solid wastes can be extremely beneficial in the burgeoning field of nanobiotechnology. Valorization of agro-industrial waste extracts for the biological fabrication of NPs is a preferred method over the chemical and/or physical methodologies because of its rapidity, non-toxic effects, eco-friendliness, cost-effectiveness (Zamani et al., 2019). Fig. 9.2 demonstrates the usage of different biological entities (e.g. bacteria, yeast, fungi, viruses, algae and agroindustrial wastes) for the biological fabrication of nanomaterials.

9.3.1 Biologically fabricated NPs for the removal of hazardous water pollutants

9.3.1.1 Biologically fabricated NPs using bacteria and actinomycetes

Ralstonia eutropha (*Cupriavidus metallidurans*) mediated the biogenic synthesis of AuNPs (Srivastava and Mukhopadhyay, 2015). The physicochemical features of AuNPs were analyzed using UV/Visible spectroscopy, dynamic light scattering (DLS), X-ray diffraction (XRD), scanning electron microscope/energy dispersive X-ray (SEM/EDX), and transmission electron microscope (TEM). The incubation of chloroauric acid ($HAuCl_4$) with biomass of *R. eutropha* resulted in a gradual change in color from light transparent yellow to dark pink color within 24 h. The color change appeared due to the surface plasmon resonance (SPR), which originated from

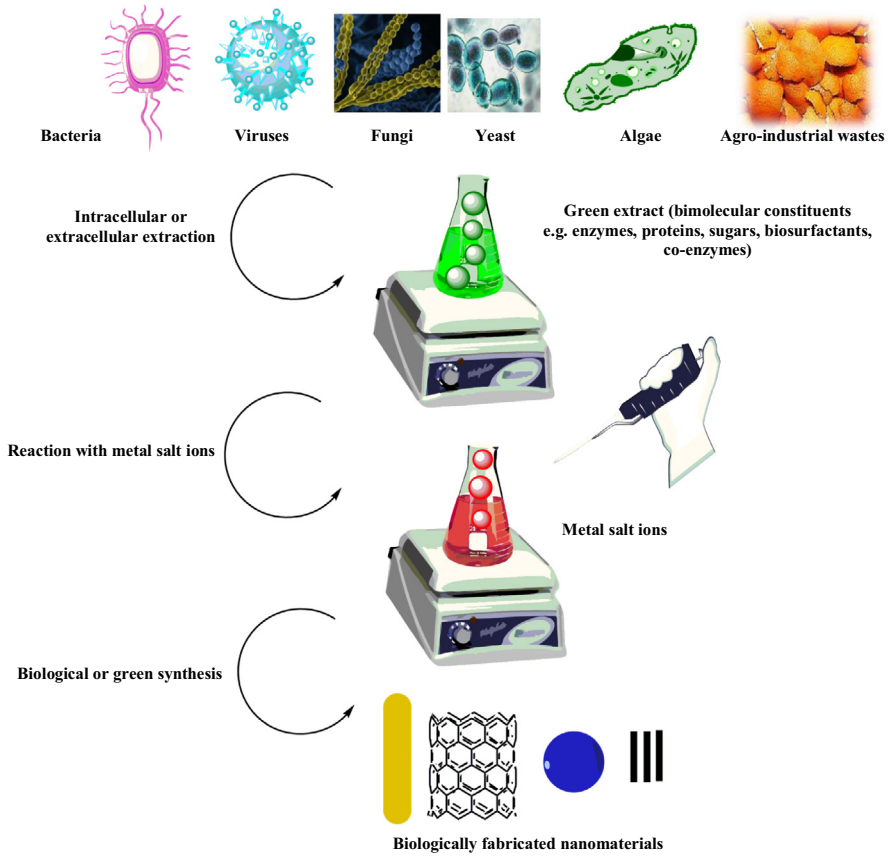

FIG. 9.2 A graphical illustration showing a mechanistic scheme for the biological / green synthesis of nanomaterials using different biological entities.

the coherent oscillation of conduction electrons on the absorbed visible light at the surface of the prepared AuNPs. A very low absorption peak appeared after 12 h of incubation. Whereas, a maximum absorption peak at 542 nm was noticed after 48 h. Till 96 h, the band intensity remained stable. A red shift was noticed after 120 h of incubation and AuNPs SPR intensity started to decrease. This red shift and decreased peak intensity indicated the agglomeration of AuNPs in the reaction mixture. SPR band of AuNPs was found to be stable after 30 days of incubation. TEM micrographs revealed the presence of spherical-shaped particles with a size particle ranging from 10 to 30 nm. Small-sized particles 2-8 nm were also observed. The AuNPs showed excellent dechlorination and degradation activities towards 100 ppm of 2, 4 dichlorophenol (DCP). Degradation of 2,4 DCP was monitored using UV/Vis spectroscopy. The 2, 4 DCP displayed an absorbance peak at 284 nm. After treatment with AuNPs, the absorption peak started to decrease rapidly. Reaction was terminated within

15-120 min. The recorded removal percentage was 82% in photocatalytic conditions, whereas in non-photocatalytic conditions, the removal percentage reached 61.5%. Henceforth, photocatalytic degradation of 2, 4 DCP depicted higher effectiveness when compared with the non-photocatalytic process. Authors attributed this result to the excitation of surface electrons under UV irradiation. The degradation potential followed first-order reaction kinetics.

Several toxic effluents are generated from tannery industry, among which is the hexavalent chromium Cr (VI) as reported by Albadarin et al. (2012). Additionally, unprocessed polluted water contains high rates of Cr (VI). It is highly carcinogenic and displays mutagenic and teratogenic effects in living systems. It causes severe threats to human health when mixed with water bodies. (Alvarez-Ayuso et al., 2003) reported that levels of chromium ions in drinking waters should not exceed 0.05 mg/L (IS 3025). An environmentally and non-toxic approach for the biosynthesis of palladium nanoparticles (PdNPs) was achieved using *Shewanella loihica* PV-4 for the first time as demonstrated by Wang et al. (2018). In this study, both extracellular and intracellular bioreduction of Pd (II) contributed to the biofabrication and production of 4-10 nm sized Pd^0 particles. Biosynthesis of PdNPs was affected by several factors involving; concentration of Pd (II), weak acid medium conditions, large dosage of sodium formate, and biomass concentration. The as-prepared PdNPs displayed an excellent catalytic activity for hexavalent chromium (VI) reduction. It achieved complete removal of Cr(VI) within 3 h of reaction time with a catalyst concentration of 0.5 mg mL^{-1} and an initial Cr(VI) concentration of 0.5 mM by using formic acid as an electron donor. The outstanding Cr(VI) reduction catalyzed by *S. loihica* PV-4-derived PdNPs was promoted by factors like high dosage of formic acid, low pH, and a low initial Cr(VI) concentration.

As mentioned earlier, catastrophic impacts result from the textile wastewater, which contains huge amounts of heavy metals and azo dyes. Agricultural fields are greatly affected as alterations in the physical, chemical, biological, and nutritional properties of agricultural lands take place. In a study performed by Noman et al. (2019), biogenic copper nanoparticles (CuNPs) were biologically fabricated by a low cost and an environmentally friendly approach. *Escherichia* sp. SINT7 mediated the biosynthesis of CuNPs. SEM and TEM revealed the formation of spherical-shaped particles with a size ranging between 22.33 and 39 nm. XRD illustrated that the prepared particles were crystalline in nature with an average particle size of 28.55 nm according to Scherer equation. Proteins derived from *Escherichia* sp. SINT7 functioned as capping agents around the CuNPs as demonstrated by FTIR spectra. These capping agents conferred further stabilization to the particles. Authors evaluated the photocatalytic degradation activity of the biologically fabricated CuNPs against some textile effluents like azo dyes. Azo dye degradation assays showed that CuNPs decolorized congo red (CR), malachite green, direct blue-1, and reactive black-5 with removal percentages of 97.07%, 90.55%, 88.42%, and 83.61%, respectively at a dye concentration of 25 mg L^{-1} after 5 h of exposure to sunlight. However, at 100 mg L^{-1} dye concentration, the degradation percentage displayed by the CuNPs decreased to 83.90%, 31.08%, 62.32%, and 76.84% for CR, malachite green, direct

blue-1, and reactive black-5, respectively. Hence, the prepared CuNPs can be used for the efficient removal of toxic dyes.

Liu et al. (2019) synthesized AgNPs extracellularly by an innovative green methodology using cell free filtrate (CFF) of *Lysinibacillus fusiformis*. Authors isolated *L. fusiformis* from a sewage treatment plant in Huaian and was identified by 16S rRNA gene sequencing. The CFF managed alone to bioreduce silver ions to their NP state without using any toxic organic solvents and reductants. The bioconversion occurred at pH (9.0), temperature (50°C), and- silver nitrate (5 mM). *L. fusiform*-derived AgNPs were characterized using UV/Vis spectroscopy, XRD, Fourier transform infrared spectroscopy (FTIR), TEM, EDX, and zeta potential/size distribution analysis. The as-prepared AgNPs were circular in shape with no agglomeration and with an average size of approximately 50 nm. The antifungal activity of the biosynthesized AgNPs was recorded against *Candida albicans*, *Trichophyton Rubrum*, and *T. mentagrophytes* using Oxford cup plate assay. Results showed a pronounced antifungal activity of the biosynthesized NPs against the tested pathogenic fungi. (Shahid et al., 2020) isolated *Lactobacillus brevis* MSR104 from Chinese koumiss. Authors tested the capability of *L. brevis* to mediate the biosynthesis of AgNPs. *L. brevis*-derived AgNPs were characterized using FTIR, SEM, TEM, XRD, and EDX. The average size particle of the prepared AgNPs was 45 nm. XRD confirmed the pure crystallinity of the prepared AgNPs. The antimicrobial potential of the biosynthesized AgNPs was assessed against two bacterial pathogens namely; *Escherichia coli* and *Staphylococcus aureus* using the disc diffusion assay. It was found that *L. brevis* expressed an outstanding antimicrobial potential.

Several microbial diseases such as malaria, cholera, plague, skin acne, respiratory tract infections, and many more are being treated by Tetracycline (TC). Unfortunately, intermediates released from TC causes extremely harmful impacts on human health. Moreover, their long-term exposure may cause the incidence of resistant genes in microbes. Henceforth, removal of TC from aquatic environment is of utmost importance. Lately, various methodologies have been applied for the removal of TC from wastewater like ozonation, adsorption, coagulation, ion exchange, and membrane processing. Among which; adsorption is the most effective and widely applied technique. Several studies have reported the usage of activated carbon, activated clay, graphene oxide, and carbon nanotubes (CNTs) as efficient adsorbents for the removal of TC from waste water (Marzbali and Esmaieli, 2017; Zhu et al., 2018; Maged et al., 2020). However, each material has quite few limitations, including high cost, poor reusability, and low durability, etc. In this context, Debnath et al. (2020) reported the biological synthesis of zirconium dioxide nanoparticles (ZrO_2 NPs) using *Pseudomonas aeruginosa*. The bioderived nanozirconia were characterized by DLS, field emission scanning electron microscope (FESEM), EDX, XRD, FTIR, and zero-point charge analysis. Authors evaluated the adsorption capacity of zirconia NPs towards TC at pH 6.0. The adsorption mechanism was attributed to the strong electrostatic interaction between tetracycline zwitter ions and the protonated surface of ZrO_2 NPs. Kinetic studies revealed that the adsorption phenomenon followed pseudo-second order kinetic. Accordingly, it was suggested that TC was chemisorbed over the ZrO_2

NPs. Among all the isotherm models, Langmuir isotherm model was the most fitted model. Besides, the maximum TC adsorption capacity achieved by ZrO_2 NPs was close to 526.32 mg g^{-1}. Based on this research, ZrO_2 NPs can be used as an alternative adsorbent for the removal of TC from wastewater.

In a study conducted by Hamed et al. (2020), nine endosymbiotic actinomycete strains were isolated from the marine sponge *Crella cyathophora* that were collected from Makadi Bay South Hurghada via surface sterilization and by the incubation of sponge pieces on a culture medium selective for actinomycetes. Of the nine isolated actinobacteria, two isolates were able to biosynthesize AgNPs. The two actinobacteria were further identified as *Streptomyces* sp. 192ANMG (F2) and *Streptomyces* sp. 17ANMG (F7) using 16S rDNA. The as-prepared AgNPs were characterized using DLS, zeta-potential, UV/Vis spectroscopy, and TEM. The average particle size for the synthesized AgNPs ranged from 8.66 ± 2 to 35 ± 2 nm. The produced particles were monodispersed with no aggregation and were mainly spherical in shape. The synthesized AgNPs displayed a significant antimicrobial potential towards pathogenic microbes, particularly against *P. aeruginosa* and *E. cloacae*. A notable decrease was observed in the growth curve dynamics of both *P. aeruginosa* and *E. cloacae* in accordance with the increase in AgNPs concentration. Hamed and co-authors measured the anti-biofilm activity of the AgNPs. It was found that the AgNPs exhibited a high biofilm inhibition potential against *P. aeruginosa*, *B. subtilis*, and *S. aureus*.

9.3.1.2 Biologically fabricated NPs using fungi

Bhadwal et al. (2014) conducted a study in which biomass of *Trichoderma harzianum* was tested for its potential to mycosynthesize cadmium sulphide NPs (CdS NPs) at ambient laboratory conditions. The biologically fabricated NPs were characterized via UV/Vis spectroscopy, TEM, XRD, and FTIR. A characteristic absorption peak of CdS NPs appeared at 332 nm as revealed via the UV/Vis spectroscopy. The energy band gap of CdS NPs was 3.31 eV, which was larger than their bulk counterparts because of the quantum confinement effect. The mycosynthesized CdS NPs were highly stable with no aggregation for approximately two months. The photocatalytic activity of CdS NPs was evaluated against methylene blue. The removal degradation efficiency of methylene blue by CdS NPs was 37.15% after 60 min. Results showed that the synthesized CdS NPs displayed a good potential for the degradation of methylene blue dye. Venkatesh et al. (2016) reported the ability of *Fusarium solani* (i.e. plant pathogenic fungus) to synthesize cerium oxide NPs (CeO_2) NPs. Thermogravimetric/differential thermal analysis (TG/DTA) elucidated that the crystalline nature of CeO_2 nanopowder remained stable at 400°C. Raman spectroscopy and XRD showed that CeO_2 NPs were cubic fluorite in structure. FTIR illustrated that the CFF of *F. solani*-derived functional groups might have facilitated the synthesis of CeO_2 NPs. FESEM and TEM revealed the homogenous distribution of spherical shaped CeO_2 NPs with size ranging from 20 to 30 nm. Selected area electron diffraction (SAED) revealed the polycrystalline nature of CeO_2 NPs, which was consistent with the XRD resultant data. X-ray photoelectron spectroscopy (XPS) clearly revealed the presence of CeO_2 NPs oxidation states Ce(3d) and O (1s). Furthermore,

the antibacterial and antibiofilm activities of the biogenic CeO_2 NPs were evaluated against Gram-negative bacteria (e.g. *P. aeruginosa*, *K. pneumoniae*, and *Escherichia coli*) and Gram-positive bacteria (e.g. *Staphylococcus aureus*). Maximum zone of inhibition (ZOI) emphasized the high antibacterial activity of CeO_2 NPs against *P. aeruginosa* and *K. pneumoniae*. Authors suggested that CeO_2NPs significantly inhibited the bacterial growth via the generation of reactive oxygen species (ROS) such as hydroxyl and oxy radicals ($^{\cdot}OH$ and $O_2^{\cdot -}$). ROS cause the incidence of an oxidative stress and consequently lead to cell death. Additionally, authors postulated that CeO_2NPs might have caused disruption to DNA replication, cellular respiration, and cell division through binding with mesosome existed in the cell membrane. Confocal laser scanning microscope (CLSM) was used to study the biofilm inhibition by CeO_2NPs. CLSM clearly indicated the disintegration of bacterial cell surface by the effect of CeO_2NPs.

The potential of *Aspergillus brasiliensis* ATCC 16404 mycelial cell free filtrate (MCFF) to mycosynthesize AgNPs was investigated by (Omran et al., 2018). A gradual change in color from yellow to brown was noticed, hence indicating the mycosynthesis of AgNPs as demonstrated in Fig. 9.3. Further confirmation was performed via UV/Vis spectrophotometer, which depicted an absorption silver characteristic peak at λ_{440}. The one-factor-at-a-time-technique (OFAT) was applied to reveal the optimum conditions to obtain maximum production of AgNPs. The optimum conditions were 72 h for reaction time, 20°C for temperature, 7 for pH, and 2 mM $AgNO_3$ using 6% (w/v) of *A. brasiliensis* MCFF under fluorescent light and static conditions. The mycosynthesized AgNPs were monodispersed and circular in shape with size particle ranging between 6-21 nm. Interestingly, the mycosynthesized AgNPs remained highly stable for 2 months without any change in peak intensity as revealed by UV/Vis spectrophotometer. The mycosynthesized AgNPs showed a good antimicrobial effect against some pathogenic microorganisms including; Gram-positive *Bacillus subtilis* (ATCC 6633) and *Staphylococcus aureus* (ATCC 35556), Gram-negative *Pseudomonas aeruginosa* (ATCC 10145) and *Escherichia coli* (ATCC 23282) and a yeast *Candida albicans* (IMRU 3669). Antimicrobial effect was investigated using the agar well diffusion assay.

Bioinspired platinum nanoparticles (PtNPs) were successfully prepared using *Fusarium oxysporum* MCFF via the reaction between *F. oxysporum* MCCF and hexachloroplatinic acid (H_2PtCl_6) (Gupta and Chundawat, 2019). PtNP characteristics, antimicrobial potential, and photocatalytic activity were further studied. UV/Vis spectrophotometer displayed a characteristic absorption peak of H_2PtCl_6 at 261 nm. Upon reaction with *F. oxysporum* MCFF, bioreduction of Pd ions to their NP state took place and the characteristic peak of H_2PtCl_6 completely disappeared. FTIR emphasized that most of the major fungal peaks were found in the spectra of the produced PtNPs. However, these peaks appeared with minor alterations and with low intensities. It was manifested that amides, proteins, polysaccharides, and long chain fatty acids were majorly responsible for the capping and stabilization of the prepared PtNPs. SEM illustrated the synthesis of cubical, circular, and truncated triangular-shaped particles. XRD patterns affirmed the high crystallinity of the

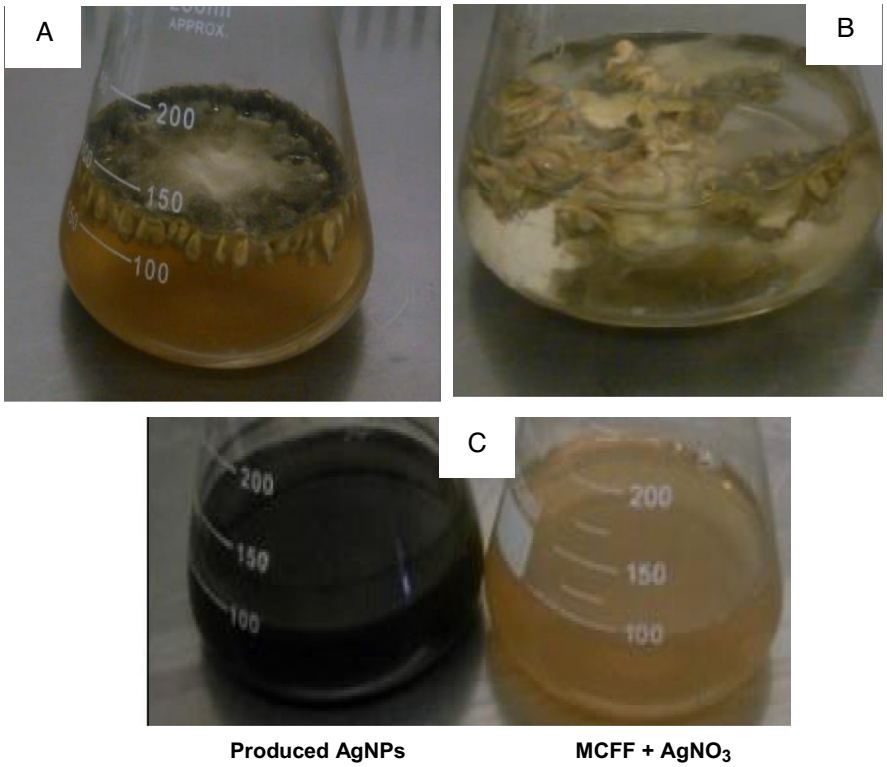

FIG. 9.3 Preparation of *Aspergillus niger* ATCC 16404 biomass (A); preparation of MCFF (B); the visual observation indicating the production of AgNPs (C).

biosynthesized PtNPs. The antimicrobial potency of the fabricated PtNPs was evaluated against three bacterial strains *Klebsiella pneumonia*, *Pseudomonas aeruginosa,* and *Escherichia coli*. Maximum ZOI was attained against *K. pneumonia* (24 mm), followed by *P. aeruginosa* (18 mm), and then *E. coli* (14 mm). However, the antimicrobial activity of the PtNPs was less against *Aspergillus niger* than the two tested bacterial strains. The photocatalytic capacity of the biologically synthesized PtNPs was assessed towards methyl orange (MO) dye under the influence of solar irradiation. The characteristic absorption peak of MO solution appeared at 465 nm. A drop in the peak intensity was noticed upon incubation with the fungal biosynthesized Pt nanocatalysts. Hence, degradation of MO dye was confirmed. The photocatalytic degradation of MO was carried out using different concentrations of PtNPs ranging from 0.2 to 0.6 mg ml^{-1}. It was found that by increasing the concentration of the catalyst, the degradation rate-of MO increased in accordance. Though, no satisfactory data was obtained upon the usage of 0.2 mg ml^{-1} of catalyst. Meanwhile, 0.4 mg ml^{-1} and above concentration showed better results.

In an attempt to treat chromium containing solutions, Mahanty et al. (2019) isolated five fungal isolates from Rhizo sediment samples from intertidal region of Sundarbans, India. The fungal isolates were identified as *Candida* sp., *Curvularia* sp., *Phoma* sp., *Trichoderma* sp., and *Penicillium* sp. The CFFs of the isolated fungal strains were evaluated for their potential to hydrolyze a mixture of ferrous chloride ($FeCl_2$) and ferric chloride ($FeCl_3$) salts to mediate the production of iron oxide NPs (IONPs). A color change from brown to black was observed after 5 min of reaction with agitation at ambient temperature. Formation of IONPs was further monitored using UV/Vis spectrophotometer. Authors suggested that IONPs were synthesized in a three-step process. The first step involved the dissociation of iron salts of chlorine complexes upon reaction with the CFF. The dissociation resulted in the release of ferric (Fe^{3+}) and ferrous (Fe^{2+}) ions. In the second step, different extracellular fungal proteins, polysaccharides, enzymes, and secondary metabolites acted as hydrolyzing agents. Different types of bondages like covalent, van der waals, and hydrogen bonds were formed with the Fe^{3+} and Fe^{2+} ions. Eventually, bonds between the fungal biological moiety and metal ions were broken down by the aid of extracellular reductase enzymes. Afterwards, nucleation and coprecipitation of metal ions occurred and resulted in the synthesis of IONPs in the solution. FTIR spectroscopy illustrated the involvement of fungal proteins in the stabilization of IONPs. IONPs were spherical in shape as demonstrated by FESEM and TEM. The size of the IONPs ranged between 2-16 nm. Peaks of elemental iron were detected via EDX. SAED and XRD patterns assured the crystalline and elemental nature of the mycosynthesized IONPs. Vibrating sample magnetometry (VSM) confirmed the supermagnetic properties of IONPs. Batch studies were conducted to determine the potential of IONPs for the treatment of Cr (VI) contaminated solution. Effect of reaction time (15, 30, 45, 60, and 120 min), adsorbent dose (0.2-1 gL^{-1}), pH (2-8), and temperature (293-313 K) were optimized. The high removal of Cr(VI) was attained at pH 2, adsorbent dosage of 1 gL^{-1} at 313K at a reaction time of 120 min. The removal mechanism of Cr (VI) by IONPs was found to be chemisorption in nature and followed Langmuir adsorption isotherm and pseudo second order kinetic models. IONPs showed a high adsorption capacity which was recorded to be 4.623 mg g^{-1}.

Omran et al. (2019) investigated the mycosynthesis of cobalt oxide nanoparticles (Co_3O_4) NPs using the MCFF of *A. brasiliensis* ATCC 16404. A preliminary indication was observed by the change in color from yellow to reddish-brown as revealed in Fig. 9.4. UV/Vis spectroscopy illustrated the presence of a sharp absorption peak at λ_{230} nm, hence mycosynthesis of Co_3O_4 NPs was confirmed. OFAT technique was applied to determine the best conditions needed for maximum production of Co_3O_4 NPs. The optimum reaction time was 72 h, 11 for pH, 30°C for temperature, 100 rpm for agitation rate using 4 mM of $CoSO_4.7H_2O$, and 55% of *A. brasiliensis* dry weight mycelium (w/v) in dark conditions. The prepared metal oxide NPs were quasi-spherical in shape and monodispersed with a size ranging between 20-27 nm as revealed by TEM and FESEM. XRD and EDX analyses indicated the crystallinity and purity of the mycosynthesized Co_3O_4 NPs. FTIR spectroscopy confirmed the involvement of biomolecules driven from *A. brasiliensis* MCFF during the

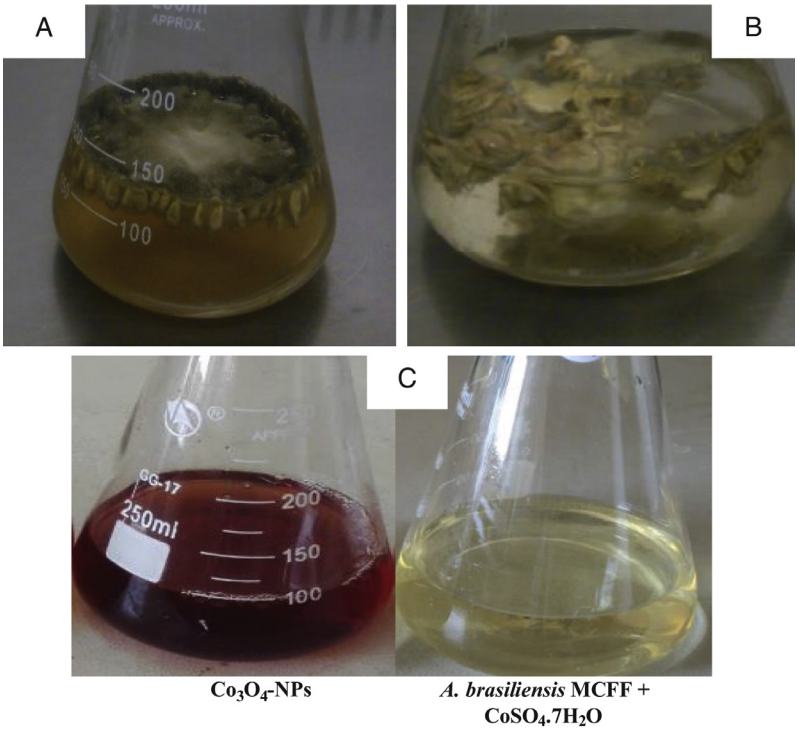

FIG. 9.4 Cultivation of *Aspergillus brasiliensis* ATCC 16404 (A) preparation of *A. brasiliensis* mycelial cell free filtrate (MCFF) (B); the visual observation indicates the mycosynthesis of cobalt oxide.

mycosynthesis, capping, and stabilization of the metal oxide NPs. The magnetic properties were evaluated using VSM. Data showed that Co_3O_4 NPs possessed ferromagnetic properties. The recorded values for remnant magnetization (Mr) and coercivity (Hci) were 012 emu g^{-1} and 29 g, respectively and the Mr/Ms value was 7.05. The antimicrobial potential of Co_3O_4 NPs was determined against pathogenic microorganisms e.g., Gram-positive *B. subtilis* ATCC 6633 and *S. aureus* ATCC 35556, Gram-negative *P. aeruginosa* ATCC 10145 and *E. coli* ATCC 23282 and a yeast *C. albicans* IMRU3669 using the agar well diffusion assay. Results were compared with positive controls involving; streptomycin (10 μg), ampicillin (10 μg), gentamycin (10 μg) and erythromycin (15 μg). The prepared Co_3O_4 NPs expressed antimicrobial activity against the tested pathogenic strains. Where, 5 mg ml^{-1} of Co_3O_4 NPs expressed zones of inhibition; 15.6±0577 mm, 20 mm, 11.3± 0.577 mm, and 12 mm against *B. subtilis*, *S. aureus*, *P. aeruginosa,* and *E. coli*, respectively as represented in Fig. 9.5. The mycosynthesized Co_3O_4 NPs displayed a better antimicrobial activity towards the tested Gram-positive bacteria than Gram-negative bacteria. Nevertheless, no antimicrobial activity was observed against the tested yeast strain, *C. albicans.*

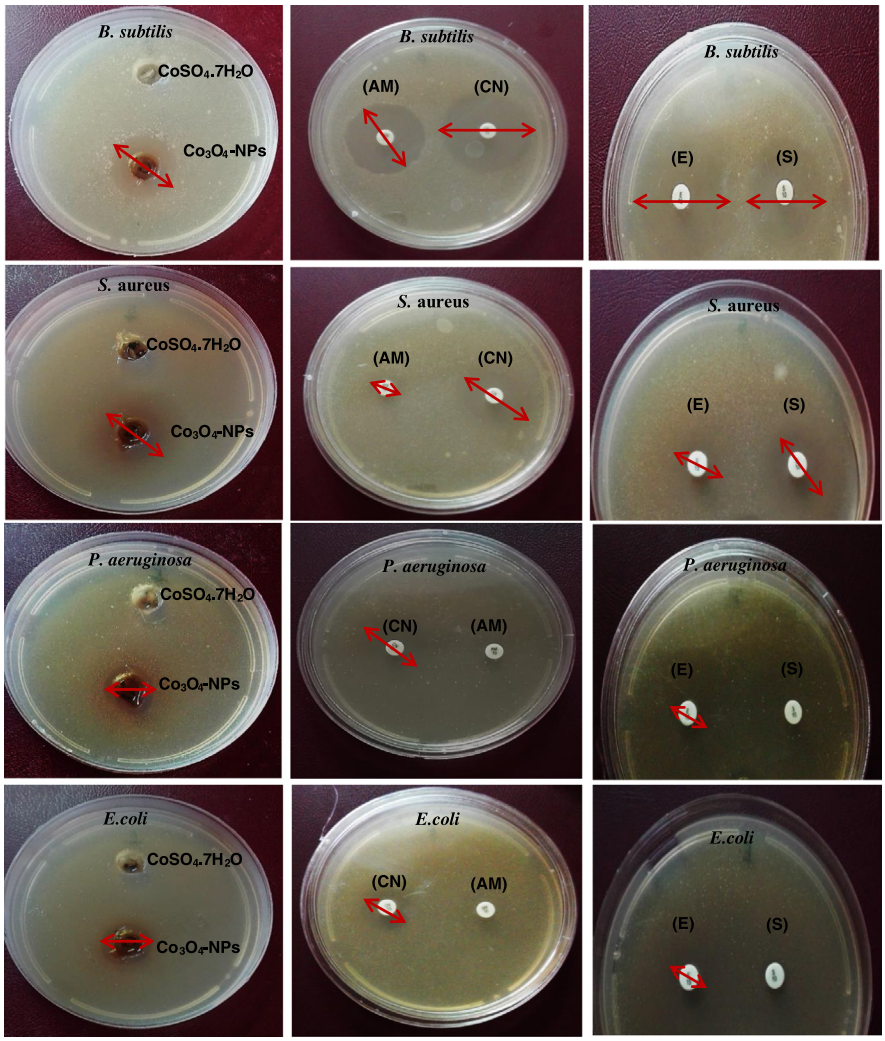

FIG. 9.5 Antibacterial activity of the mycosyntheszied Co_3O_4-NPs (5 mg ml^{-1}), 1mM $CoSO_4.7H_2O$ and some standard antibiotics; Gentamycin (CN), Ampicillin (AM), Erythromycin (E) and Streptomycin (S) against *Bacillus subtilis* (A), *Staphylococcus aureus* (B), *Pseudomonas aeruginosa* (C) and *Escherichia coli* (D), respectively. Abbreviations; AM: Ampicillin (10 mcg), CN: Gentamycin (10 mcg), S: Streptomycin (10 mcg), E: Erythromycin (15 mcg).

9.3.1.3 Biologically fabricated NPs using yeast

For the first time, Eugenio et al. (2016) demonstrated the potential of yeast strains to biologically fabricate silver and silver chloride NPs (Ag/AgCl NPs). Fifteen yeast isolates were isolated from the gut of 10 termites belonging to *Cornitermes cumulans*. The yeast strains were identified using the automated microbial and identification

system VITEK2 (bioM´erieux, Inc.). The isolates were found to belong to *Candida lusitaniae*. Changes in color were observed from pale yellow to dark brown. Formation of Ag/AgCl NPs was confirmed by UV/Vis spectroscopy via the appearance of a characteristic peak between 350-450 nm. XRD analysis affirmed the crystalline nature of Ag/AgCl particles and elucidated the presence of diffraction peaks, which corresponded to metallic silver and silver chloride NPs. The prepared particles were circular in shape with a diameter ranging between 2-10 nm as revealed by TEM images. Ultra-thin sections were imaged by TEM. The images illustrated that Ag/ AgCl NPs were mostly found between the cell wall and the plasma membrane. Focused ion beam scanning electron microscope (FIB/SEM) was used to demonstrate and map a three-dimensional structure of the spatial distribution of the synthesized NPs. Maps showed non-agglomerated Ag/AgCl NPs with a diameter of 35 nm. The antimicrobial activity of the biologically fabricated Ag/AgCl NPs was evaluated against cultures of Gram-positive *Staphylococcus aureus* and Gram-negative *Klebsiella pneumoniae* cultures. Resultant data revealed the strong antimicrobial potential as revealed by optical density measurements.

9.3.1.4 Biologically fabricated NPs using algae

Kashyap et al. (2019) screened the potency of four microalgal strains to synthesize Ag/AgCl nanohybirds. The four tested microalgae were *Chlorella* sp., *Lyngbya putealis*, *Oocystis* sp., and *Scenedesmus vacuolatus*. *Chlorella* sp. was the most fitted for the biosynthesis of the nanohybirds. It was found that the biological molecules existed within the alcoholic extract of *Chlorella* sp. assisted in the biological fabrication of the nanohybirds by facilitating the bioreduction of the metal ions and the further capping and stabilization of the prepared Ag/AgCl nanohybirds. DLS showed that the prepared particles were 90.6 nm in size. Authors tested different $AgNO_3$ concentrations (1, 0.5, 0.1, and 0.2 mM). The best $AgNO_3$ concentration was 0.5 mM. The produced AgNPs remained stable for 192 h. XRD patterns confirmed the crystalline cubic phase of AgCl NPs. SEM and TEM illustrated the presence of circular shaped particles with a size ranging between 10-20 nm. The prepared nanohybirds exhibited an antimicrobial potential against *Bacillus subtilis*, *Bacillus sphaericus*, *Bacillus pasteurii,* and *E. coli* (DH5-a).

9.3.1.5 Biologically fabricated NPs using plant extracts

Das et al. (2012) described a simple and one-pot reaction for the biological fabrication of AuNPs using the protein extract of *Rhizopus oryzae*. Proteins were the leading molecules for the bioreduction of chloroauric acid ($HAuCl_4$). The size of the biosynthesized AuNPs ranged in size from 5 to 65 nm. The AuNPs exhibited an excellent stability over a wide range of pH, ionic strength, and temperature. Authors suggested that the conjugated proteins conferred stability to the prepared particles via electrostatic repulsion forces, which arose from the negative charges of the conjugated proteins. The as-synthesized AuNPs protein conjugates displayed size- and shape-dependent catalytic potential for borohydrate-mediated reduction of *p*-nitrophenol. The obtained results showed that the catalytic activities of the AuNPs were significantly better than those of chemically synthesized AuNPs.

Manjumeena et al. (2014) introduced a study in which nanosilver was biologically synthesized and incorporated into reverse osmosis (RO) membrane. Leaf extract of *Rosa indica wichuriana* was used for the biomimetic synthesis of AgNPs. The formation of AgNPs was confirmed using UV/Vis spectrophotometer, which revealed a SPR peak at 427 nm that was characteristic to AgNPs. High resolution transmission electron microscope (HRTEM) depicted the size of the AgNPs, which was in the range of 15 to 25 nm. The crystalline nature of the *R. indica*-driven AgNPs was assured by XRD. Morphology and surface topography of the uncoated and AgNPs-coated RO membrane were investigated using SEM and atomic force microscope (AFM). SEM and AFM revealed the uniform distribution of AgNPs on the membrane surface. FTIR spectra identified new bands at 3685 and 1342 cm^{-1}, which corresponded to H-bonded-OH groups and methylene CH bend vibrations, respectively. Contact angle measurement for the AgNPs-coated RO membrane showed the increase in the hydrophilicity, which was a good achievement as this would trigger the incidence of chemical fouling. Furthermore, the AgNPs-coated RO membrane exhibited a significant antimicrobial potential against pathogenic yeast strains, involving *Candida albicans*, *C. tropicalis*, *C. glabrata,* and *C. krusei* obtained from VHS hospital, India. Additionally, a remarkable antibacterial potential was recorded against *Micrococcus luteus* (ATCC 4698), *Staphylococcus aureus* (ATCC 6538), *Pseudomonas aeruginosa* (ATCC 15442), and *Klebsiella pneumoniae* (ATCC 13883).

Biomimetic synthesis of AgNPs using the aqueous leaf extract of *Piliostigma thonningii* was reported by Shittu and Ihebunna (2017) for the purification of simulated waste water. Optimization of different parameters affecting the synthesis process was performed. The optimized parameters included temperature, time, $AgNO_3$ concentration, volume of leaf aqueous extract, and pH. The optimum conditions that led to maximum production of AgNPs were 6.5 for pH, 65°C for temperature, 1.25 mM for $AgNO_3$ concentration, and 5 ml of leaf aqueous extract of *P. thonningii*. TEM and nanosizer revealed the size of the biogenic AgNPs within the range of 50-114 nm. Elemental analysis of the prepared AgNPs was confirmed by EDX through the occurrence of silver peaks at 2.60 keV. Qualitative analysis of aqueous leaf extract of *P. thonningii* revealed the presence of active phytochemicals such as tannins, alkaloids, phenols, anthraquinones, saponins, terpenoids, glycoside, steroids, and flavonoids. FTIR depicted the involvement of hydroxyl (OH) functional groups along with –C=C stretching vibrations as capping agents. The synthesized AgNPs exhibited a high efficiency towards the removal of several heavy metals involving iron, magnesium, and copper. Usage of the leaf extract of *Momordica charantia* (Bitter guard) for the biosynthesis of AgNPs was proposed by Mishra and Pani (2017). *M. charantia* is a climbing tree that belongs to the cucurbitaceae family. It grows in Africa and Asia. The optimum conditions for maximum production of AgNPs were 10^{-3} M of $AgNO_3$, pH 5.3, and by using 10 ml of aqueous leaf extract at ambient temperature. The prepared AgNPs were spherical in shape with a size of 12.15 nm as demonstrated by TEM images. The AgNPs possessed a significant catalytic potential towards the degradation of MO dye. Assessment of the catalytic degradation activity was performed using UV/Vis spectrophotometer. The λ_{max} of

pure MO appeared at 460 nm. After treatment with the bioinspired AgNPs, the absorbance peak decreased gradually with the increase in reaction time. Authors suggested that AgNPs acted as a redox catalyst. In other words, it accepted electrons from plant extract. Additionally, AgNPs acted as a donor (i.e., donated electrons to MO). This phenomenon is referred to as "electron relay effect."

Flower extract of *Hibiscus sabdariffa* mediated the biogenic synthesis of iron nanoparticles (FeNPs) (Alshehri and Malik, 2017). The natural plant extract acted as a non-toxic, biodegradable, and cost-effective reductant for the biomimetic synthesis of FeNPs. Different complementary characterization techniques were employed to investigate the optical, morphological and structural properties of the synthesized FeNPs such as UV/Vis spectroscopy, FTIR, TEM, XRD, DLS, and TGA-DSC. The reduction of Fe^{3+} to Fe^{0} was evident by the change in color from yellowish to brown upon mixing of *H. sabdariffa* extract with $FeCl_3$. UV/Vis spectrophotometer displayed three peaks at 287, 322, and 519 nm, which were characteristic to the biological moieties present in the extract of *H. sabdariffa*. After reacting with $FeCl_{3,}$ a strong peak was observed at 335 nm, which was characteristic to FeNPs. TEM depicted the fabrication of spherical-shaped particles with a size of 100 nm. Based on DLS data, the hydrodynamic radius was calculated according to Stokes–Einstein equation and was in the range of 10 to 100 nm. FTIR revealed the involvement of H. *sabdariffa* extract in the bioreduction and stabilization of the synthesized FeNPs. Fig. 9.6 demonstrates the most common constituents of *H. sabdariffa* flower extract, which include cyanidin 3-glucoside, cyanidin 3-sambubioside, delphinidin 3-glucoside, and petunidin 3-glucoside. The photocatalytic degradation activity was further assessed against the toxic organic dyeCR. It has been designated as one of the most hazardous dyes that could be carcinogenic and can result in extremely harmful effects to the surrounding biota. Determination of the photocatalytic performance of the FeNPs was performed via UV/Visible spectroscopy under UV irradiation. This was attained by inspection of the decolorization of the aqueous solution of CR dye treated with the bio-fabricated Fe NPs. Results showed a high photocatalytic activity against CR dye. Authors proposed a mechanistic pathway for the photocatalytic degradation of CR dye by FeNPs. The phot-generated holes in the valance band of FeNPs reacted with H_2O and hydroxyl radical ($^{\bullet}OH$) to boost the generation of reactive $^{\bullet}OH$ and H^{+} species. Besides, an electron resonance plasma is created around the surface of FeNPs by the help of electrons (e^{-}) in the conduction band and react with O_2 to produce superoxide radical anions ($O_2^{\bullet-}$). The $^{\bullet}OH$ and $O_2^{\bullet-}$ created within the FeNPs facilitated the oxidation process on the surface of the NPs and resulted in enrichment of CR dye simultaneously. These free radicals caused bleaching of CR dye within a short time (i.e., 10 min). The degradation of CR dye and the generation of the intermediate products is illustrated in Fig. 9.7.

Nickel hydroxide NPs ($Ni(OH)_2$NPs) were prepared using the aqueous fruit extract of *Illiciumverum* sp. (Nagajyothi et al., 2019). Different characterization techniques were employed to study the morphological, optical, and crystalline nature of the prepared NPs involving; FTIR, XRD, XPS, HRTEM, EDX, SEM, and SAED. The biologically synthesized Ni $(OH)_2$NPs exhibited several morphological

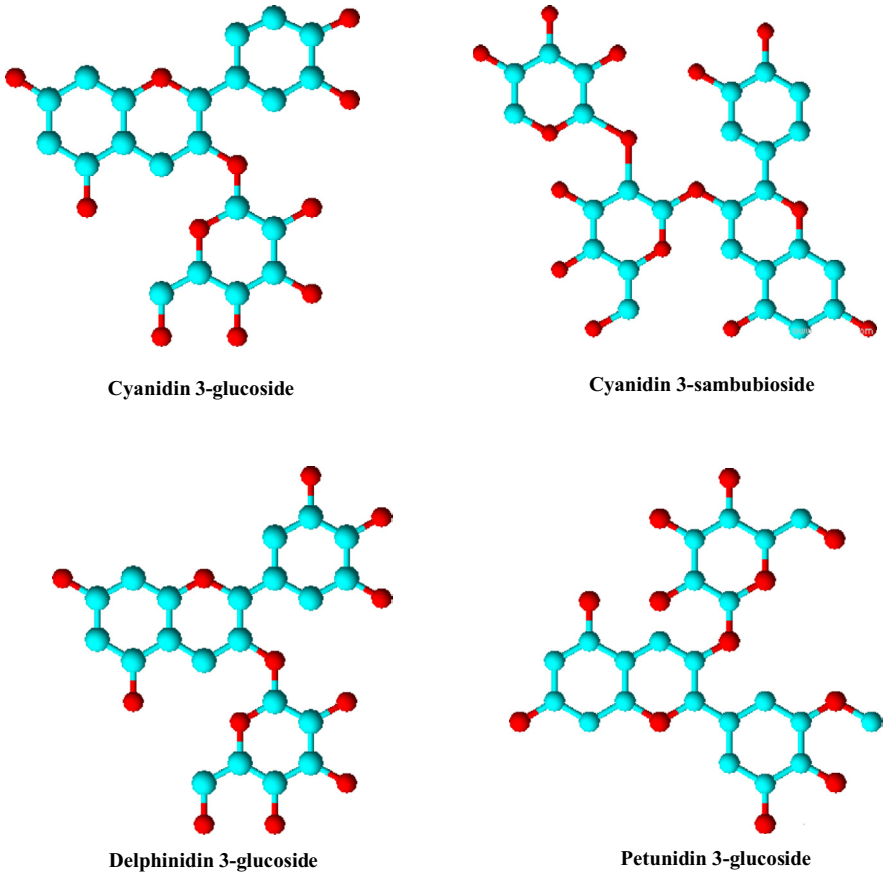

FIG. 9.6 Major phytochemical constituents in *H. sabdariffa.*

structures, involving spherical, hexagonal, and rod shapes. Ni $(OH)_2$NPs acted as a highly effective biocatalyst against the degradation of two cationic dyes; rhodamine B and rhodamine 6G (RhB and Rh6G). *Solanum nigrum* (Black Nightshade) extract mediated the biological synthesis of copper oxide NPs (CuO NPs) as illustrated by Lakshmi et al. (2019). Absorption spectroscopy, XRD, FTIR, EDX, and TEM analyses were used to study the optical, morphological, and crystalline properties of CuO NPs. Lakshmi et al. evaluated the degradation efficiency of *S. nigrum* derived CuO NPs for a wide range of industrial dyes involving; MO, MB, safranin O, and coomassie brilliant blue R-250 (CBB). Reaction of 10 ppm of CBB R-250 dye solution (50 ml) and CuONPs (10 mg) was carried out under sunlight. Photo-degradation of MB dye was achieved based on Behera and Giri method by which 10 mg of CuONPs were dispersed in 50 ml MB dye solution (20 ppm) and stirred constantly under sunlight radiation. Samples were further collected at fixed time intervals and separated

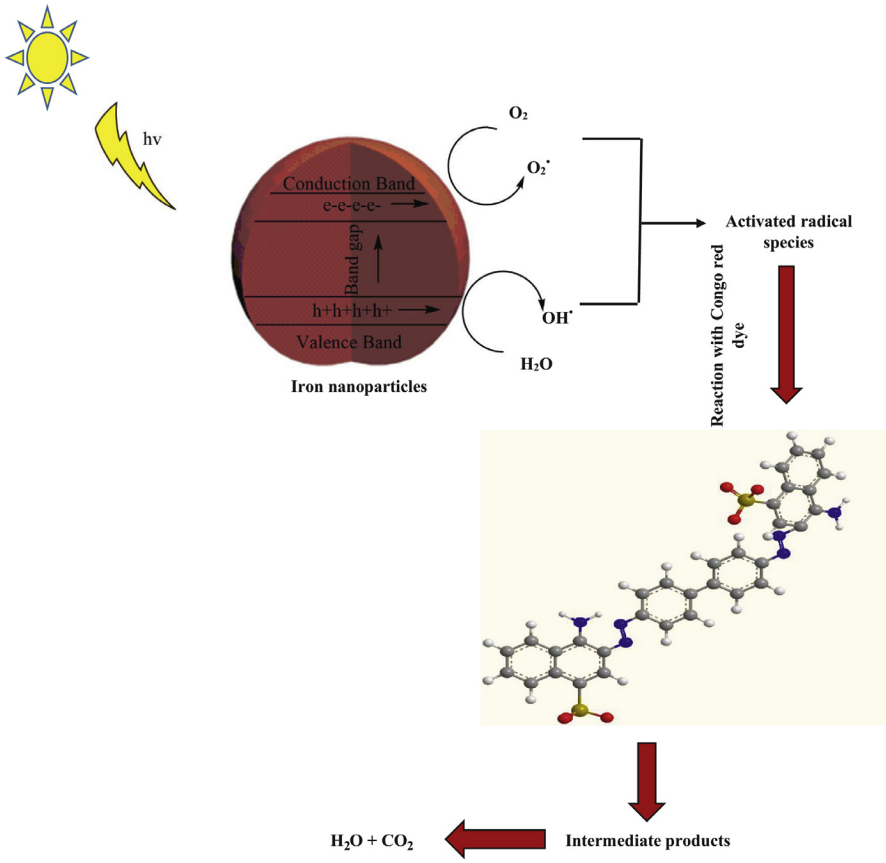

FIG. 9.7 A schematic representation of the photocatalytic degradation mechanism of Congo red dye using iron nanoparticles under UV irradiation.

via centrifugation at 10,000 rpm for 10 min. Monitoring degradation of CBB R-250 and MB dye was assessed by observing the changes of the dye absorbance peak at 554 and 502 nm, respectively. Dye degradation percentage was calculated according to the following formula (1):

$$\%\ Degradation : (A_{0-A} / A_0) \times 100 \tag{9.1}$$

Where, A_0 denotes the absorbance of the blank dye solution and A indicates the absorbance of the test solutions.

The degradation efficiencies of CBB R-250 and MB dyes were found to be 75.302 ± 2.072% and 89.339 ± 0.739%, respectively. The effect of different parameters that might affect the process of dye degradation such as pH, irradiation time, dye concentration, and catalyst load was studied. The optimum dye concentration was 5 ppm,

catalyst load (25 mg), and pH (7.0). Recyclability experiments elucidated that the used NPs were recyclable for three successive rounds.

Copper nanoparticles (CuNPs) were biologically fabricated using the aqueous fruit extract of *Ficus carica* (Fig fruit) (Usman et al., 2019). Fig fruit contains several bioactive molecules involving; polyphenolic compounds (e.g. polyphenolic flavonoid and quercetin-3-O-glucoside), phytosterols, coumarins, triterpenoids, organic acids (e.g. chlorogenic acid), and several other volatile compounds. Extract of this fruit is extensively used in a wide range of applications, including cosmetics and food and medical products. The photocatalytic potential of the CuNPs was evaluated against toxic organic dyes such as Alizarin Yellow R (AYR). Maximum degradation activity of CuNPs towards AYR dye reached 89.71%. The parameters that might influence the degradation performance such as catalyst concentration, time, temperature, and pH were investiagted. Formulating the solution pH towards more acidic ranges resulted in enhancing the degradation kinetics. The degradation reaction increased by the increase in temperature owing to the endothermic nature of the degradation reaction. Increasing the concentration of CuNPs led to increase in the degradation rate due to the availability of extra reactive sites. It was observed that by increasing the reaction time from 6 to 36 h, the degradation rate efficiency increased accordingly. After 36 h, no changes in the degradation removal percentage took place. It was observed that, all the catalytic experiments carried out under solar radiation resulted in excellent degradation efficiency of AYR dye. The kinetic study of the degradation process followed the pseudo-first-order reaction. Regarding CuNPs reusability, it was found that after four cycles of usage, a slight loss of photocatalytic degradation was observed. In another study, IONPs were biologically fabricated via a cost-effective, non-toxic, and environmentally friendly approach using aqueous leaf extract of *Teucrium polium* (Amin et al., 2019). Secondary metabolites acted as reducing and capping agents of IONPs. The prepared NPs were characterized by particle size analyzer (PSA), VSM, TEM, XRD, FTIR spectra, and TGA. The biogenic IONPs were spherical in shape and slightly aggregated with a size range of 5.68 to 30.29 nm. Size estimated by PSA was higher than the one recorded by TEM because PSA estimated the hydrodynamic diameter of the NPs along with the biological shell coating introduced by the used biological entity. XRD showed that the prepared particles were amorphous in nature. VSM identified the magnetic properties of the IONPs at room temperature from -10000 to +10000 Oe. The magnetization curve of IONPs was found to be linear with no hysteresis loop, indicating that the produced NPs possessed paramagnetic properties. The dye degradation activity of IONPs towards MO dye was evaluated. The decolorization efficiency of green synthesized IONPs reached 73.6% in a 6-h reaction.

According to Riaz et al. (2019), green synthesis of silver nickel bimetallic NPs was carried out using the plant extract of *Salvadora persica*. Assessment of optical properties was performed using UV/Vis spectroscopy. A broad absorption band was recorded in the wavelength range of 400-450 nm. FTIR illustrated the presence of bands characteristic to hydroxyl, ketonic, and amine groups. SEM images elucidated

the structural appearance of silver nickel bimetallic NPs. SEM revealed the presence of cluster shapes with a size average of 24 nm. EDX spectra revealed distinctive signals related to silver and nickel. The average diameter of the prepared bimetallic NPs was 23.67 nm according to Scherer equation (Eq. 9.2):

$$D = \frac{K\lambda}{\beta \cos\theta} \tag{9.2}$$

The biogenic bimetallic silver nickel NPs were further used for the removal of hexavalent chromium Cr (VI) and Congo red dye. Different factors such as temperature, contact time, pH, concentrations of adsorbent and adsorbate were optimized for the ultimate removal of both contaminants. Effect of different temperatures on Cr (VI) removal was studied (25°C, 35°C, 45°C, 55°C, and 65°C) using 10 mg of Ag-Ni bimetallic NPs. Maximum removal was noticed at 45°C. Authors attributed that increasing the temperature enabled the mobility of ions towards active sites, hence; adsorption was increased. Generally, pH affects the charge density around the surface of adsorbents. Different pH values were tested from 2-10. pH value 2 resulted in maximum absorption of Cr (VI). Number of positive charges on adsorbents was enhanced in acidic conditions owing to the high rate of protonation which increased the removal efficiency of Cr metal anions. Whereas, at pH range from 4 to 10, removal of Cr (VI) was decreased. The effect of different concentrations of adsorbate (10, 20, 30, 40, and 50 mgl^{-1}, V = 25 ml) was estimated. Usually, a direct relation occurs between the available site number and the concentration of adsorbed metals on NPs. Increasing the concentration of metal ionsled to increasing the concentration of Cr (VI) adsorbed on the surface of Ag-Ni bimetallic NPs. Increasing the temperature above 55°C led to a decrease in the removal efficiency of Congo red. Results depicted that the highest dye adsorption was obtained at low pH values. Effect of different dye concentrations was studied (5, 10, 15, 20 and 25 mgl^{-1}, V = 25 ml). The rate of adsorption was increased by increasing the concentration of adsorbate molecules. Beyond a particular concentration of adsorbate (20 mgl^{-1}), negligible change was noted in adsorbed concentration, which was attributed to the increase in attraction rate between the dye and the Ag–Ni bimetallic NPs till all the available sites become occupied.

Malini et al. (2019) synthesized AgNPs using the leaf extract of *Prosopis juliflora* and further encapsulated the prepared particles into chitosan. A change in color occurred from light green to dark brown; which was considered as a preliminary indication for AgNPs formation. Physicochemical characterization of the green synthesized AgNPs and the nanoencapsulated particles were performed using UV/Vis spectrophotometry, FTIR, XRD, and SEM. Authors evaluated the antimicrobial potential of AgNPs embedded in chitosan using the agar well diffusion assay. A high ZOI was attained against *E. coli* and reached 22 mm. Authors attributed the large ZOI to the antimicrobial potency of both AgNPs and chitosan. Furthermore, the photocatalytic degradation of the toxic rose bengal dye by the prepared nanobiosorbent by monitoring the dye concentration in various time periods. Almost, 83% of the dye was degraded using the chitosan-embedded AgNPs within 2 h. It was noticed

that the absorbance intensity decreased with the increase in the exposure time. The aqueous extract of palm (*phoenix dactylifera*) argonne was tested for its capacity to biologically fabricate Ag nanospheres (Salih et al., 2019). Argonne is a curved side in the palm, which helps in holding dates. The synthesized AgNPs were characterized via UV/Vis spectroscopy, FTIR, XRD, EDX, SEM, and TEM. The prepared particles remained stable for 30 days without any agglomeration. Disk diffusion assay determined the anti-*E. coli* activity. Disks were soaked in different concentrations of AgNPs (126, 63, 31.5, 15.75, and 7.875 μg ml^{-1}). The measured ZOI were 22, 18, 11.5, 8.7, and 5.4 mm for 126, 63, 31.5, 15.75, and 7.875 μg ml^{-1} AgNPs, respectively. SEM was further used to detect the effects of AgNPs on the tested bacterial cells. After nine hours of exposure, disruption of bacterial cells was observed and wrinkled structures appeared.

Sutherlandia frutescent is referred to as bush cancer tea and belongs to the Fabaceae family. It usually occurs in Southern Africa. It is a medicinal plant that has been reported to provide immune support, blood cleansing, and mental stress decrease. Zinc oxide NPs (ZnO NPs) were biologically synthesized using the plant extract of *S. frutescent* as demonstrated by Mbita et al. (2019). Morphological, structural, and functional characteristics; elemental mapping; and mass to charge ratio analyses were characterized using TEM, SEM, SAED, FTIR, and EDX. The prepared ZnO NPs displayed a sphericalshaped morphology with a particle size ranging from 5 to 25 nm. FTIR corroborated the formation of ZnO NPs by the appearance of a peak in the characteristic fingerprint region of ZnO. FTIR further affirmed the corporation of the phytochemical functional groups existed in the plant extract. Authors identified the presence of bioactive molecules extracted from *S. frutescent*. Among which; canavanine, flavanol, sutherlandin B, sutherlandioside B, and flavanol. EDX showed the characteristic Zn and O elemental peaks. *S. frutescent*-derived ZnO NPs displayed exceptional antibacterial potential against Gram-negative (*Escherichia coli* and *Pseudomonas aeruginosa*) and Gram-positive (*Staphylococcus aureus* and *Enterobacter faecalis*) bacterial strains. Different concentrations were employed (0.005, 0.01, 0.02, and 0.05 mg ml^{-1}). The prepared ZnO NPs caused a 95% inhibition of *E. coli* at the lowest concentration and 100% inhibition in case of *P. aeruginosa* at all concentrations. Whereas, the effect of ZnO NPs was dose-dependent in case of *S. aureus* (i.e., increasing the concentration of ZnO NPs resulted in further decrease in bacterial growth). Meanwhile, the effect of ZnO NPs on *E. faecalis* was found to be plateau after treatment with 0. 01 mg ml^{-1}. Authors attributed the weak effect of the prepared ZnO NPs to the high resistance of *E. faecalis* and to its potential to produce spores that confer a high protection levels against antimicrobial agents.

Seed coat of *borassus flabellifer* was utilized for the biomimetic fabrication of IONPs as elucidated by Sandhya and Kalaiselvam (2020). *Borassus flabellifer* is also referred to as Palmyra palm. It belongs to the family Arecaceae. It is an easily cultivated tree and it is abundant in Indian and South East Asian countries. The tree bears fruits that contain soft edible jelly seeds inside kernels. The jelly seeds are enclosed within a thin yellowish inedible brown coating. The fruit seeds are edible while the

seed coating is discarded and becomes a waste. According to Alamelumangai et al. (2014), the extract of the seed coating contains several phytochemicals such as tannins, saponins, flavonoids, terpenoids, and glycosides that possess an antimicrobial and free radical scavenging activities. Authors manifested that the presence of bioactive moieties facilitated the bioreduction, capping, and stabilization of the prepared particles. Formation of magnetic IONPs was confirmed via XRD by the incidence of diffraction patterns with the presence of magnetite phase and low traces of hematite phases. The average crystallite size was 35 nm using Scherer equation. UV/Vis spectrophotometer depicted an absorption peak at 352 nm. According to Devi et al. (2019), magnetic NPs showed absorption peaks in the range of 330-350 nm because of light scattering and absorption by the NPs. FTIR of the synthesized IONPs revealed bands corresponding to amines, polyphenols, aliphatic amines, and amino groups. Hexagonal-shaped particles were displayed by SEM images and the particles- size was in the range of 30-200 nm. However, minor irregular shapes were observed as well. EDX revealed the elemental composition of the with a structural composition of 52.81% iron and 29.7% oxygen. Other elements were detected like sodium, sulphur, and potassium with minor percentages. Authors attributed the occurrence of sulphur to the organosulfur compounds within the extract. Agar well diffusion assay was used to study the antimicrobial action of the prepared particles against *E. coli*, *S. aureus*, *Shigella*, *B. Subtilis*, *A. niger,* and *C. albicans.* Three different concentrations were tested 50, 100 and 500 μg ml^{-1}. The ZOI reached the maximum at a concentration of 500 μg ml^{-1}. ZOI recorded 23, 20, 22, 26, 15, and 13 mm for *E. coli*, *S. aureus*, *Shigella*, *B. subtilis*, *A. niger,* and *C. albicans*, respectively.

Water and alcoholic extracts of *Rhododendron ponticum* were tested for the biomimetic synthesis of AgNPs as conducted by Korkmaz et al. (2020). UV/Vis spectrophotometer depicted absorbance peaks at 431 and 439 nm for the AgNPs derived from the water and alcoholic extracts, respectively. The crystalline nature was manifested by XRD and the mean particle diameter of the AgNPs was calculated using Scherer equation and was found to be 20 nm. The water and alcoholic *R. ponticum*-driven AgNPs were circular in shape with a size of 12-19 and 10-21 nm, respectively. The biosynthesized AgNPs was tested for its antibacterial activity against eight Gram-positive bacteria (*Bacillus subtilis*, *Enterococcus durans*, *Staphylococcus* aureus, *Enterococcus faecalis*, *Enterococcus faecium*, *Listeria* monocytogenes, *Listeria innocua*, and *Staphylococcus epidermis*) and eight Gram- negative bacteria (*Klebsiella* pneumonia, *Enterobacter aerogenes*, *Escherichia coli* CFAI, *Pseudomonas aeruginosa*, *Salmonella infantis*, *Salmonella kentucky*, *Salmonella typhimurium*, and *Salmonella enteridis*). AgNPs derived from the water extract of *R. ponticum* displayed a significant effect against Gram-negative bacteria except for *S. typhimurium*. No effect was observed against the three Gram-positive bacteria including; *E. faecium*, *S. aureus*, and *S. epidermis*. Meanwhile, AgNPs synthesized by the alcoholic extract of *R. ponticum* was less potent. It only showed antimicrobial potential against two Gram-positive (*B. subtilis* and *L. innocua*) and two Gram-negative (*E. coli* CFAI and *E. aerogenes*) bacteria. Moreover, authors investigated the biofilm inhibition capacity of the as-prepared AgNPs. All the tested concentrations of AgNPs exhibited

an anti-biofilm activity. The maximum biofilm inhibition was attained at the highest concentration 1 mg ml^{-1}. In another investigation, biogenic synthesis of AgNPs using the aqueous extract of Umbrella plant (*Schefflera arboricola hyata*) was reported by Elemike et al. (2020). *S. arboricola* is an ornamental plant and it is native to China and Taiwan. It is usually 2-3 meters high. It is rich with fumaric acid, flavones, steroids, lipids, phenols, essential oils, saponins, carbohydrates, and amino acids. The biologically fabricated AgNPs were characterized using UV/Vis spectrophotometer, XRD, TEM, and FTIR. The synthesized AgNPs were investigated for its photocatalytic degradation potential of methyl red. The degradation reaction was assessed for 2 hrs. Unfortunately, the degradation efficiency was poor as the maximum degradation percentage reached only 29% after 120 min.

As mentioned earlier, the levels of phosphorous and nitrogen reached high levels in water bodies (e.g., lakes and rivers) owing to the rapid industrialization and developments in human activities. In this context, several methodologies have been applied for the removal of phosphorous and nitrogen such as ion exchange, adsorption, biological removal, precipitation, and crystallization (Huo et al., 2012). However, adsorption is the best remediation technique because of the low energy consumption and cost effectiveness. Among the important natural adsorbents is zeolite. Xu and co-colleagues decorated nanozero valent iron particles (ZVI) on zeolite as a natural support (Xu et al., 2020). According to previous studies, ZVI NPs have been reported as effective adsorbents of phosphate and ammonia from water. However, the high surface of ZVI NPs limits its effective application due to agglomeration in aqueous solutions. For this reason, Xu and co-authors investigated the dispersion of metal NPs on zeolite in a way to increase zeolite's dispersibility and reactivity. This study investigated the feasibility of using biologically fabricated IONPs using the leaf extract of *Eucalyptus* sp. and dispersing them onto zeolite to help in the removal of phosphates and ammonia from aqueous solutions. SEM and XRD showed the successful dispersion of iron oxide NPs onto zeolite. The synthesized materials removed 43.3% of NH^{4+} and 99.8% of PO_4^{-3} (at an initial concentration of 10 mg l^{-1} for each). The removal capacity was impacted by the ratio of zeolite to *Eucalyptus* derived IONPs, solution pH, temperature and initial ion concentration. The adsorption of both ions followed the pseudo-second-order kinetic reaction, confirming the chemisorption of ammonia and phosphate, while interaction between NH^{4+} and PO_4^{-3} with the synthesized material might have occurred through either ligand exchange or electrostatic adsorption. The overall results obtained in this study pointed out that decorating zeolite with IONPs possessed a significant potential as a nanoremediation technique for the simultaneous removal of anionic phosphate and cationic ammonium from wastewaters.

9.3.1.6 Biologically fabricated NPs using agro-industrial waste extracts

Cupric oxide (CuO) has been extensively used in several applications including; catalysis, batteries, solar energy conversion, magnetic storage media, gas sensing, electronics, sensors, field emission transistors, and energy conversion and storage (Zhang et al., 2006). A simple, efficient, and an eco-friendly route for the

biosynthesis of cupric oxide (CuO NPs) was reported by Tamuly et al. (2014). CuO NPs were synthesized using the peel extract of *Musa balbisiana. M. balbisiana* peels were burnt in a muffle at 500°C for 1 h. Copper sulfate pentahydrate ($CuSO_4.5H_2O$) reacted with the alkaline precursors (e.g., K^+, Na^+, CO_3^{-2}) to form copper (II) hydroxide $Cu(OH)_2$. Afterwards, $Cu(OH)_2$ was exposed to calcination at high temperature 500°C for 1 h, leading to the fabrication of CuO NPs. CuO NPs were characterized using XRD, XPS, SEM, TEM, and photoluminescence spectroscopic (PL). XRD patterns depicted the presence of significant peaks at 2θ values of 18.2, 24.6, 33.3, 34.9, 35.5, 38.6, and 42.3 without the appearance of peaks related to Cu $(OH)_2$ and Cu_2O. XPS spectra of CuO NPs showed peaks at 941 and 961 eV, which corresponded to to Cu $2p_{3/2}$ and Cu $2p_{1/2}$, respectively. In addition, another peak was observed at 951 eV, which corresponded to Cu $2p_{3/2}$. XPS analysis revealed absence of any impurities related to Cu $(OH)_2$ and Cu_2O. SEM images demonstrated a 3d flower-like hierarchical CuO architecture with a diameter ranging between 200-400 nm. HRTEM illustrated the presence of spherical and cubic structures along with flower like shapes. The size of CuO NPs was found in the range of 10.0 ± 0.2 to 40.0 ± 1.3 nm. Photoluminescence spectra showed the emergence of two emission peaks at 398 nm (violet) and 470 nm (blue) corresponding to the band-edge emission and to artefact, respectively. The catalytic performance of CuO NPs was evaluated towards aldehyde oxidation. Results showed that aldehydes were smoothly oxidized to carboxylic acids, indicating their potential for removal of aldehydes.

Biosynthesis of novel Ag, Cu, and Ag@Cu alloy NPs was attained using fruit peelextracts of *Aegle marmelos* and *Citrus limetta* (Kushwah et al., 2019). Formation of Ag, Cu, and Ag@Cu alloy NPs were preliminarily indicated by the change in color into yellow-green, red-brown, and dark brown colors, respectively. UV/Vis spectroscopy revealed SPR peaks at 438 nm and 675 nm, which were characteristic for AgNPs and CuNPs, respectively. Whereas, the Ag@Cu alloy NPs exhibited two lower peaks and were slightly shifted towards a lower wavelength referred to as "blue shift". Authors ascribed the biosynthesis mechanism of Ag@Cu alloy NPs to the reaction of galvanic displacement. This displacement took place during the second stage of surface nucleation and growth. The fruit peel- extracts were rich with catechol derivatives, coniferol [(Hydroxy-1-propenyl)-2-methoxyphenol], and stigmasterol. These biological active molecules aided in the bioreduction, capping, and stabilization of the prepared alloy NPs. The Ag@Cu alloy NPs exhibited a face-centered-cubic structure as demonstrated by XRD. The average size was detected via TEM and were 15, 3, and 6 nm for AgNPs, CuNPs, and Ag@Cu alloy NPs, respectively. The prepared particles were monodispersed and spherical in shape. The photocatalytic activities of the biosynthesized AgNPs, CuNPs, and Ag@Cu alloy NPs were tested against methylene blue (MB). The characteristic blue coloration of the dye disappeared gradually upon reaction with the alloy NPs. The photocatalytic activity was assessed using UV/Vis spectrophotometer. MB characteristic peak appeared at 664 nm. A decrease in the intensity of the MB peak was observed. The photocatalytic strength followed the order of Ag@Cu NPs

> CuNPs > AgNPs. By increasing the concentration of MB, the reaction degradation rate decreased. As the concentration of MB became higher, the photocatalyst surface became fully occupied and consequently the reaction rate started to slow down. Additionally, Kushwah and co-authors assessed the antibacterial potential of AgNPs, CuNPs, and Ag@Cu alloy NPs against *E. coli* and *S. aureus*. The Ag@Cu alloy NPs (100 μg ml^{-1}) displayed a ZOI of 18 mm and 19 mm against *S. aureus* and *E. coli*, respectively

Chen et al. (2019) conducted a study in which ZnO NPs were biologically fabricated from the fresh leaf extract of *Phyllanthus emblica*. Based on Scherer formula, the average size particle was 19.56 nm. XRD peaks revealed the hexagonal pure wurtzite crystalline nature of ZnO NPs. TEM images illustrated the presence of spherical-shaped particles. FTIR spectra affirmed the synthesis of ZnO NPs by the incidence of a significant band at 876 cm^{-1} that corresponded to Zn-O vibrations. The prepared ZnO NPs exhibited an antibacterial potential against two bacterial strains e.g., *Proteus vulgaris* and *Staphylococcus aureus*. A higher antibacterial effect was attained against the Gram-positive bacterium *S. aureus* (12 mm) than the Gram-negative bacterium *P. vulgaris* (5 mm). Moreover, the photocatalytic activity against malachite green (MG) was analyzed under UV irradiation. Approximately, 91.8% of decolorization of the characteristic dye color occurred within 60 min.

Srivastava and Choubey (2019) performed a study in which *Citrus limetta* (Mosambi) peel extract mediated the biological synthesis of AgNPs. The change in the reaction solution color to brown indicated synthesis of AgNPs. Synthesis of AgNPs was further confirmed via UV/Vis spectroscopy. SPR peak characteristic to AgNPs occurred at 432 nm. The synthesis reaction took place in a basic medium. By increasing the pH from 7 to 12, the intensity of the SPR peaks increased gradually. Authors suggested that this might have been related to the ionization of phenolic groups within the peel extract. DLS showed a high negative value of zeta potential which confirmed the high stability of the prepared particles. The polydispersed index (PDI) ranged between 0.2 and 0.4. The shape and size of the bioderived AgNPs were characterized using TEM. Particles were spherical in shape and the average size was around 61.53 nm. XRD patterns illustrated the crystalline nature of the AgNPs with a face-centered-cubic structure that was confirmed by the appearance of XRD peaks corresponding to (111), (200), (220), and (311) planes. Authors examined the catalytic degradation potential of the produced AgNPs against the two azo dyes MB and MO in the presence of sodium borohydride ($NaHBO_4$). It is important to keep in mind that $NaHBO_4$ acts as a reducing agent to convert dyes into simple mineral forms. AgNPs catalytic degradation activity was assessed by tracking the maximum absorbance peaks of both dyes with respect to time using UV/Vis spectrophotometer. First, change in coloration took place from blue and red to colorless in cases of MB and MR, respectively, which indicated the degradation of both dyes. For more confirmation, MB absorption peak was recorded at 664 nm. In case of using $NaBH_4$ alone, the absorption peak started to decrease indicating the degradation of MB. However, the reaction pace was slow. While, upon treatment with two different concentrations of AgNPs (5 mg/100 ml) and (10 mg/100ml), a rapid decrease in the absorbance peak

was noticed, which in turn indicated the rapid degradation of MB. In this context, the increase in AgNPs concentration led to an acceleration of the reaction and to a high degradation efficiency. Amazingly, the absorbance peak at 664 nm completely disappeared within 4 min. The degradation of MO was similar to that of MB. The absorption peak of MO was noticed at 464 nm. The degradation of MO with $NaBH_4$ alone without the catalyst (i.e., *C. limetta* derived AgNPs) was extremely slow. Whereas, upon treatment with AgNPs, a complete degradation of MO was observed via the complete disappearance of MO absorbance peak. It is important to clarify that $NaBH_4$ alone did not have the ability to degrade the two dyes completely owing to the kinetic barrier. Henceforth, a catalyst was required to relay electrons from $NaBH_4$ to dyes. Usually, during dye degradation, transfer of electrons occurs from BH_4^- to dye molecules (act as acceptors). Meanwhile, in case of the catalyst (i.e., AgNPs), the metal NPs displayed an electrochemical mechanism. The AgNPs behaved as an acceptor and then as an electron donor. The BH_4^- ions acted as a nucleophile while dye molecules acted as an electrophile with respect to AgNPs. As a result, an electron transfer from the nucleophilic $NaBH_4$ to AgNPs took place. Meanwhile, the electrophilic dye captured the electrons released from AgNPs.

Nickel oxide (NiO) NPs were successfully bio-fabricated via the leaf extract of *Euphorbia heterophylla* (L.) (Lingaraju et al., 2020). *E. heterophylla* (Linn.) belongs to the Euphorbiaceae family. *E. heterophylla* has been well known to possess a medicinal value for the treatment of various diseases and disorders. XRD patterns of NiO NPs revealed the face-centered-cubic structure. UV/Vis spectrophotometer displayed an absorption peak at 321 nm with an optical band gap of 3.24 eV. A stretching vibration band of Ni-O was detected at 452 cm^{-1} by FTIR. The prepared NiO NPs exhibited rhombohedral shape and were quite agglomerated with a size range of 12 to 15 nm. The antibacterial activity of *E. heterophylla*-derived NiO NPs was evaluated against Gram-positive bacterium *Staphylococcus aureus* and Gram-negative bacteria *Escherichia coli*, *Pseudomonas desmolyticum*, and *Klebsiella aerogenes* via the agar well diffusion assay. Highly significant antibacterial potential was noted against *E. coli* and a moderate inhibition potential was observed against *S. aureus*, *K. aerogenes*, and *P. desmolyticum*.

9.3.2 Possible mechanisms involved in biomimetic synthesis of NPs

9.3.2.1 Role of enzymes and proteins

According to Gahlawat and Choudhury (2019), several investigations claimed the possible involvement of proteins and enzymes as the main reactive moieties during the synthesis of NPs. Basically, it has been denoted that microorganisms mediate biosynthesis of NPs in order to protect themselves against the lethal effects of metal ions (i.e., a way of defense mechanism). Different defense mechanisms have been evolved by microbes to guarantee their own protection against metal toxicity including; reduction of metal ions, precipitation, complex formation, and dissimilatory oxidation (Tanzil et al., 2016). Earlier studies endorsed that NADH-dependent

nitrate reductases might have been responsible for metal bioreduction. Karthik and co-authors introduced a study, which showed a possible mechanism for the biological bioreduction of silver ions into AgNPs by *Streptomyces* sp. LK3 (Karthik et al., 2014). The resultant data revealed that the nitrate reductase enzyme in *Streptomyces* sp. LK3 was the the key cause for the bioreduction process as shown in Fig. 9.8. It was demonstrated that nitrate was reduced to nitrite and afterwards nitrite was further reduced to nitrogenous gases. The prepared AgNPs were quite stable for several months without the need to add any capping agents. In addition, no agglomeration was observed in the fabricated particles which validated their long-term stability.

In a study performed by Divya et al. (2019), monodispersed AgNPs were biologically fabricated by the bacterial strain *Alcaligenes faecalis*. This study revealed that NADH and NADH-dependent reductases acted as reductants for the synthesis of AgNPs. In 2017, Hamedi and colleagues evaluated the potential of cell free supernatant of *Fusarium oxysporum* to synthesize AgNPs (Hamedi et al., 2017). Results illustrated that during the stationary phase, the rate of AgNPs production reached the maximum due to the high levels of the extracellular enzyme nitrate reductase.

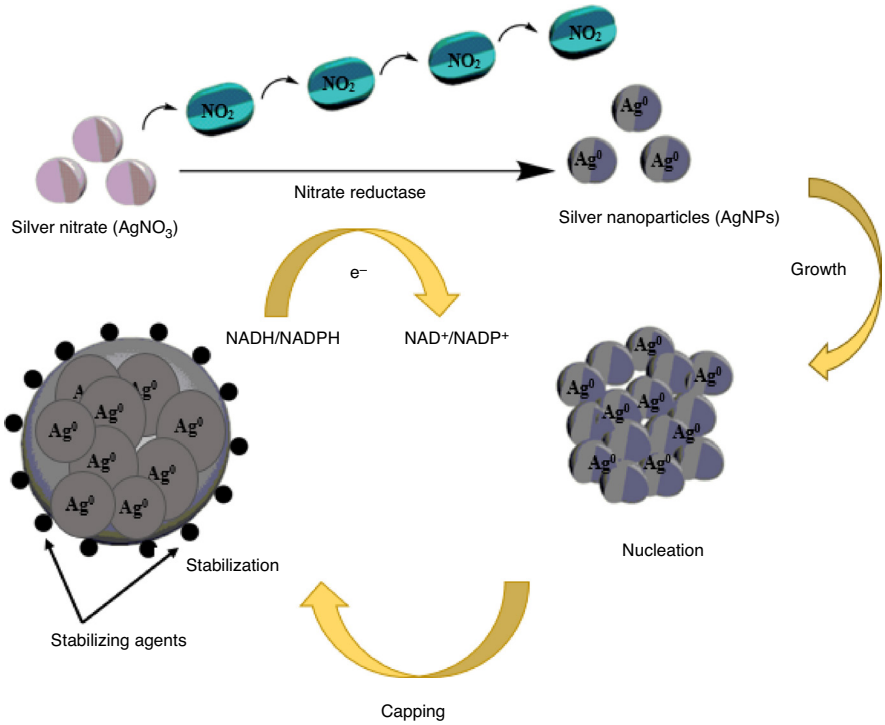

FIG. 9.8 Bioreduction, capping, and stabilization of silver nanoparticles by nitrate reductase enzyme.

Several researchers revealed the role of conductive pili and cell surface proteins during electron transfer, which leads to subsequent reduction of metal ions (Cologgi et al. ,2011; Reguera, 2012; Kitching et al., 2016). Cologgi et al. (2011) illustrated the biomineralization potential of *Geobacter sulfurreducens* to convert uranium metal ions to uranium NPs. This study highlighted the importance of pili in the bioreduction of metal ions. Pili are bacterial external appendages that contain pilin proteins. Authors compared between the potential of pilin presence and absence to induce formation of uranium NPs. Amazingly, it was evidenced that pilin- deficient mutants produced uranium NPs inside the periplasmic space. Meanwhile, strains containing pilins managed to produce uranium NPs extracellularly. Henceforth, it can be concluded that pilin expression affected the rate of uranium biomineralization and prohibited its localization inside the periplasm. Likewise, another pioneer investigation carried out by Reguera (2012) illustrated the importance of pili in the bioreduction of uranium ions by *Geobacter* spp. It was observed that pilin proteins played a major role in *Geobacter* immobilization and extracellular reduction of uranium. Kitching et al. (2015) reported one-pot reaction for the synthesis of AuNPs using the purified cell surface protein of *Rhizopus oryzae*. It was elucidated that the cell surface protein had a major impact in determining the size and morphology of the fabricated AuNPs. Biosynthesized AuNPs expressed good stability and were compatible for different biomedical applications. An in-depth investigation was carried out by Vasylevskyi et al. (2017) to evaluate the ability of *Geobacter sulfurreducens* to biologically reduce silver ions to AgNPs. Authors suggested a hypothesis, which chiefly clarified that reduction of Ag^+ ions to their nanoscale form was an endergonic reaction. This hypothesis was suggested by the authors via the conduction of several experiments that revealed the photo-induction of electron transfer via tetrapeptide/Ag^+ solution. Authors showed that at N-terminal, electron transfer was not able to generate AgNPs via tetra peptide-1 containing histidine. Whereas, at C-terminal region, tyrosine present at tetra peptide1 produced tyrosyl radicals and electrons. At N-terminal, Ag^+ ions combined with histidine at N-terminal were not reduced into AgNPs. Accordingly, it was strongly revealed that imidazole side chain of histidine inhibited the fabrication of AgNPs by photo-induction.

9.3.2.2 Role of exopolysaccharides

Exopolysaccharides (EPSs) are biological molecules secreted extracellularly by microorganisms. EPSs confer protection against stress environmental factors, facilitate surface adherence, and induce cellto cell interactions. EPSs are chiefly composed of carbohydrates such as monomers of D-glucose, D-mannose, L-fucose, D-galactose, L-rhamnose, D-galacturonic acid, D-glucuronic acid, L-guluronic acid, D-mannuronic acid, N-acetyl-D-glucosamine, and N-acetyl D-galactosamine. Besides, they are composed of noncarbohydrate moities for instance; carboxyl, phosphate, sulfate, and pyruvate substituents. The noncarbohydrate part confers an anionic nature to EPSs and also increases the lipophilicity of EPSs (Freitas et al., 2011). Sathiyanarayanan et al. (2017) reported that when metal ions get in contact with EPSs containing reducing sugars, they become chelated, reduced, and stabilized. Sathiyanarayanan

et al. revealed that polyanionic groups are the best-known biological moieties to be incorporated for metal ion reduction and stabilization to metal NPs. It was observed that presence of functional cationic and anionic groups such as hydroxyl, carboxylic, phosphoric, amino, and hemiacetal of EPS aided in the synthesis of metal NPs (Banerjee et al., 2017). In relation with the above, hydroxyl groups endorsed the coordination ability with metal ions. In fact, during the reducing process, oxidation of hydroxyl groups to form carbonyl groups as well as oxidation of alcoholic and aldehydic groups to form carboxylic groups were reported as critical factors during the synthesis of metal NPs.

EPSs have been tested as green biological molecules that can play a role in bioreduction, capping, and stabilization of nanomaterials (Gahlawat and Choudhury, 2019). In 2016, Kang et al. (2014) introduced a study that illustrated the role played by EPSs of *Escherichia coli* during the bio-fabrication of AgNPs. FTIR and nuclear magnetic resonance (NMR) revealed that hemiacetal groups of rhamnose sugars were involved in the biosynthesis process. Additionally, the aldehyde groups in pyranose and rhamnose sugars were oxidized to carboxyl groups by silver ions. Authors concluded that aldehyde and hemiacetal functional groups present in the EPSs acted as reducing agents. Choudhury et al. (2014) synthesized AuNPs using pullulan as reducing agent. FTIR illustrated that the basic structural composition of pullulan was not affected during the preparation of AuNPs. In this context, it was notified that α-1,4 and α-1,6 linkages in pullulan remained sustained. It was hypothesized that biomineralization of gold ions occurred due to the oxidation of aliphatic alcoholic groups of pullulan molecule. As a result, it was concluded that the free CH_2OH groups of pure pullulan polymers were oxidized to COO^- carboxyl groups, which in turn resulted in the bioreduction of Au^{3+} to Au^0. Likewise, AgNPs synthesized by *Ochrobactrum rhizosphaerae* were mediated by the active moiety of EPSs (Gahlawat et al., 2016). Further characterization studies were carried out by biochemical techniques and revealed that the involved EPSs were glycoprotein in nature. This study was the first to report an investigation that demonstrated the tremendous role played by glycoproteins secreted by *O. rhizosphaerae* during the biological fabrication of AgNPs. Raj et al. (2016) tested the potential of a marine bacterium *Pseudomonas aeruginosa* JP-11 to synthesize sphericalshaped cadmium sulfide (CdS) NPs. The synthesized NPs were characterized using UV/Vis spectroscopy, Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectrometry, XRD, FESEM, and TEM. FESEM and TEM illustrated the presence of circular shaped (CdS) NPs with a size ranging between 20-40 nm. XRD assured the high crystallinity of the prepared particles. Surface functionalization of EPSs with specific functional groups had a positive effect in increasing metal adsorption. Sulphur is mostly preferred as an important functional group owing to its high affinity toward metals. Hence, sulphur interacted easily with cadmium ions and resulted in the successful synthesis of (CdS) NPs. In 2017, Yumei et al. (2017) reported that EPSs derived from *Arthrobacter* sp. B4 mediated the biological synthesis of AgNPs. FTIR analysis revealed the involvement of –C=O and –OH absorption peaks during the biosynthesis of AgNPs.

9.4 Advantages, limitations, drawbacks, and future perspectives of nanobiotechnology

A tremendous progress has been observed over the last decade in the field of nanobiotechnology. Biological synthesis of metal and metal oxide nanoparticles possess numerous advantages. Among which, biologically synthesized NPs are benign, cost-effective, and environmentally-friendly in addition to their high biocompatibility (Singh et al., 2016). As clearly proved, biosynthesized NPs are free from toxic chemical constituents that is considered a fundamental and a desirable feature for biomedical applications (Ahmed et al., 2016). Besides, biogenic synthesis of NPs does not require an additional step of capping or stabilization because the needed capping and stabilizing agents are naturally introduced by the biological entities themselves. Furthermore, the time needed for biological synthesis of NPs is much lessthan that of the physical- and chemical-based methodologies.

To obtain maximum yield of NPs, a number of controlling parameters that are involved in the nucleation and subsequent formation of stabilized NPs need to be optimized, among which pH, reactant concentrations, reaction time, illumination/darkness, agitation rate, and temperature (as mentioned earlier). Apart from optimizing such parameters, usage of biofilms for efficient biosynthesis of NPs is a very interesting approach (Tanzil et al., 2016). According to Ikuma et al. (2015), biofilms are recognized as the most active growth mode for bacteria. Biofilms display outstanding properties such as high catalyzing potential, active reducing matrix, and high ability to control electrochemical interactions, which introduce a favorable environment for effective synthesis of NPs than planktonic cells. Additionally, biofilms provide protection against the external environment due to diffusion limitations; hence the entire synthetic process becomes free of contaminants, which is preferred during synthesis of NPs. Biological fabrication of NPs in the biofilm mode offers additional advantages, involving large surface area and high biomass concentration, which in turn leads to more efficient and scalable biosynthesis routes. Teitzel and Parsek (2003) reported that biofilms are 600 times more resistant to metals than their planktonic counterparts. In addition, biofilms possess the potential to catalyze electrochemical redox reactions by the provision of a suitable environment with naturally occurring reducing agents (e.g., peptides, proteins, and heterocyclic compounds) that are necessary for metal transformation to NPs (Khan et al., 2014). However, very few studies investigated the biological fabrication of NPs in biofilm mode. Henceforth, an in-depth understanding of the molecular mechanisms operated by biofilms during synthesis of NPs will extremely assist future researchers to reach robust microbial biosynthesis of NPs with the desired shapes and sizes. Interestingly, understanding those mechanisms may allow genetic modification of particular bacterial strains to facilitate the synthesis of morphologically-controlled NPs (Faramarzi and Forootanfar, 2011).

Biological synthesis of metal NPs has evolved as a significant branch of nanotechnology, and bio-agents serve as important nano-bio-factories for the production

of NPs. Nonetheless, there are certain limitations for successful production of biologically-driven NPs that need to be addressed by the scientific community. One of the major limitations for the biogenic synthesis of NPs is the detailed and thorough understanding of the mechanistic aspects involved in the biofabrication of NPs. Despite, the presence of some reports in literature that have identified the bioactive moieties responsible for biomineralization of metal ions by biological extracts, much detailed analysis of the biochemical pathways is further required for the improvement of tailor-made NPs. Particularly for biomedical applications, it is absolutely necessary to figure out how and which active moieties from different biological resources bind to the NP surface. Large-scale production is another utmost bottleneck issue in the commercialization and development of biocompatible nanostructures with definite shapes and sizes. Lately, researchers have focused on large-scale cultivation methodologies for NP production that can be reproducible and scalable. In this context, large-scale cultivation of NPs is usually hampered by factors such as high energy requirement and high costs. However, the biological fabrication of NPs at ambient room temperatures via the employment of natural active biomolecules without any external reducing agents could make large-scale fermentation more economic and less energy consuming. Overall, the collaborative focus on the development of fermentation processes along with understanding the mechanistic aspects, how to- scale-up the production processes, and exploration of other biological agents will result in expediting the process of cost-effective tailor-made synthesis of NPs.

9.5 Conclusions

The major progress of scientific cognizance and the advent of innovative technologies have paved the route towards a revolutionized nanoage. In nanobiotechnology, biological entities mediate the biological fabrication of green, cost-effective, and non-toxic NPs. Additionally, biologically driven NPs can be effortlessly scaled-up and they are biocompatible from the ecological point of view. These biological entities involve microorganisms (i.e., bacteria, yeast, and fungi), extracts of different plant parts, and agro-industrial wastes. Several biological reducing agents such as proteins, enzymes, carbohydrates, polyphenols, flavones, amines, etc. are involved in the synthesis mechanisms of NPs. Nanobiotechnology applies green strategies by excluding the usage of expensive harmful chemicals and replacing them with eco-friendly, biologically oriented, and renewable materials. Reactions usually take place at neutral pH and at ambient pressure- and temperature. Nanobiotechnology applies green chemistry principles by introducing simple, safe, clean, and controllable alternatives for the manufacturing ofNPs with well-defined shapes and sizes and desired characteristics. Accordingly, the biologically-driven NPs can be imparted the utmost attention for application in diverse fields. The wide range of reported investigations of the green synthesized NPs via natural biological entities can oust the conventional methodologies by overcoming their drawbacks. Hence, the current chapter addresses the significance of the green synthesis of metal and metal oxide NPs. Besides, this

chapter emphasizes the potential use of biologically originated nanomaterials in wastewater treatment applications as better alternatives for the hazardous chemical agents by referring to the numerous updated studies investigated so far. It also highlights the advantages and the main drawbacks for their wide-scale applications.

Abbreviations

Ag/AgCl NPs	Silver and Silver Chloride Nanoparticles
AgNPs	Silver Nanoparticles
ATCC	American Type Culture Collection
ATR-FTIR	Attenuated Total Reflectance-Fourier Transform Infrared
AuNPs	Gold Nanoparticles
AYR	Alizarin Yellow R
CBB	Coomassie Brilliant Blue R-250
CdS NPs	Cadmium Sulphide Nanoparticles
CeO_2 NPs	Cerium Oxide Nanoparticles
CFF	Cell Free Filtrate
CLSM	Confocal Laser Scanning Microscope
CNS	Central Nervous System
CNTs	Carbon Nanotubes
Co_3O_4 NPs	Cobalt Oxide Nanoparticles
CR	Congo Red
CTAB	Cetyl Trimethylammonium Bromide
CuNPs	Copper Nanoparticles
CuO NPs	Cupric Oxide Nanoparticles
CuONPs	Copper Oxide Nanoparticles
CVD	Chemical Vapor Deposition
DCP	Dichlorophenol
DLS	Dynamic Light Scattering
EDX	Energy Dispersive X- Ray

EPSs	Exopolysaccharides
FeNPs	Iron Nanoparticles
FESEM	Field Emission Scanning Electron Microscope
FIB/SEM	Focused Ion Beam Scanning Electron Microscopy
FTIR	Fourier Transform Infrared Spectroscopy
GLP	Glycoprotein
Hci	Coercivity
HRTEM	High Resolution Transmission Electron Microscope
IMRU	Institute of Microbiology, Rutgers University
IONPs	Iron Oxide Nanoparticles
MB	Methylene Blue
MG	Malachite Green
MIT	Massachusetts Institute of Technology
MO	Methyl Orange
Mr	Remnant Magnetization
NADH	Nicotinamide Adenine Dinucleotide (NAD) + Hydrogen (H)
NADH	Nicotinamide Adenine Dinucleotide Hydrogen
$Ni(OH)_2$ NPs	Nickel Hydroxide Nanoparticles
NiO NPs	Nickel Oxide Nanoparticles
NMR	Nuclear Magnetic Resonance
NPs	Nanoparticles
OFAT	One-Factor-at-a-Time Optimization
PDI	Polydispersed Index
PdNPs	Palladium Nanoparticles
PL	Photoluminescence
PPCPs	Pharmaceuticals and Personal Care Products
PSA	Particle Size Analyzer
PtNPs	Platinum Nanoparticles

PVP	Polyvinyl Pyrrolidone
Rh6G	Rhodamine 6G
RhB	Rhodamine B
RO	Reverse Osmosis
rpm	Round Per Minute
SAED	Selected Area Electron Diffraction
SOPE	Sweet Orange Peels Extract
STPs	Sewage Treatment Plants
SWM	Solid waste management
TC	Tetracycline
TCPs	Total Cell Proteins
TEM	Transmission Electron Microscope
TGA/DTA	Thermogravimetric/Differential Thermal Analysis
UV/Vis	Ultraviolet/Visible spectroscopy
VSM	Vibrating Sample Magnetometry
XPS	X-ray Photoelectron Spectroscopy
ZOI	Zone of Inhibition
ZrO_2 NPs	Zirconium Dioxide Nanoparticles
ZVI	Zero Valent Iron Particles

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CHAPTER

10

Removal of emerging contaminants from pharmaceutical wastewater through application of bionanotechnology

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10.1 Introduction

The rapid increase in population, changing climate, prolonged droughts, and exhausting water resources are the various challenges faced by humanity across the globe. Chemical pollution of water is one of the major issues faced in this centenary. The emerging chemical pollutants of water includes pharmaceuticals and personal care products. Interest in pharmaceuticals and their byproducts has gained more attention recently in the 1970s and currently sufficient data is available that can address their impact on the living organisms and the environment (Debska et al. 2004; Fatta et al. 2007; Kummerer, 2009; Zuccato et al. 2006). Pharmaceuticals are molecules that are active at very low concentrations resulting in therapeutic effect. Pharmaceuticals include prescription drugs, over the counter medicines and veterinary drugs. They enter the environment mainly by wastewater and further can contaminate the surface and ground water. Various primary sources of pharmaceutical contamination include wastewater from household, industries and hospital, effluents from sewage treatment plants, seepage from landfills sites, aquaculture, and runoff from animal wastes (Patneedi and Prasadu, 2015). The pharmaceutical compounds generally have complex chemical structures, some are toxic in nature, some are antimicrobials, and some others are radioactive or hazardous. Moreover, once in the environment, they are very difficult to remove. There is insufficient knowledge available in public domain about the usage of these compounds (Daughton, 2003; Kummerer, 2008).

Larson et al. (2007) and Bottoni et al. (2010) reported the presence of hormones, antibiotics (both human and veterinary use), anti-inflammatories, steroids, blood lipid regulators, estrogens, painkillers, disinfectants, plasticizers, fire retardants,

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insecticides, antioxidants, antiepileptics, and detergents in wastewater. They can reach up to a level of water concentrations of ng/L to μg/L. Pharmaceuticals in wastewater may have adverse impact on human health and aquatic ecosystem that can result in morphological, metabolic and sex alterations in aquatic organisms, and antibiotic resistance in pathogenic microorganisms and will interfere with the biodegradation activities (Bottoni et al. 2010). Pharmaceutical compounds, even at low concentrations, are found to influence the stream biota by showing behavioral changes (Gaworecki and Klaine, 2008; Stanley et al. 2007), reproductive damage (Nentwig, 2007) and inhibition of cell proliferation (Pomati, 2006) when exposure is for long duration. Similarly, several studies on fishes exposed to negligible amount of birth control pharmaceuticals in the wastewater results in decrease in reproductive rate (Sanderson, 2004).

The pharmaceutical manufacturing industry generates wastewater during the synthesis and formulation of various drugs which involves chemical synthesis (organic or inorganic) or biological reactions. The amount of wastewater generated is huge as in pharmaceutical industries the reactor and separators used are mainly oversized or are utilized inefficiently. Moreover, it is difficult to characterize the generated waste product as large number of subprocesses are involved in the industry. On the basis of manufacturing processes involved, the pharmaceutical industry is divided into subcategories (Browner, 1998) involving: fermentation plants, organic chemicals plants, fermentation or synthesized organic chemicals plants, natural or biological product extractions (antibiotics/vitamins/enzymes, etc.) and drug mixing, formulation, and preparation plants (tablets, capsules, and solutions, etc.). In order to manufacture drugs possessing specific pharmacological action/intermediates, chemical synthesis processes using organic/inorganic chemicals was utilized. It is usually a multistep process involving several byproducts and intermediates that needs large usage of raw water almost at every step. This may result in release of considerable amount of volatile solvents into water and air (Gadipelly et al. 2014). Wastewater is generated at almost every stage of the chemical synthesis operation (during manufacturing, purification, cleaning, washing, and maintenance). The mother liquor produced includes products, byproducts, unreacted reactants and substrates. There will be simultaneous production of acids and bases, cyanides, metals, halides, nitrates, and sulfates that will increases the toxicity level of wastewater. Such wastewaters need immediate treatment as they have high levels of biological oxygen demand (BOD), chemical oxygen demand (COD), and total suspended solids (TSS). The pH is found to be ranging from 1.0 to 11.0 (Browner, 1998).

Various treatment processes were employed by pharmaceutical industry for wastewater treatment and disposal methods (Struzeski, 1980) that can reduce the concentrations of pharmaceuticals in wastewater. However, waste-treatment operational costs, energy requirements and generation of residuals or by-products are the gray areas which needs to be worked upon. Nanotechnology has shown promising results in solving wastewater issues in recent years. Nanomaterials such as carbon nanotubes (CNTs), nanofiltration, and dendrimers are contributing to an efficient wastewater treatment processes (Obare and Meyer, 2004). Thus, the focus of this

chapter is to emphasize the role of nanomaterials and their applications in removal of pharmaceutical contaminants present in wastewater. It includes nanosorbents (nanotubes and zeolites), nanofiltration (NF), and advanced oxidation processes (AOPs). These nanomaterials have healthy prospects for future applications in research for the recovery and reuse of the pharmaceutical wastewaters.

10.2 Overview of contaminants in pharmaceutical wastewater

Pharmaceutical compounds present in the water resources raises concern worldwide as it is estimated that more than half of the pharmaceutical wastewaters produced are discarded without any treatment process (Enick and Moore, 2007; Lange, 2006). These compounds are persistence in nature, possess intrinsic biological activity, and act as toxins for aquatic and terrestrial organisms. Patneedi and Prasadu (2015) reported higher concentrations of antibiotic compounds affecting microbial community structure and ultimately food chains. They reported nonsteroidal drugs such as diclofenac, ibuprofen, and naproxen in sewage and surface water. In surface water, various antibiotic compounds, ibuprofen, ketoprofen, naproxen, indomethacin, diclofenac, acetyl salicylic acid, and phenazone have been found. Diclofenac in water bodies is found toxic for vultures and cattle (Kreisberg, 2005). Similar study reported three most frequently detected antibiotic compounds, diclofenac, carbamazepine, and amoxicillin in the aquatic environment (Ortiz et al. 2013). These compounds are not completely removed from wastewater by traditional treatment processes as they have low biodegradability and thus, pose great risk of accumulation of these contaminants in water bodies. Lower concentrations of these may result in cytological damages in aquatic and terrestrial ecosystems. Diclofenac (1 μg/L concentration) can changes the liver glycogen and ultrastructure, and kidney protein of a rainbow trout (Triebskorn et al. 2007) whereas, at lower concentration (10 ng/L) it can weaken the osmoregulatory ability of a green shore crab (Eades and Waring, 2010). Carbamazepine will impair the antioxidant enzymes, affects the mortality and fertility potential of midge *Chironomus riparius* (Heya, 2016). Amoxicillin in the range of 50 ng/L to 50 mg/L can inhibit photosynthesis and is toxic to the algae *Cyanophyta Synechococcus leopolensis* (Andreozzi et al. 2004). Due to the ill effect of these contaminants, there is strong need to remove these contaminants from wastewater prior to discharge in receiving waters.

Pharmaceutical products (PhPs) in the wastewater/water streams results in the development of microbes with antibiotic resistance, retardation of nitrite oxidation, and increased toxicity of chemical combinations and metabolites (Kummerer, 2001; Dalrymple et al. 2007). The PhPs can lead to feminization in fish (Orlando et al. 2004) and alligators (Guillette et al. 2000) and can affect migratory and behavioral patterns of salmon. Many of the compounds in these PhPs have low biodegradability and thus can't be removed efficiently by conventional treatment methodologies resulting in high level accumulation. Persistence of various pharmaceutical compounds such as

cyclophosphamide, flumequine, oxolinic acid, ivermectin, oxytetracycline, and clofibric acid were confirmed by scientists in soil, sediments, and aquatic environment despite treatment by biological degradation. These compounds are highly stable and have even more than 100 days of half-lives and sometimes even longer (Sorensen et al. 1998; Hartmann et al. 1999; Winkler et al. 2001).

Kolpin et al. (2002) reported approximately 90 organic contaminants from 139 water bodies investigated in United States in water bodies near the urban areas and livestock farming sites. Out of 90 contaminants, 21 were antibiotics (both human and veterinary), 19 were prescription medicines, and 14 were hormones and steroids. Sacher (2001) studied ground water wells samples, in which around 39 pharmaceutical compounds were detected belonging to group of antibiotics, analgesics, beta-blockers, antiepileptics, antirheumatics, and iodinated X-ray contrast. Carbamazepine (at 1.1 μg/L concentration) was reported from 21 ground water samples studied. Some of the pharmaceutical compounds were detected in higher concentration whereas, some others, such as analgesics phenanzone, propy-phenanzone, dimethyl-amino-phenazone, and lipid regulators gemfibrozil, were detected in ng range (Reddersen and Heberer 2002; Daughton and JL 2001).

10.3 Applications of nanomaterials for the removal of pharmaceutical contaminants

Over the past few years, pharmaceutical industry wastewater containing active pharmaceutical ingredients, solvents, intermediates, and raw materials have gained much attention. Various conventional treatment methodologies were widely used for the removal of pharmaceutical residues, but as they suffer several disadvantages, thus, they are not very effective. As the awareness of the inefficiencies of the individual treatment technologies for the removal of hazardous substances in pharmaceutical wastewater is increasing, the integration and combination of treatment technologies may provide a more effective, albeit expensive solution in the future.

This chapter will present review on the use of nanomaterials and their applications in the removal of pharmaceutical contaminants from wastewater. It includes NF, AOPs, and nanosorbents (Nanotubes and Zeolites).

10.3.1 Nanofiltration

NF is one of the essential processes used in the area of wastewater treatment. NF process falls between ultrafiltration (UF) and reverse osmosis (RO). NF is a membrane process that is powered by pressure and used to extract molecular weight solutes ranging from 200-1000 $gmol^{-1}$, mainly from aqueous solutions. NF membranes have pore sizes between 1 and 10 nanometers. These pore sizes are smaller than those used in microfiltration (MF) and UF, but in RO they are larger. NF extracts most organic compounds, nearly all bacteria, most natural organic matter and a wider range of salts. Nanofiltration is used mainly to soften hard water as it eliminates compounds

that make water hard like divalent ions. NF can separate small solutes from large molecules by two processes that occur in the solution. The first method is the separation of molecules based on their charge. The other method is to isolate unloaded solutes by weight of the molecules. In the science community the first mechanism is most common.

Advantages of Nanofiltration

Nanofiltration provides many benefits such as operation at low pressures, retention of multivalent anion salts is high, relatively less investment, and maintenance costs are low. NF successfully demonstrated the efficient removal of organic materials. NF processes are used in desalination. The desalination process refers to the removal of salt from seawater or brackish water and other inorganic ions with a final goal for providing safe and accessible water. NF is distinguished by the elimination of inorganic ions, during filtration, resulting in water softening, and no addition of sodium ions relative to ion exchange units. NF does not require special treatment, which automatically reduce the costs of separation. Further, no mechanical stirring is required separation of molecules. NF has the tremendous advantage of holding a consistently large quantity of feed and a smooth permeate flow rate (Rao, 2014; Rahimpour, 2010; Labban et al. 2017).

Disadvantages of Nanofiltration

Because of the porous nature of the membrane NF has not very high application in industry. Replacement of NF membranes are very fast, which is a big drawback of this process and it increases the cost of the NF (Mohammed, 2007). Using the NF systems, energy requirements for water treatment have risen by 60–150 percent. Consumption of energy is very high with NF than in UF and MF (0.3 to 1 kWh/m^3) and pretreatment is required (Sombekke, 1997). For some highly polluted waters, a tedious process of pretreatment is required with NF. There is not much retention of salts and univalent ions with NF. NF membranes are more expensive than RO membranes.

Applications of Nanofiltration

Within this purview of desalination, NF as a subset of membrane processes has found wide application.NF has been used for both RO and thermal processes in a desalination facility, resulting in an increased output of desalinated seawater. Many uses include extracting divalent ions from seawater, leachate heavy metals and solutions for electrolysis plating. Another use is to create a value-added product in an effluent process (Peters, 1998; Treboute et al. 2001; Wang et al. 2009). The retentate and permeate of these processes are effectively used by biotechnological means to generate enzymes and itaconic acids, respectively. The other applications of NF used in the industry are isolation of chemicals and solvents from solution, the processing of biomaterials, the food industry and flavors hence NF plays main role in the technology of separating solutes from solution. RO is replaced by NF membranes in applications such as drinking water. NF is used to extract fine and costly materials in order to make profits and reduce energy costs. NF has the unique appeal in numerous applications including water reuse, municipal wastewater treatment, and

drinking water (Koschuh et al. 2005; Drioli et al. 2011; Lipnizki et al. 1999; Yorgun, 2008). NF systems have softening units which use water processes such as the heat exchanger, water can be filtered by removing the ions that shape the scale in potable water pipes and equipment (Blocher et al. 2002; Vellenga and Tragardh, 1998). Comparative account of different nanomaterials used for wastewater treatment processes is as mentioned in Table 10.1.

10.3.2 Advanced oxidation process

Advanced oxidation processes (AOPs) are the processes used for oxidation by generation of hydroxyl radical (•OH). Such processes have been applied to eliminate or degrade harmful contaminants (Glaze, 1987). In AOPs mostly free radicals are synthesized, most predominant is the hydroxyl radical (•OH). The definition of AOP with sulfate radicals (SO_4^-) has been applied to oxidative processes. Hydroxyl radicals (OH^-) or sulfate radicals ($SO_4^{-)}$ are produced in enough amounts during wastewater treatment at AOP to remove both inorganic as well as organic contaminants (Cho et al. 2005; Ikai et al. 2010). As common oxidants both decontamination and disinfection play dual roles. These radicals act as a strong oxidizing agent and convert wastewater contaminants into less toxic compounds. Over the past decades, AOPs have gained growing interest in researching and implementing wastewater treatment technologies (Tchobanoglous et al. 2003; Huang et al. 1993). Processes like Fenton's process, hydroxyl radical generation, etc. have been used to eliminate or degrade recalcitrant contaminants to convert contaminants into simple compounds.

The different methods of AOPs include

a. AOP using ozone: ozone degrades into oxygen without the oxidation reaction creating self-derived byproducts. It is commonly used in drinking water purification, wastewater treatment and plant water management, water sterilization in artificial ponds.

- **(i)** O_3/UV Process: hydroxyl radicals are formed by lysis of ozone in the presence of light and water as shown in the following: $O_3 + hv + H_2O \rightarrow 2\cdot OH + O_2$ (Vilhunen et al. 2010; Muruganandham and Swaminathan, 2004).
- **(ii)** $O_3/UV/H_2O_2$: this combined approach will produce numerous ways to create hydroxyl radicals and is the most efficient treatment solution for highly polluted effluents. The process of UV/H_2O_2 is a uniform AOP using hydrogen peroxide from UV radiation. Hydrogen peroxide is activated by UV light which act as external source and hydroxyl radical ($\cdot$ OH) is generated by photolysis of H_2O_2 by UV light. Photolysis can also occur by solar light, but is less efficient (Matilainena and Sillanp, 2011; Wu et al. 2008).
- **(iii)** Catalytic ozonation process: catalytic ozonation is a form of AOP that joins both the properties of adsorption and oxidation of ozone with the catalyst that acts as solid phase in which decomposition of pollutants occurs at room temperature.

Table 10.1 Table showing comparative account of nanomaterials used for wastewater treatment processes.

Treatment Processes	Advantages	Disadvantages
Nanofiltration	1. Operates at low pressures and retention of multivalent anion salts is high. 2. Relatively less investment needed with no use of chemicals. 3. The membrane has very tiny holes so most molecules cannot go through. 4. Maintenance costs are low.	1. Soluble elements cannot be separated from water. 2. NF membranes are more expensive than reverse osmosis (RO) membranes. 3. There is not much retention of salts and univalent ions with NF.
Advanced oxidation process (AOP)	1. AOP can completely remove organic compounds and multiple organic pollutants can be extracted simultaneously. 2. AOP designs can cause disinfection of water at a fast reaction rate. 3. Easily managed and controlled processes. 4. Solar energy can be used.	1. AOP requires continuous input of costly chemicals thus is very expensive process. 2. Ozone is highly toxic gas which need good controls. 3. Risk of scaling on quartz sleeves, especially for high alkalinity wastewaters. 4. Catalyst separation can be difficult, potential for catalyst carry-over into treated wastewater.
Nano-sorbents (Nano-tubes and Zeolites)	1. NTs have a broad specific surface area which helps to adsorb pollutants. 2. Porous structure of NTs facilitates the transfer of reactants. 3. Functionalization of NTs is easy. 3. Zeolites are highly resistant, and they have water softening capacities. 4. Zeolites have high ion exchange capacity.	1. Zeolites are highly sensitive and can be deactivated by irreversible adsorption or steric blockage of heavy secondary products. 2. Zeolites cannot be used for the synthesis of bulky molecules. 3. NTs lack their solubility in aqueous media and are extremely small so are difficult to work with. 4. Process of production of nanotubes is relatively expensive.

In terms of energy efficiency, catalytic ozone decomposition is beneficial as compared with heat decomposition in respect to energy efficiency, as it does not involve heating of large volumes of air (Mahamuni and Adewuyi, 2010)

b. Photocatalysis: heterogeneous photocatalysis creates hydroxyl radicals on a semiconductor surface either by UV illumination or by visible light. in the presence of catalysts or oxidants photons excite hydroxyl radicals. The most common catalyst is titanium dioxide (TiO_2), with oxidative potential of TiO_2 particles, a semiconductor of the form RO (Muruganandham et al. 2007).

c. Fenton and photo-Fenton processes (Fe^{2+}/H_2O_2 and Fe^{2+}/H_2O_2/UV): wastewater is treated with hydrogen using iron salt using the Fenton process or homogeneous AOP. In photo-Fenton reaction UV light is combined with Fenton reagent. The illumination by UV light increases the efficiency of Fenton process. In Fenton process hydroxyl radical produced because of the iron catalyzed decomposition of H_2O_2 as shown in the following: $Fe^{2+} + H_2O_2 + hv = {}^{\cdot}OH + Fe^{3+} + OH^-$ (Muruganandham et al. 2010; 2012).

d. Other approaches for treating wastewater under AOPs are irradiation by ultrasonic waves [ultrasound (US)] and irradiation by electronic beam. In these processes, high frequency waves, 16kHz-100MHz, high temperature (4000-5000K), and a high pressure (150-500atm) lead to hydroxyl radicals being produced in these processes (VanHoof et al. 1999).

Advantages of AOPs

In an aqueous environment, they can completely remove organic compounds, rather than absorb or move contaminants to another environment. Owing to the extraordinary reactivity of •OH, it interacts with virtually any aqueous pollutant without any discriminating. Thus, AOPs are in many, if not all, cases where multiple organic pollutants must be extracted simultaneously. In aqueous phase they can completely remove contaminants, rather than storing or moving them to another phase. Certain AOP designs can cause disinfection of water, which is an effective solution to some water quality problems. Because the maximum reduction product of •OH is H_2O, technically no new dangerous compounds are introduced into the water by APOs. AOPs have fast reaction rates and are easily managed and controlled.

Disadvantages of AOPs

Most importantly, AOPs is expensive as it requires continuous input of costly chemicals. Some techniques require pretreatment of wastewater to ensure consistent performance, which could be potentially expensive and challenging. For example, presence of bicarbonate ions (HCO_3^-), due to scavenging processes that yield H_2O and a much less reactive species, $\bullet CO_3^-$ may significantly decrease the concentration of •OH. Bicarbonate is also washed out of the network.

Using only AOPs to handle a large volume of wastewater is not cost effective; rather, AOPs are introduced at the last stage after an enough proportion of pollutants have been effectively eliminated by primary and secondary treatment. The chemistry is dynamic and must be adapted to different applications. The quenching of excess peroxide is needed for certain applications.

Applications of AOPs

The AOPs have extensively investigated the removal of aromatic compounds because these compounds are toxic for the water (Liu et al. 2009; Sivasankar and Moholkar, 2009b). AOP has been used for removal of dyes from industries (Akpan and Hameed, 2009). These dyes may have harmful effects on microorganisms, marine life and human beings. waters (Akpan and Hameed, 2009; AlHamedi et al. 2009). AOPs are used to remove several pharmaceutical compounds because their presence in both aquatic environment and pure drinking water causes serious effects (Ikehata et al. 2006; Sanchez-Polo et al. 2009; Yang et al. 2009; Yu et al. 2008). Various insecticides and microbiocides, which has been widely used in agricultural and nonagricultural sectors, contaminate the groundwater and are removed by AOPs. The advanced oxidation processes were often used to handle certain toxins, such as carboxylic acids, heavy metals, bacteria, and actual industrial wastewaters (Kishimoto et al. 2005; Song et al. 2008a; Dutta et al. 2005; Neppolian et al. 2009; Chakinala et al. 2009; Kallel et al. 2009).

10.3.3 Nanosorbents (nanotubes and zeolites)

Our body requires low metal ion doses such as Zn ions, but their excess amounts can cause eminent health issues (Molinari et al. 2004; Al-Degs et al. 2006; Sadegh et al. 2015; Babel and Kurniawan, 2003; Karimi and Zohoori, 2013; Islam et al. 2017; Bansal and Goyal, 2005; Khlifi and Hamza-Chaffai, 2010; Ernhart, 1992). To protect health and environment removal of toxic materials from wastewater is necessary. Heavy metal ions are the most common toxic materials in wastewater that are responsible for health problems. Most wastewater treatment plants worldwide work according to the adsorption theory (Zare et al. 2015; Sadegh et al. 2015; Rao et al. 2006; Biskup and Subotic, 2005; Gupta et al. 2016). Some adsorbents such as activated charcoal, bio-sorbents, mineral adsorbents have been studied for their potential in the removal (adsorption) of various types of contaminants (Ekmekyapar et al. 2006; Arias et al. 2002; Gupta et al. 2015; Chu, 1999; Sublet et al. 2003). However, certain materials adsorption efficiency is poor. So, seeking more effective adsorbents has become important. An ideal adsorbent for wastewater treatment purposes should meet the following criteria as it should be ecofriendly, be simple to remove the adsorbed contaminants from its surface, be recyclable (Machida et al. 2006; Sharma et al. 2009; Ali, 2012). Several studies have shown that most of these criteria are fulfilled by the nanomaterials. The nanomaterials can be used successfully as powerful, less expensive and ecofriendly adsorbents for the removing different toxic substrates from wastewater such as heavy metals, etc. (Zwiener et al. 2007; Carballa et al. 2004; Joss et al. 2006; Lissemore et al. 2006; Andersen et al. 2003; Miao et al. 2004; Sadegh et al. 2016; Savage and Diallo, 2005; Machida et al. 2006; Sharma et al. 2009; Ali, 2012; Chen and Wang, 2006; Wang et al. 2013; Luo et al. 2010; Singh et al. 2013; Feng et al. 2010; Tuzen and Soylak 2007; Moradi et al. 2015; Zhao et al. 2010). Activated carbons (ACs), carbon nanotubes (NTs), zeolites and resins are the common adsorbents. Various nanomaterials and their advantages and disadvantages are as mentioned in Table 10.1.

a. Nanotubes (NTs)

Nanotubes (NTs) are considered as one of the most promising adsorbents for wastewater treatment because they have special structural and semiconductor. NTs have been commonly used in wastewater treatment to extract heavy metals and dyes. Just a few studies were reported on the application of NTs to extract dye from aqueous solution have been published. Among the modifications in NTs like introduction of functional groups, oxidation is a simple way to inject hydroxyl and carbonyl groups into the sidewalls of NTs. Oxidized NTs have been found to be efficient in extracting dyes aqueous solutions. The ability of NTs depends on the nature and type of adsorbent.

Advantages of NTs

The NTs have a broad specific surface area. The broad area of surface helps to adsorb pollutants. Functional groups like carbonyl and hydroxyl molecules could be easily attached to NTs by acid treatment, and these groups could be further changed to enhance adsorption tolerance to other different chemicals, resulting in process of "selective degradation" such as pollutant degradation. The porous structure of NTs facilitates the transfer of reactants from solution to the catalyst's active sites. NTs are stable thermally and resistant to acids and bases and may be used in harsh conditions.

Disadvantages of NTs

NTs lack their solubility in aqueous media. NTs are extremely small so are difficult to work with. The process of production of nanotubes is relatively expensive.

Applications of NTs

NTs are used to extract organic and inorganic pollutants as adsorbents. They are used as catalysts or cocatalysts for biorefractory and persistent organic pollutants. They are also used in photocatalysis. NT filters are used as antimicrobial materials. NT filters can effectively eliminate bacteria and viruses by adsorption and killing of microbes. They function as antifouling membrane additives. Polymer membranes mixed with NT have better antifouling property and become stronger and more permeable to water.

b. Zeolites

The water treatment industry is actively studying, evaluating, and developing new and improved methods of handling wastewater and drinking water in ways that are both efficient and environmentally sustainable. It may form zeolite when volcanic rock or ash reacts with alkaline waters. Zeolite is a mineral that can turn into a variety of aluminum, silica, and oxygen arrays known as aluminosilicates structures for example clinoptilolite. Their structure and composition make them microporous. The degree of the exchange properties varies from type to type and is significantly lower due to possible impurities in naturally occurring zeolites. However, zeolites can also be produced synthetically using solution of alumina, silica, and sodium hydroxide which is preheated. Since medias of zeolite have several pores, they catch

the particles as well as absorb them into their pores. This is achieved in part through the cation exchange potential of zeolite minerals, whereby positive ions are removed from the water. Also, zeolite is less susceptible to rapid clogging, indicating a lower pressure drop felt during treatment. Different natural zeolites around the world showed varying ion-exchange capabilities for cations like ammonium and heavy metal ions. Some zeolites also exhibit anion and organic adsorption from aqueous solution. Modification of natural zeolites can be achieved in many methods such as acid treatment, ion exchange, and surfactant functionalization, resulting in a higher adsorption potential of the modified zeolites for organics and anions.

Advantages of zeolites

Different advantages of zeolites are that they are highly resistant and have water softening capacities. They have high ion exchange capacity.

Disadvantages of zeolites

Zeolites are highly sensitive and can be deactivated by irreversible adsorption or steric blockage of heavy secondary products. Zeolites cannot be used for the synthesis of bulky molecules.

Applications of zeolites

Zeolites are used for pollution management, wastewater treatment. It is used for treating drinking water and grey water. Zeolites can reduce the sodium adsorption ration (SAR) and total dissolved solids (TDS). It is also used in fishing industry and radioactive water treatment.

10.4 Concluding remarks

Pharmaceutical compounds are contaminating the water and environment due to their inappropriate disposal from the pharmaceutical industries. These units are generating huge amount of waste that have hazardous effects on human health and environment. Wastewater is generated at almost every stage of chemical synthesis operation (during manufacturing, purification, cleaning, washing, and maintenance). Traditional treatment processes employed by pharmaceutical industry were inefficient in resolving the issue. Moreover, waste-treatment operational costs, energy requirements and generation of residuals, or byproducts are the gray areas that need to be worked upon. Thus, nanotechnology was used which has shown promising results in solving wastewater issues. Nanomaterials such as nanosorbents, NF, and AOPs are contributing for an efficient wastewater treatment processes. NF is useful for more than 80% recovery of antibiotic from the waste stream. It can lead to increase in the production capacity, can reduce the need of raw water, and decreases the cost of waste disposal. AOP is used mainly for the removal of recalcitrant compounds which are nonbiodegradable. Nanosorbents play significant role in removal of organic and toxic compounds from wastewater. Wastewater treatment utilizing different nanomaterials have healthy prospects for future applications in research for the recovery and reuse of the pharmaceutical wastewaters.

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CHAPTER

11

Recent advances in pesticides removal using agroindustry based biochar

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11.1 Introduction

Pesticides are a class of chemicals mainly used in agricultural practices in order to check the growth of pests, weeds, or to prevent the plants from contracting various diseases. It includes insecticides, herbicides, fungicides, nematicides, rodenticides, weedicides, etc. (Fig. 11.1) (Sharma et al., 2019). The use of pesticides has derived many benefits such as improved productivity, quality of food, protection of crop losses and control of vector-borne diseases like malaria (Aktar et al., 2009). Pest infestation leads to the loss of approximately 45% of the annual crop yield, therefore the use of synthetic pesticides has become very significant to curb these pests (Abhilash and Singh, 2009).

However, along with the industrial and agricultural revolutions in the late nineteenth century, use of pesticides has increased tremendously leading to detrimental effects on the natural environment. The unwise use of pesticides has led to devastating repercussions through bioaccumulation in higher trophic levels, long half-life, and slow decomposition rate (Sharma et al., 2019). The initial objective of pesticides was to inhibit the growth of certain target pest organisms but now they are known to cause detrimental effects to other nontarget organisms including human being (Nicolopoulou-Stamati et al., 2016; Aktar et al., 2009). The numerous health effects of pesticides to humans take account of neurotoxic, carcinogenic, endocrine-disrupting, reproductive, dermatological, and gastrointestinal effects, and high exposure may result in fatalities (Nicolopoulou-Stamati et al., 2016; Alewu and Nosiri, 2011; WHO, 1990). Notably, about 1 million deaths per year have been accounted to pesticide poisoning (Environews Forum, 1999).

The pesticides being used in agricultural practices are synthetically manufactured and get absorbed into the soil by surface runoff from the crops. The residues of these compounds further contaminate the groundwater table through the process of leaching, thus affecting the production of other agricultural crops as well (Sharma et al., 2019). The leached pesticides also contaminate water bodies as is evident in Kenya, where the catchment area of Lake Victoria is fed by six rivers that carry contaminants to the lake, which leads to poisoning of fishes in the lake (Sharma et al., 2019;

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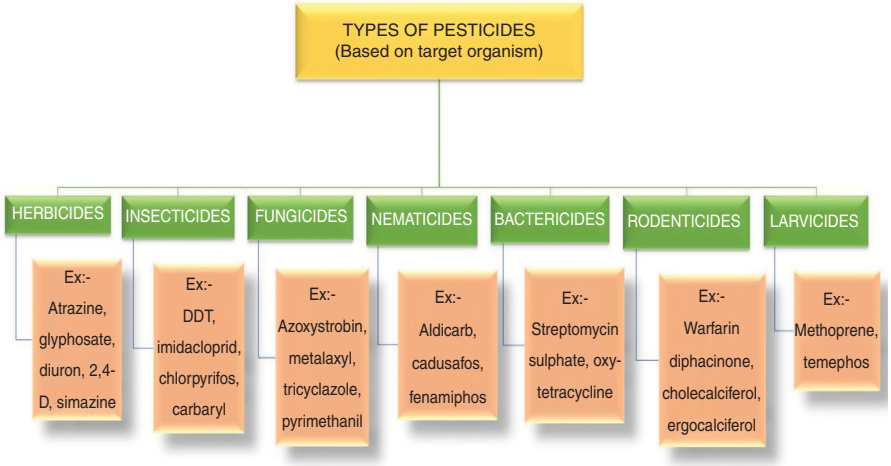

FIG. 11.1 Major types of pesticides on the basis of target organisms.

Abong'o et al., 2014). High quantities of malathion, γ-HCH and dieldrin were found in the groundwater and the Ganges River in the city of Kanpur, India (Sankararamakrishnan et al., 2005). Herbicide runoffs from agricultural catchments on the shores of Australia have led to deterioration of the coastal ecosystems in the Great Barrier Reef, leading to a loss of biodiversity as well (Brodie et al., 2012).

Pesticide contamination drastically changes water quality, soil ecosystem, and might change the interaction of the soil microbes with each other, thus disrupting the biochemical and physiological pathways, like symbiotic nitrogen fixation, between leguminous plants and symbiotic bacteria (Fox et al., 2007). Kostik et al. (2014) determined the residues of pesticides in fresh vegetables and fruits and found high concentrations of metalaxyl and imidacloprid, which may cause serious health effects to the consumer. Therefore, it is the need of hour to find potential technology to eliminate the pesticide residues from the environment. Various methods of remediation such as washing with extractants, bioremediation, and chemical oxidoreductive methods were tried for pesticide remediation (Morillo and Villaverde, 2017). However, though effective, these methods have some problems like low efficiency, high costs, loss of fertility, soil erosion, and leaching of nutrients (Liu et al., 2018; Kong et al., 2014). In contrast, adsorption of pollutants using biochar prepared from agro-industrial waste material has proven promising method of remediation. Use of biochar for the elimination of toxicants like pesticides, textile synthetic dyes, antibiotics, and heavy metals is a current topic of interest among researchers (Vyavahare et al., 2019, 2017; Liu et al., 2018; Peiris et al., 2017; Yan et al., 2015; Cao et al., 2009). Biochar is a cost effective, high efficient, and ecofriendly method of adsorption and possesses development of successful technology from lab to land (Liu et al., 2018). Biochar application is also reported in the areas of waste management, climate change mitigation, and generation of energy. Due to its high organic carbon

content, biochar acts as an efficient soil conditioner, and increases the water holding potential of the soil (Ahmad et al., 2014).

With this background, present chapter discusses concept of biochar with its characteristics and various applications. Further efforts have been made to review sorption of pesticides using direct and modified biochar.

11.2 What is biochar?

Biochar is a porous carbon rich material, which is obtained from pyrolysis of biomass such as residues from agricultural crops, wood, and waste usually in the limited or absence of oxygen (Liu et al., 2018; Khorram et al., 2016; Lehmann et al., 2006). Initially it was introduced as an amendment to improve the fertility of the soil, increasing crop yield, and to reduce the necessities of irrigation and chemical fertilizer. Also, biochar plays effective role in carbon sequestration and reduction in the emissions of greenhouse gases (Liu et al., 2018; Khorram et al., 2016). However, in recent years, it has become tremendously popular as a remediation method for hazardous chemical pollutants like pesticides, synthetic dyes, heavy metals, antibiotics, etc. (Vyavahare et al., 2019, 2017; Liu et al., 2018; Peiris et al., 2017; Mukherjee et al., 2016; Yan et al., 2015; Chen et al., 2012; Cabrera et al., 2011; Cao et al., 2009). Biochar possesses high sorption ability due to porosity and presence of phenolic, carboxyl, hydroxyl, etc. functional groups (Liu et al., 2018; Ahmad et al., 2014). Biochar assisted pesticide removal in the agricultural fields may reduce contamination of the underground water via lessening the leaching of pesticides (Khorram et al., 2016; Ahmad et al., 2014).

11.3 Characteristics of biochar

Efficiency of biochar for the remediation of pollutants is largely depends on the raw feedstock material and pyrolysis temperature used for its preparation. Number of studies has shown that, increase in temperature enhances the ability of biochar to adsorb the pollutant (Gámiz et al., 2019; Vyavahare et al., 2019, 2017). The effective sorption of pollutants using biochar usually depends on a number of characteristics including porosity, charge on surface, carbon content, pH, functional groups, surface area, aromatic structure, and mineral composition (Liu et al., 2018; Ahmad et al., 2014). The prominent biochar characteristics have been reviewed below and shown in Fig. 11.2.

11.3.1 Porosity and surface area

Pore filling is very important mechanism in the sorption of pollutant on biochar. Hence, the larger the pores or the higher the porosity, the more will be the sorption capacity of the biochar. Porosity can be brought about during pyrolysis in the dehydration step, where loss of water occurs (Bagreev et al., 2001). Porosity of biochar can affect the release behavior and bioavailability of the pollutants (Kookana, 2010);

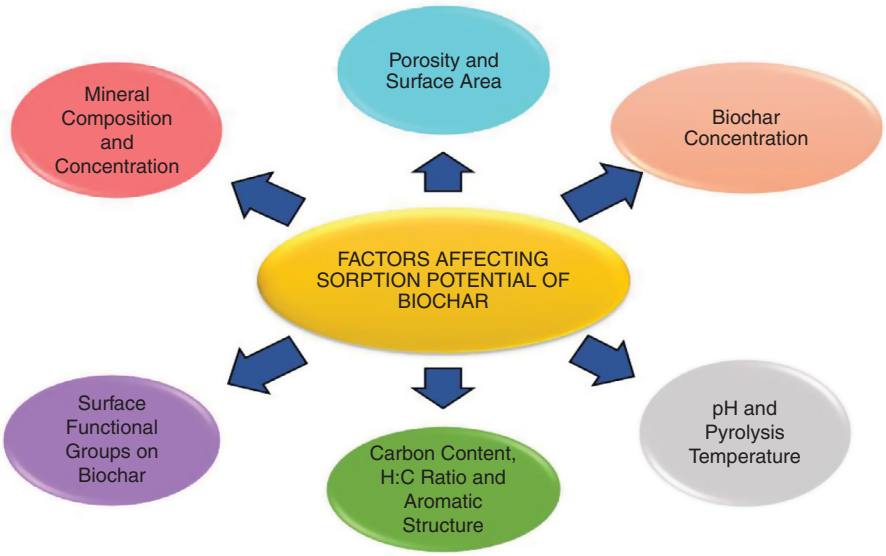

FIG. 11.2 Different factors affecting pollutant adsorption potential of biochar.

moreover, biochar with pores of smaller size, cannot trap the contaminant molecules, which are generally large (Liu et al., 2018). Surface area also affects the sorption of the pollutant in similar way as porosity. Higher surface area results in higher sorption (Liu et al., 2018; Bagreev et al., 2001).

11.3.2 pH

Higher pH of biochar has been shown to accelerate the sorption processes of organophosphates and carbamates by alkali catalysis (Zhang et al., 2012). Generally, biochar is alkaline in pH and the pH increases with an increase in temperature of pyrolysis (Cantrell et al., 2012). Depending on raw material of the biochar, there may be exceptions, for example, biochar that was produced from wheat straw and wastewater sludge at low pyrolysis temperature was reported to be acidic in pH (Hossain et al., 2011).

11.3.3 Functional groups at the surface

The biochar adsorption capacity of the largely dependent on the functional groups present on its surface. Types and quantity of surface functional groups present in biochar is generally determined by the pyrolysis temperature and raw material (Chen et al., 2015). The presence of functional groups reduces with higher temperatures due to a reduction in the H:C, O:C and N:C ratios (Liu et al., 2017).

11.3.4 Carbon content and aromatic structures

Both of these factors plays key role in determining the extent of pollutant sorption on the biochar (Liu et al., 2018; Cabrera et al., 2014). Aromatic structure is also important in determination of how sustainable the biochar behavior is, in the soil (Xiao and Chen, 2017). The ration of H:C reflects the aromatic structure of the compound and this determines the surface area and size of the pores in the biochar material (Xiao et al., 2016).

11.3.5 Mineral composition

The mineral composition of biochar is responsible for cation exchange potential of biochar; hence, it plays a very vital role in determination of the effectiveness of the biochar in sorption of the contaminant compound (Dias et al., 2010). Raw material used for biochar preparation determines mineral composition and concentration. Surface chelation and/or acidity mechanisms are the methods through which the availability of pollutants can be reduced (Wei et al., 2001). Further, temperature used for pyrolysis and type of raw material also affects the mineral composition of biochar. Higher temperatures lead to enriched mineral composition of biochar (Liu et al., 2018; Subedi et al., 2016).

11.4 Modified biochar

Though biochar has promising capability of chemical waste removal, it has low capacity when compared to absorbents like clays and activated carbon (Antón-Herrero et al., 2018; Liu et al., 2018). Therefore, in recent years, increase in porosity, surface area, and presence of different functional groups has been brought about in order to alleviate its sorption capacity popularly known as 'modified biochar'. Some frequent modification methods include loading of organic functional groups, activation with alkalis and nanoparticles (Rajapaksha et al., 2016). Researchers have also tried for enhancing mineral content of biochar using haematite, magnetite, calcium oxide, zero valent iron, etc. (Wang et al., 2015a; Agrafioti et al., 2014). Nanoparticles such as crystals of ZnS have been used for increasing biochar surface area (Yan et al., 2015). However, while selecting a method for chemical modification of biochar, it should be kept in mind that the method should be economical and should not in turn cause further environmental contamination (Liu et al., 2018).

11.5 Hazards of pesticides to environment and health

Overuse of pesticides has posed a great environmental challenge. The safe storage and disposal of pesticides are serious concern that needs to be tackled (Sharma et al., 2019).

Pesticides cause about 1 million deaths and chronic disease cases to humans per year as per the Environews Forum (Environews Forum, 1999). They are widely known to be endocrine-disruptors, and either mimicking or acting against the natural role of hormones in the body. This leads to severe health effects such as immunosuppression, mental retardation, disruption in hormonal functionality, reproductive disabilities, and cancers. Consumption of commodities sprayed with excessive pesticide is a serious health issue (Nicolopoulou-Stamati et al., 2016; Aktar et al., 2009).

Nontarget plants and animals are widely targeted by pesticide poisoning through contamination in soil and other nearby water bodies. Through runoff, pesticides reach surface water and further dissipate into the groundwater by leaching. This disrupts the overall quality of the soil and water, disturbing the entire environment causing detrimental effects (Aktar et al., 2009). Thus, even though pesticides are considered as a quick and easy way to control pests in agricultural fields, it is imperative that they should be used judiciously. Uncontrolled use of pesticides causes more harm than benefits (Sharma et al., 2019; Aktar et al., 2009).

11.6 Recent development in pesticides sorption on biochar

Various chemical, physical, and biological methods are being developed for pesticides remediation worldwide; however, higher technology cost, production of harmful intermediate metabolites and limitations for field application are the prominent disadvantage (Paul et al., 2005; Vyavahare et al., 2019, 2017). In recent years, researchers are trying for elimination of pesticide using sorption on agricultural waste-based biochar, which is thoroughly discussed below and presented in Table 11.1.

11.6.1 Herbicides sorption

The role of biochar in the sorption of herbicides has been studied extensively, especially on the more polar ones that undergo leaching and spread into the groundwater and surface water (Loffredo et al., 2019). The biochar surface contains specific adsorption sites that lead to more selective interactions with the herbicides like diuron and 2-methyl-4-chlorophenoxyacetic acid (MCPA) (Tatarková et al., 2013; Yang et al., 2006).

Yang et al. (2005) used a wheat-straw derived biochar to determine the bioavailability of the herbicide diuron to the microorganisms and barnyard grass in the soil. Study found wheat straw is highly effective for the sorption of diuron; however, it leads to a direct loss in the bioavailability of the pesticide which reduces its efficacy towards pests. Previously the same group of scientists had studied the sorption capacity of wheat and rice derived biochars for diuron, and reported diuron sorption to be 400-2500 times more than the sorption by a soil having 2.1% organic matter (Yang and Sheng, 2003a). Additionally, soil alteration with 1% wheat char showed improved diuron adsorption (Yang and Sheng, 2003b). In Yu et al. (2006), attempted research to determine the sorption of diuron onto a red gum (*Eucalyptus* spp.) derived charcoal

Table 11.1 Overview of various pesticides adsorption on agro-industry based biochar.

Pesticide	Feedstock Material	Pyrolytic Temperature (in °C)	References
Diuron	Wheat straw, rice straw	100	Yang and Sheng (2003a, b)
	Wheat straw	100	Yang et al. (2005)
	Red gum (*Eucalyptus* spp.) wood	450, 850	Yu et al. (2006)
Diuron, atrazine	Papermill sludge, poultry litter	550	Martin et al. (2012)
Diuron, monuron, linuron	enhanced biochar, hog waste, turkey litter, walnut shell and wood feedstock	510-900	Wang et al. (2015)
Diuron, glyphosate, bentazone, MCPA, chlorpyrifos	*Skogens kol* (80% hardwood such as birchwood, and 20% Norway spruce)	380-430	Cederlund et al. (2016
Diuron, glyphosate, MCPA	*Skogens kol* (80% hardwood such as birchwood, and 20% Norway spruce)	380-430	Cederlund et al. (2017)
Atrazine, simazine	Elm, maple, oak wood chips and bark	450	Zheng et al. (2010)
Atrazine	Dairy manure	200, 350	Cao et al. (2009)
	Corn straw	450	Zhao et al. (2013)
	Pine wood chip	300-550	Delwiche et al. (2014)
	Sludge	400	Zhou et al. (2015)
	corn cob, corn stalk, rice straw, soybean straw	450	Ouyang et al. (2015)
	soybean, corn stalks, rice stalks, poultry manure, pig manure and cattle manure	450	Liu et al. (2015)
	Corn straw	500	Tan et al. (2016)
	Pig manure	300, 700	Ren et al. (2016)
	Wheat straw	350, 550, 700	Yang et al. (2017)
	Corn straw	200, 400, 500, 600, 700	Yang et al. (2018)
	Cassava waste	200-750	Li et al. (2018)
Atrazine, acetochlor	Woodchips	500	Spokas et al. (2009)
Deisopropylatrazine, malathion, parathion, diazinon	Cottonseed hulls, flax, and rice husk	350, 650, 800	Uchimiya et al. (2012)
Atrazine, isoproturon	Rice straw, pig manure and wheat straw	300, 450, 600	Jin et al. (2016)
Atrazine, nicosulfuron	Peanut shells	300, 450, 600	Wang et al. (2019)

(continued)

Table 11.1 Overview of various pesticides adsorption on agro-industry based biochar. *Continued*

Pesticide	Feedstock Material	Pyrolytic Temperature (in °C)	References
Atrazine, carbaryl	Pig manure	350, 700	Zhang et al. (2012)
Terbuthylazine	Sawdust	350, 700	Wang et al. (2009)
Fluometuron, MCPA	from hardwood sawdust, macadamia nut shells, oak/hickory hardwood, bituminous coal, wood pellets, olive oil waste and organoclay	200	Cabrera et al. (2011)
Fluridone, norflurazon	Wood and grass	200, 300, 400, 500, 600	Sun et al. (2011)
	Poultry waste, wheat straw, swine waste	250, 400	Sun et al. (2012)
MCPA	Wheat straw	300	Tatarková et al. (2013)
Aminocyclopyrachlor, bentazone, pyraclostrobin	wood pellets, macadamia nut shells, and hardwood (oak or hickory)	500-850	Cabrera et al. (2014)
Imazamox, methyl-desphenyl-chloridazon, metazachlor oxalic acid, metazachlor sulfonic acid	beech wood, manure and straw	<550	Dechene et al. (2014)
MCPA, terbuthylazine, nicosulfuron, fluoroethyldiamino-triazine, indaziflam	macadamia nut shells	850	Trigo et al. (2014)
pyrazosulfuron-ethyl	Wheat and rice straw	400, 600	Manna and Singh (2015)
Fomesafen	rice hulls	600	Khorram et al. (2015)
Metolachlor	Rice husks	300, 500, 750	Wei et al. (2016)
	macadamia-nut shell	550, 850	Trigo et al. (2016)
Bentazone, pyrimethanil, boscalid	Pine wood chips	400	Mukherjee et al. (2016)
Metribuzin	Switchgrass	425	Essandoh et al. (2016)
	Grapevine pruning residues, red spruce wood	<550	Loffredo et al. (2019)
2,4-D	tea, bur cucumber and hardwood	400, 700	Mandal et al. (2017)
Imazapic, imazapyr	empty fruit bunches of the oil palm and rice husks	300, 500, 700	Yavari et al. (2017)

Table 11.1 Overview of various pesticides adsorption on agro-industry based biochar. *Continued*

Pesticide	Feedstock Material	Pyrolytic Temperature (in °C)	References
2,4-D, MCPA	Switchgrass	425	Essandoh et al. (2017)
Glyphosate	hardwoods like pecan, apple and cherry wood chips, wood pellets	350, 500, 700, 900	Hall et al. (2018)
Acetochlor	Crofton weed, wood chips, rice hull	500	Li et al. (2018)
2,4-D, MCPA, metolachlor, carbaryl, carbofuran	Wheat straw	550	Ćwieląg-Piasecka et al. (2018)
mesotrione	Oak wood	550	Gámiz et al. (2019)
acetamiprid	Red gum (*Eucalyptus* spp.) wood	450	Yu et al. (2011)
Pymetrozine	Spent brewer's grain	300, 400, 500, 600, 700	Xi et al. (2014)
Carbaryl	rice straw, pig manure and maize straw	350, 700	Ren et al. (2015)
DDT	Burt's and Blue Leaf	Not mentioned	Denyes et al. (2015)
Imidacloprid	wheat straw, pig manure and rice straw	300, 450, 600	Jin et al. (2016)
Imidacloprid, atrazine	Rice straw	600	Mandal and Singh (2017)
Carbofuran	Tea waste	300, 500, 700	Mayakaduwa et al. (2016)
	Rice husk	300, 500, 700	Mayakaduwa et al. (2017)
Thiacloprid	Magnolia wood chips	500	Li et al. (2016)
Chlorpyrifos	*Cyperus alternifolius*	450	Tang et al. (2017)
	Rice husk	700	Okoya et al. (2020)
Imidacloprid, clothianidin, thiacloprid	maize straw and pig manure	200-700	Zhang et al. (2018a)
Thiacloprid	Maize straw, pig manure	300, 500, 700	Zhang et al. (2018b)
Fipronil	Maize straw	600-800	Qu et al. (2018)
Chlorpyrifos, chlorpyrifos-methyl	giant reed	300, 350, 400, 500, 600	Zheng et al. (2019)
Thiamethoxam, clothianidin	woodchips	450	You et al. (2020)
Diazinon	Coconut shell	700	Baharum et al. (2020)

(continued)

Table 11.1 Overview of various pesticides adsorption on agro-industry based biochar. *Continued*

Pesticide	Feedstock Material	Pyrolytic Temperature (in °C)	References
Pyrimethanil	Red gum (*Eucalyptus* spp.) wood	450, 850	Yu et al. (2010)
Azoxystrobin	Red gum (*Eucalyptus dunni*) wood	500	Sopeña and Bending (2013)
Tricyclazole	alperujo compost, woody debris and rice hull	400, 500, 550, 700	García-Jaramillo et al. (2015)
Metalaxyl	Olive mill waste	400	Gámiz et al. (2016)
	grapevine pruning residues and spruce wood	550	Parlavecchia et al. (2019)
Fenamiphos, cadusafos	Date palm and *Eucalyptus* waste	450	Abdel Ghani et al. (2018)

and it was shown to affect the sorption-desorption behavior of diuron majorly. Sorption of atrazine and diuron on biochars derived from papermill sludge and poultry litter was conducted by Martin et al. (2012). Both chars effectively adsorbed atrazine and diuron. The poultry litter derived biochar amounted to an increase in the sorption capacity of atrazine and diuron by 448% and 515% respectively. Wang et al in 2015, reported that the use of five biochars viz. enhanced biochar, hog waste biochar, turkey litter biochar, walnut shell biochar, and wood feedstock biochar, proved effective for the sorption of three phenylurea herbicides—monuron, diuron, and linuron. The sorption of the herbicides was highest in the walnut shell biochar, and the sorption intensity for herbicides was decreased in the sequence linuron > diuron > monuron.

Cederlund et al. (2016) used the commercial biochar *Skogens kol,* which has been derived from 80% hardwood, such as birchwood, and 20% Norway spruce, by slow pyrolysis at temperatures of 380-430°C, to test adsorption of diuron, glyphosate, bentazone and MCPA. The biochar was treated thermally and chemically using iron, which was believed to enhance its adsorptive properties. It was shown that heat treatment increased the surface area of biochar and increased sorption of MCPA and bentazone, while the iron treatment decreased the specific surface area but led to increase in glyphosate adsorption. Later on, Cederlund et al. (2017) used the same commercial wood-based biochar *Skogens kol,* and its effects on leaching of three herbicides, diuron, glyphosate and MCPA, were determined. The impact of this biochar was only seen significantly on diuron and MCPA, because of their higher mobility, as compared to glyphosate. Zhelezova et al. (2017) carried out research to determine the adsorption of diuron and glyphosate, using aged version of the wood-based commercial biochar *Skogens kol* in two different soil types – clayey and sandy. Adsorption of diuron increased with the addition of fresh biochar to both types of soils. However, sorption of glyphosate reduced in the sandy soil, probably due to soil pH increase after adding the biochar. The ageing of the biochar resulted in a decrease in adsorption of both herbicides due to a further increase in the pH of the soil.

Many studies have been conducted for the removal of atrazine, as is one of the most widely used herbicides in the United States and known to adversely affect human health and natural ecosystem (Delwiche et al., 2014). The question whether atrazine leaching could be reduced by increased sorption to biochar was addressed by Zheng et al in 2010 by using a greenwaste biochar derived from elm, maple and oak wood chips and bark. The sorption capacity of this biochar was tested on two triazine group pesticides viz., simazine, and atrazine. The sorption affinity was seen to increase at low pH and as the solid-to-solution ratio decreased. Decline in solid-to-solution ratio from 1:50 to 1:1000, showed increase in sorption of atrazine from 451 to 1158 mg/kg and that of simazine increased 243 to 1066 mg/kg. Cao et al. (2009) showed that biochar derived from dairy manure could effectively sorb atrazine and lead. Spokas et al. (2009) used a woodchip-based biochar to test its effect on the sorption of atrazine and acetochlor in agricultural fields. Biochar was capable of enhancing sorption of the pesticides and reduced the possibility of leaching and runoff.

A pig-manure derived biochar was used to study the adsorption of atrazine on original and deashed biochars (treated with HCl). The adsorption was shown to significantly increase in case of the deashed biochar (Zhang et al., 2012). Cottonseed hulls, flax, and rice husk (activated with KOH) biochars were used to determine the adsorption of deisopropylatrazine, a metabolite of atrazine (Uchimiya et al., in 2012). The rice husk derived biochar activated by KOH proved to be very useful in adsorption of deisopropylatrazine as it removed almost half of its own weight of the metabolite.

Zhao et al. (2013) performed a study on corn straw biochar, with and without pretreatment with ammonium dihydrogen phosphate and investigated sorption behavior of atrazine. The results indicated that atrazine sorption potential of modified biochar was enhanced and acidic conditions with higher temperature were favored for it (Zhao et al., 2013). Another research conducted by Delwiche et al in 2014, showed reduction in atrazine leaching by 52% using pine chip biochar. The soil structure may affect the leaching of atrazine, irrespective of biochar (Delwiche et al., 2014). Sludge-derived biochar was employed and the role of humic acids from the soil in the sorption process of atrazine was tested. Humic acids resulted in a suppression of atrazine sorption due to the increase in hydrophilicity of the biochar surface and pore blockage in the presence of these acids (Zhou et al., 2015). At the same time, a study was published in which five modified biochars from four different sources viz. corn cob, corn stalk, rice straw, soybean straw and corn stalk treated with ammonium dihydrogen phosphate (5%) were used for the sorption of atrazine in two different concentrations (1 mg/L and 20 mg/L). Modified corn stalk biochar showed the largest sorption capacity, while the unmodified rice straw and corn stalk biochars were also performed considerably (Ouyang et al., 2015).

In an extensive study, Liu et al. (2015) examined the sorption capacities for atrazine in biochars derived from soybean, corn stalks, rice stalks, poultry manure, pig manure and cattle manure. The results showed that the sorption of atrazine on the biochars reduced in the order soybean > rice stalks > cattle manure > corn stalks > poultry manure > pig manure due to the respective pore volume of the biochars. A

corn-straw based biochar was used by Tan et al in 2016, to prepare KOH and Na_2S-modified biochars as well as biochar using activated carbon. The sorption ability of these biochars for aqueous Hg (II) and atrazine were checked, either alone or in a mixture. The modified biochars showed an increase in sorption capacity by 46.39%, 38.66%, and 47 times for atrazine in case of KOH modified, Na_2S modified and activated carbon biochars respectively, as compared to the normal corn straw derived biochar. Its high surface area is the reason that activated carbon proved as the best sorbent for the removal of atrazine.

A biochar derived from pig manure, produced at two different temperatures, 300 and 700°C, was used to detect the sorption of atrazine and the effect of ageing of the biochar on the sorption was further studied. It was concluded that soils freshly amended with the biochar showed up to 23.4 times increase in atrazine sorption as compared to the soils without biochar. Furthermore, results indicated, biochar produced at 300°C has an increase in the atrazine sorption after ageing. However, biochar prepared at 700°C showed a marked decrease in the sorption capacity, but the sorption was still 56.3% higher than original soil (Ren et al., 2016).

Jin et al in 2016, attempted a study on the adsorption of atrazine and isoproturon, using biochars prepared from raw rice straw, pig manure and wheat straw at three different temperatures (300, 450 and 600°C). They found increase in biochar and pyrolytic temperature led to increase in sorption capacity of the mixtures. The plant residue derived biochars showed a higher enhancement of sorption capacity than the pig manure derived biochar. An amendment of wheat-straw derived biochars in black soil has enhanced sorption capacity and microbial transformation of atrazine (Yang et al., 2017). Mandal and Singh (2017) used rice straw derived biochars to evaluate atrazine sorption, using normal and modified biochar with phosphoric acid. The Freundlich adsorption coefficient for atrazine was higher in the case of phosphoric acid treated biochar (Mandal and Singh, 2017).

Corn straw was used to produce biochar at various temperatures by Yang et al in 2018, and concluded that corn straw biochar colloids are perfect for atrazine sorption, under high temperature and high surface area condition. Cassava waste biochar addition to latosol as a sorbent material for atrazine resulted in increased adsorption of atrazine from 1.7-fold by the latosol to 36-fold (X Li et al in 2018).

A study on the sorption of atrazine and nicosulfuron onto nine biochars produced by pyrolysis of peanut shells, was conducted by Wang et al., in 2019. The biochars were pyrolyzed at three different temperatures and samples of each of the biochars were treated either with deionized water or 1M HCl for 24h. These biochar were effective in immobilizing atrazine from travelling to surface or ground water. However, the deashed biochars showed a reduction in sorption capacity, with the HCl deashing proving more effective than water deashing.

Apart from the studies included above, a number of other experiments have been conducted to test the sorption of the herbicides 2,4-D, bentazone, glyphosate, MCPA, fluridone, norflurazon, fluometuron, pyrazosulfuronethyl, imazapic and imazapyr, aminocyclopyrachlor, imazamox, methyl-desphenyl-chloridazon, metazachlor oxalic acid, metazachlor sulfonic acid, mesotrione, nicosulfuron, terbuthylazine,

indaziflam, acetochlor, fomesafen, metolachlor, metribuzin, and fluoroethyldiaminotriazine using biochar.

Wang et al. (2009), observed the sorption of terbuthylazine onto biochars produced from sawdust and commercially available charcoal at 700°C and 350°C. The results of the study showed that addition of biochars into soils greatly improved the adsorption of terbuthylazine, as the values of the adsorption coefficients enhanced from 1.80 L kg^{-1} for unamended soil, to 115.6 and 6.69 L kg^{-1} for the biochar produced at 700°C and 350°C respectively. The biochar was also reported to have reduced the possibility of terbuthylazine leaching to groundwater.

The herbicides fluometuron and MCPA were examined for the sorption onto six different biochars, derived from hardwood sawdust, macadamia nut shells, oak/hickory hardwood (a sample of which was thermally activated), wood pellets (a sample of which was chemically activated using H_2O_2), bituminous coal (activated with steam), organoclay, and olive oil waste. The biochar derived from bituminous coal, organoclay, and wood pellets (both inactivated and activated by H_2O_2) showed high sorption for both fluometuron and MCPA (Cabrera et al., 2011).

Sun et al. (2011) produced a number of biochars from wood and grass feedstocks to investigate the sorption of the fluorinated herbicides fluridone and norflurazon. Study found that, higher sorption occurs on biochar produced at low pyrolyzing temperature which may be due to reduced mobility of fluridone and norflurazon.

Further investigation of fluridone and norflurazon sorption behavior on thermal and hydrothermal biochars was reported by Sun et al. (2012). Thermal biochars were obtained from poultry waste and wheat straw with HCl treatment. While, hydrothermal biochars (heated in the presence of water) were derived from swine waste and poultry waste respectively. Results showed that, due higher organic functionalities, hydrothermal biochar showed higher sorption capacity as compared to thermal biochar. Tatarková et al in 2013, reported that biochars derived from wheat-straw, increased the sorption of MCPA from biochar-amended soils, by 2.53 times more than that of soil without amendments, and soil modification with biochar addition led to a reduction in leaching and dissipation of MCPA.

The sorption of herbicides aminocyclopyrachlor and bentazone was determined in the study conducted by Cabrera et al., in 2014, in which wood pellets, macadamia nut shells, and hardwood (oak or hickory) were used to derive biochars. The sorption capacity of wood pellet-derived biochar was greater than macadamia nut shell-derived biochar. This might be because of the competition for the sorption sites among dissolved organic carbon (DOC) from nut shells and herbicides. Thus, this study revealed that mobile pesticides can be easily sorbed by biochars with low DOC content.

Polar herbicide imazamox and some metabolites of herbicide (methyl-desphenylchloridazon, metazachlor oxalic acid, metazachlor sulfonic acid) were examined for their sorption onto fresh biochar derived from beech wood, and composted biochar obtained on composting it in a mixture of manure and straw. Three out of the four tested compounds (imazamox, metazachlor sulfonic acid and metazachlor oxalic acid) didn't show any difference in sorption or desorption on addition of the biochars,

but methyl-desphenyl-chloridazon sorbed stronger to the soil which was amended with biochar by two times (Dechene et al., 2014).

Trigo et al in 2014 macadamia nut shells biochar (fresh and aged) for studying sorption of various herbicides including MCPA, terbuthylazine, nicosulfuron, fluoroethyldiaminotriazine and indaziflam. In the study, nicosulfuron did not show sorption on the fresh biochar, whereas, terbuthylazine exhibited higher sorption with sorption coefficient of 595. The aged biochars did not show any progress in the sorption of nicosulfuron. An increase in sorption of indaziflam and fluoroethyldiaminetriazine on aged biochar as compared to fresh had been seen. The sorption of terbuthylazine and MCPA decreased with the application of the aged biochar (Trigo et al., 2014).

Wheat and rice biochars were used to study the sorption of pyrazosulfuron-ethyl, a sulfonylurea herbicide used to control grassy weeds in paddy cultivations (Manna and Singh, 2015). Pyrazosulfuron-ethyl was weakly adsorbed in sandy loam soil, but rice biochar proved more effective even when compared with biochar derived from wheat. The pesticide fomesafen was tested for its sorption onto biochar produced from rice hulls, and it was shown that addition of the biochar into the soil increased the sorption of fomesafen and reduces its mobility (Khorram et al., 2015).

Rice husks were used to derive biochar for the sorption of the acetanilide herbicide metolachlor, and it was reported that a higher pyrolytic temperature resulted in an increase in the sorption of metolachlor due to increase in pore diameter and surface area (Wei et al., 2016). A biochar produced from pine wood chips was used in the sorption of bentazone (Mukherjee et al., 2016). In the study, biochar addition led to a decrease in the mineralisation of the pesticide and non-extractable residues formation. This resulted in enhanced pesticides dissipation due to sequestration in soils.

A study by Trigo et al. (2016), used three macadamia-nut shell biochars aged zero, one and two years respectively, along with two wood biochars aged zero and five years respectively. These biochars were used to determine the sorption and desorption of herbicide metolachlor. The fresh macadamia nut biochar increased the apparent sorption coefficient of the herbicide by 2.4 times, while the 1-year-aged and 2-year-aged biochars showed an increase in apparent sorption coefficient by 2.5 and 1.9 times. The fresh wood biochar showed a 2-fold increase in the apparent sorption coefficient, while the aged wood biochar showed a 1.4-fold increase in the same. The study concluded that increasing sorption coefficients were due to degradation in solution of the metolachlor, which could then sorb onto lesser accessible sorption sites.

Adsorption of the herbicide metribuzin from aqueous solution using modified switchgrass biochar, as a cost-effective and sustainable source of biochar has been investigated. Modified biochar was prepared by precipitation of iron oxide onto the surface of the switchgrass biochar, using an aqueous solution of Fe^{3+}/Fe^{2+} followed by treatment with NaOH. It was observed that a low solution pH facilitated the adsorption of metribuzin onto original as well as modified biochar. Though magnetic treatment have not shown any enhanced adsorption effect but according to researcher it could be easily separated from the contaminated solution after adsorption (Essandoh et al., 2016).

Mandal et al in 2017, studied the mechanism of 2,4-dichlorophenoxy acetic acid (2,4-D) sorption using biochar, in aqueous conditions, using biochars derived from various green waste such as tea, bur cucumber and hardwood at two different pyrolysis temperatures (400 and 700°C). Further, tea waste biochar was modified using steam showed the highest sorption capacity of 2,4-D. Yavari et al., in 2017 used empty fruit bunches of the oil palm and rice husks to derive biochars. Study was aimed to determine sorption of imidazolinone herbicides, imazapic and imazapyr. The empty fruit bunch biochar was found to be more effective in the sorption of the herbicides, especially imazapyr, as compared to the rice husk-derived biochar. Low-cost switchgrass biochar was successfully used to sorb the herbicides 2,4-D and MCPA from aqueous solutions (Essandoh et al., 2017). In an aqueous condition, three-dimensional swelling of the biochar occurs, which provide additional sorption sites for the adsorbates.

A study by Hall et al (2018) was conducted on the herbicide glyphosate, to investigate the sorption-desorption behavior on biochar produced from different hardwoods like pecan, apple and cherry wood chips. Another biochar sample was used which contained wood pellets, in addition to chemically modified biochars prepared by combining wood pellets with 10% w/w Fe_2O_3, and another treated with 5% w/w Cu_2SO_4. However, the hardwood biochars were deemed inefficient for glyphosate sorption in soils with high phosphate content. The hardwood biochars pyrolyzed at 700°C showed sorption capacity in the order of pecan > apple > cherry. In this study, chemically modified biochars did not show any significant enhancements in glyphosate sorption.

Three biochars derived from crofton weed, wood chips, and rice hull were produced to explore their effect on the sorption of acetochlor. The rice-hull derived biochar was most efficient in the sorption of acetochlor, owing to a high specific surface area. Among the remaining two biochar, crofton weed biochar was more effective than wood chip biochar due to its higher carbon content (Li et al., 2018).

Sorption potential of wheat straw-derived biochar was examined for herbicides 2,4-D, MCPA and metolachlor in which higher sorption was obtained for metolachlor, due to its non-ionic nature and high hydrophobicity (Ćwieląg-Piasecka et al., 2018). Recently, Gámiz et al in 2019 had produced oakwood biochar (fresh and field-aged) and applied to soil to check the herbicide mesotrione sorption. The aged biochars were aged at three different places around the United States – Wisconsin, Idaho and South Carolina – for six months each. The fresh sample showed low sorption capacity, while the field-aged biochar aged at Wisconsin showed high sorption for mesotrione. This demonstrates that there can be variations in biochar sorption capacities due to soil exposure which alter the behavior of the herbicide.

Tw raw material viz., residues of grapevine pruning and red spruce wood were used to produce biochars to check their effect on the sorption of metribuzin, and both biochars exhibited a relevant sorption capacity towards metribuzin. The greater sorption potential of grapevine pruning biochar as compared to red spruce wood biochar was accounted to its higher porosity (Loffredo et al., 2019).

11.6.2 Insecticides sorption

A number of insecticides like imidacloprid, carbaryl, carbofuran, chlorpyrifos, fipronil, thiamethoxam, acetamiprid, pymetrozine, diazinon, thiacloprid, malathion, parathion, clothianidin, and DDT have been studied for their sorption onto various agroindustrial based biochars. The following studies have been conducted on these insecticides.

A red gum wood (*Eucalyptus* spp.) was used to derive a biochar to sorb the pesticide acetamiprid in three different Chinese soils – paddy soil, red soil and black soil. The amendment contributed enhancement in sorption of 52.3%, 27.4%, and 11.6% respectively in the soil (Yu et al., 2011). Uchimiya et al in 2012, used wastes from a cotton mill, consisting of a mixture of hulls and cottonseeds, to produce a biochar at 350, 650 and 800°C, as well as steam activated biochar produced from flax shive, and Rice husk KOH activated carbon, to study the sorption of three insecticides – diazinon, malathion and parathion. The degree of sorption followed the order of parathion > diazinon > malathion.

Zhang et al., in 2012, tested pig manure-derived biochar (untreated and deashed with HCl and HF) for the sorption of carbaryl, and the study showed that the pesticide was significantly sorbed to the biochar, with a highest adsorption percentage (90.6%) shown by the untreated biochar produced at 700°C, while the deashed biochar did not show much efficiency in sorption of carbaryl. A biochar produced from brewer's spent grain was produced at 300, 400, 500, 600 and 700°C and applied for the remediation of the insecticide pymetrozine from aqueous solution. High efficiency of pymetrozine sorption and potential in preventing water pollution by reusing the waste of the beer industry using biochar was obtained (Xi et al., 2014).

Three biochars derived from rice straw, pig manure and maize straw, pyrolyzed at 350 and 700°C were used for the removal of carbaryl from soil. The results showed that these amendments enhanced sorption of carbaryl with those produced at 700°C showing greater impact (Ren et al., 2015). A study by Denyes et al., in 2015, was performed to assess the bioavailability of DDT in contaminated soil after amendment with two different biochars (Burt's and Blue Leaf). The bioavailability was examined by using earthworms (*Eisenia foetida*), plants (*Cucurbita pepo*) and a polyoxymethylene passive sampler method. Though the accumulation of DDT in *E. foetida* reduced after amendment by 49%, it had no effect on the plant uptake of DDT.

The sorption of imidacloprid onto biochars derived from wheat straw, pig manure and rice straw at 300, 450 and 600°C was observed by Jin et al in 2016. The sorption of the insecticide was promising using biochar produced from rice straw and wheat straw at 300°C. Tea waste derived biochar produced at 300, 500 and 700°C were utilised for carbofuran removal. The highest sorption intensity was accomplished by the biochar derived at 700°C, and the research concluded that biochar derived from tea waste is effective in the sorption of carbofuran (Mayakaduwa et al., 2016).

Magnolia tree wood chips were used to produce a biochar by pyrolysis at 500°C, to assess its sorption capacity for insecticide thiacloprid. The sorption of thiacloprid was increased by 14 times after applying 2% of the biochar to the soil. However, during the study, environmental risk of biochar to earthworms was also observed and reported (Li et al., 2016).

A study on the insecticide chlorpyrifos was done by Cederlund et al in 2016, wherein a wood-based commercial biochar *Skogens kol* was heat-treated and chemically treated with iron salts, and utilised for the sorption of the pesticide. The sorption of chlorpyrifos was found to be increased when of heat-treated and iron-treated biochar were used equally. Chlorpyrifos sorption onto a wood-based biochar *Skogens kol* was once again studied by Cederlund et al., in 2017, and it showed the highest sorption rate among the group of pesticides tested (which were herbicides diuron, glyphosate and MCPA). Another study on chlorpyrifos published in the same year, wherein Fe-impregnated biochar derived from *Cyperus alternifolius* was used to remove the pesticide from water. The biochar impregnated with iron salts demonstrated a greater sorption capacity towards chlorpyrifos, and efficiently removed chlorpyrifos from water. It also had a encouraging effect on the degradation of chlorpyrifos in soil, possibly by altering microbial communities (Tang et al., 2017).

Rice husk-derived biochar produced at 300, 500 and 700°C and then activated by steam was applied to test sorption of the insecticide carbofuran. The steam activation was shown to increase carbofuran removal. Sorption of carbofuran was observed onto the biochar at a wide range of pH. According to study, steam-activated biochar is efficient to remove carbofuran in batch and fixed-bed sorption systems (Mayakaduwa et al., 2017). Rice straw biochar (normal and treated with phosphoric acid) had used to assess the sorption of imidacloprid (Mandal and Singh, 2017). Both types of biochar showed high adsorption capacity for 95% imidacloprid and they proved good as low-cost biochar for imidacloprid removal.

Ćwieląg-Piasecka et al in 2018, conducted a study using wheat-straw biochar to determine sorption of the two carbamate insecticides, carbaryl and carbofuran. It showed higher adsorption capacity which was 92.1% and 98.9% for carbofuran and carbaryl respectively. Study concluded that, non-ionic nature and hydrophobic effect were the responsible factors for the higher level sorption of insecticides under study. In a parallel publication, Zhang et al. (2018a) reported maize straw and pig manure derived biochar at 200-700°C further deashed by treating with Hydrochloric acid (HCl) and Hydrofluoric acid (HF). Sorption study of three neonicotinoid insecticides viz., imidacloprid, clothianidin, and thiacloprid was carried out. Higher sorption of thiacloprid on untreated biochar was observed which might be due to hydrogen bonds and hydrophobic interactions. The deashing process increased carbon content, bulk oxygen, aromaticity, and oxygen-containing functional groups, as well as the total surface area and pore volume of the biochar. The deashing however proved as a disadvantage in the higher pyrolysis temperature biochar due to the blockage of micropores by covering the inner sorption sites for organic moieties (Zhang et al., 2018a). Same researcher published sorption of thiacloprid on maize straw and pig manure-derived biochar and showed increased capacity in the soil. This was related to an organic carbon and surface area increase along with a reduced H/C ratio (Zhang et al., 2018b).

A study on the insecticide fipronil was performed in which maize-straw derived biochar was used to investigate the mitigation of fipronil in the environment to reduce its burden on loach (*Misgurnus anguillicaudatus*). The study concluded that the

presence of biochar decreased the bio-accessibility of fipronil and its metabolites (Qu et al., 2018). Recently, sorption of chlorpyrifos and chlorpyrifos-methyl onto giant reed-derived biochar is reported (Zheng et al., 2019). The biochar were produced at 300, 350, 400, 500 or 600°C, and then deashed by HCl and HF. Further biochar were treated with malic acid and citric acid. The biochar increased the sorption of both pesticides with increasing temperature, because of higher aromatic units and pores. The deashing and treatment with organic acids further favoured the exposure of carbon surfaces and made the biochar more porous, hence enhancing sorption capacity.

You et al., in 2020, studied wood-derived biochar effects on the uptake of the insecticide thiamethoxam and its toxic metabolite clothianidin by Chinese chive (*Allium tuberosum*) and their dissipation in agricultural soils. The uptake and bioavailability of thiamethoxam was decreased because of sorption on biochar. Adsorption efficiency of rice husk-derived biochar for chlorpyrifos removal from surface water was assessed. The biochar showed 94.5 ± 5.23% removal of chlorpyrifos, thus proving efficient adsorbent for chlorpyrifos remediation from polluted water (Okoya et al., in 2020).

Recently, coconut-shell modified biochar was used to determine sorption of pesticide diazinon from aqueous solutions. The modifications made to the biochar included carbonisation, thermal activation, phosphoric acid treatment and sodium hydroxide treatment. The diazinon removal was achieved about 98.96% by the acidified biochar at a pH 7. Thermally activated biochar followed by alkalified biochar also showed potential in removing diazinon from aqueous solutions (Baharum et al., 2020).

11.6.3 Fungicides sorption

Fungicides like pyrimethanil, boscalid, metalaxyl, tricyclazole, azoxystrobin and pyraclostrobin have been used in experiments to check their sorption onto various types of biochar.

The effect of red gum (*Eucalyptus* spp.) biochar on the pyrimethanil sorption, a toxic and persistent fungicide, was first reported by Yu et al., in 2010. The biochar, produced at 450 and 850°C, both showed nearly the same sorption capacity for pyrimethanil. In 2013, a study by Sopeña and Bending showed that the addition of biochar derived from Red gum wood (*Eucalyptus dunni*) did not affect the sorption of the fungicide azoxystrobin in soil even at a concentration of 2% w/w (Sopeña and Bending, 2013). Biochar prepared from Wood pellets, macadamia nut shells, and oak/hickory hardwood has been used for sorption study of pyraclostrobin. However, study showed that this fungicide is highly sorbed to soil; hence, addition of biochar did not enhance sorption in any way (Cabrera et al., 2014).

A study on fungicide tricyclazole was performed using biochar derived from alperujo compost, woody debris and rice hull. The study proved the efficiency of the biochars in the sorption of tricyclazole in water-saturated soils as they showed a very high affinity to sorb tricyclazole. The highest adsorption percentage was 90.3% which was given by the biochar produced from alperujo compost and pyrolyzed at

700°C (García-Jaramillo et al., 2015). Mukherjee et al., in 2016 used pine woodchips added to digestate material to produce a biochar for the sorption of pyrimethanil and boscalid. However, the addition of biochar led to a decrease in mineralisation of the fungicides and non-extractable residues formation, further leading to an higher dissipation of pesticides through sequestration in soil.

Olive mill waste have been tried to produce biochar for the sorption of fungicide metalaxyl and results showed great capacity to remove the enantiomers of metalaxyl from water, and immobilise these enantiomers in the soil (Gámiz et al., in 2016). Metalaxyl removal from a silty soil was studied by Parlavecchia et al in 2019, using two biochar producing using grapevine pruning residues, and spruce wood. The fungicide was successfully sorbed onto the biochar, and it was also reported that even a moderate addition of the biochar would increase the ability of the soil to retain the pesticide along with reducing leaching and contamination of natural water bodies and food chains.

11.6.4 Nematicides sorption

The nematicides fenamiphos and cadusafos, were tried for their sorption onto date palm and *Eucalyptus* waste-derived biochars pyrolyzed at 450°C. The absorption these nematicides by tomato seedlings was reported to have decreased by 97% in case of cadusafos and 85% in case of fenamiphos indicating successful sorption of nematods on biochar. The addition of biochar hence, caused an increase in the sorption capacity of the soil, decreased the nematicide bioavailability, as well as reduced the dissipation and uptake of the nematicides by tomato plants (Abdel Ghani et al., 2018).

11.7 Conclusion and future perspective

Hazardous effects of pesticides to the environment and human health have been explored by several scientific literatures. Urgent need of effective pesticides removal for the sustainable growth has given birth to number biochar based adsorption method. Agroindustry is one of the largest industries which have potential to provide huge amount of feedstock material for the production of biochar as an adsorbing material. Current scenario of research is focused on biochar assisted technology development for the pesticides removal at high concentration within limited time. However, though considerable research has been published on it, *in situ* application of this technology for the cleaning up of agriculture field and other areas is very limited. Some of the materials used for biochar production are highly promising but their availability for the large scale application is doubtful. Hence, future research can be focused on use of eco-friendly and simple as well as easily available feedstock material for biochar preparation and its on-field application along with reaction kinetics, thermodynamics, and assessment of positive and negative effects for long term.

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CHAPTER

Bioremediation – the natural solution

12

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12.1 Introduction

Water is treasured resource and its scarcity is often felt in many parts of the world, especially in the dry areas. Though approximately 75% of earth's surface is covered with water, but there is dearth of potable water. The freshwater sources are not equally spread throughout the globe and this makes the problem more acute. The water becomes wastewater after its use and the volume of waste water is quite large. The excessively growing population often faces shortage of clean drinking water and is prone to many water born diseases by consuming polluted water. Plant, humans, and animal kingdom require water for \ biological survival. Millions of people die worldwide due to water borne diseases. Besides drinking, water is required also for household, agriculture, commercial, and industrial activities.

The expansion of industrial activity has resulted contamination of surface and ground water and has affected the water quality. The discharge from industries contains a large number of toxic chemicals, dyes, heavy metals, phenols, etc. Apart from industrial pollutants, the liquid waste is generated by domestic areas, commercial properties, and agricultural sources and contains a variety of emerging contaminants, pharmaceuticals, pesticides, and personal care products. It is termed commonly as municipal wastewater resultant from different sources.

On an average, the water consumption of a person is 90–120 l/day; though the quantity varies from place to place, age, culture, race, etc. Additionally, the availability of water and the minimum level of waste water generation is 20–30 l/day/person (Li et al., 2009). The municipal wastewater is generated from household toilet flashes, bathroom, kitchen discharges, and also from hospitals and commercial places. The grey water contains organic pollutants, suspended solids, pathogens as well as nutrients. In the modern era, emphasis is given not only to the health of human beings but also to the environment and this directs the countries to dispose the wastewater wisely. Wastewater professionals are trying to reuse the stale water for

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irrigation after its treatment as a substitute water source, especially in water scarce areas. The municipal wastewater is highly biodegradable especially for the organic pollutants. The bioremediation in combination with some physical and chemical methods yields the best economic treatment for its discharge into the surface water bodies. The treated water is also reusable. It is highly beneficial as the nutrients present in wastewater reduce the fertilizer consumption. It can also be used as soil conditioner and for energy production.

12.2 Characteristics of municipal wastewater

The municipal wastewater is contaminated water and is not usable but contains 99.9% water and relatively small concentrations of impurities, such as suspended solids and dissolved organic and inorganic impurities (2). Carbohydrate, lignin, fat, soap, synthetic detergent, protein, and their decomposed products, as well as various natural and synthetic organic chemicals are the main contaminants of municipal water. In water-less areas or places with dearth of water, the consumption of water is very low and the sewage water contains large concentrations of organic and inorganic solids and considered as strong water.

12.2.1 Organic impurities

The organic compounds basically come from the living sources of plants, animals and human beings. Synthetic compounds also contribute to a large extent. Animal excreta, sewage water, plant debris and remains after collection of crop, and food wastes are organic in nature. The residuals of paper products, detergents, cosmetics, and personal care products, and various wastes generated from commercial and industrial activities are synthetic organic impurities. These left over products are present in substantial quantity in wastewater. Their main constituents are carbon, hydrogen, oxygen, nitrogen, sulfur, and some trace elements. Microbes present in the wastewater use the dissolved oxygen of water and break down the protein, carbohydrate, and fat molecules of the stale water, but in this process they produce toxic chemicals which lead to odor and pollution. Large volume of these degradable organics contaminates the water bodies, which can decrease the oxygen availability for the marine life, resulting death of fish, rising odors, and overall worsening of the water quality. Some synthetic organic compounds used by agricultural industry, personal care products, etc. do not break down easily and cause additional challenges for treatment. They are toxic to humans and aquatic lives and often are disposed off carelessly in drains and carried by rain water. The polluted water contaminates fish and crops and make them unfit for consumption, thereby, the wastewater contaminates the food chain. The polluted waste water is a threat to the food security. The synthetic organic compounds used in personal care products, pesticides, and insecticides even lower the effectiveness of the treatment processes and set challenges to the treatment processes.

12.2.2 Solids

The household wastewater carries nearly 50 percent organic solids, originated mostly from dead animal matters, plant tissues or microorganisms, and some are manmade organics. The major contents in domestic wastewater are proteins, carbohydrates, and fats and these compounds are degradable by bacteria, yeast, and other living organisms. They are combustible. The organic solids are mostly volatile compared to their inorganic counterparts who are inert and by and large nondegradable. Sulphates and some other salts are exceptions to this trait, which can be broken down under specific conditions. Sand, gravel, and mineral salts are the inorganic parts, which generate the hardness and mineral content of water. They are nonflammable.

The presence of organic and inorganic solids gives wastewater the properties known as its "strength". The concentration of the organic solids and their degradation capacity is the key factor of their strength. The higher concentration of organic or volatile solids makes the wastewater strong. The total solid content of strong water is around 1200 mg L^{-1} (3). Solids are classified based on their physical states such as suspended solids, colloidal solids or dissolved solids. Suspended solids are nearly 70 percent organic matters and can be eliminated by sedimentation or filtration process. The suspended solids are floating particles of sand, grit, clay, fecal solids, paper, wood, parts of food and garbage, and like materials. The inorganic parts are sand and grit.

The suspended solids of larger size and weight settle after a given period of time and known as settable. They are nearly 75% organic matters. Colloids are in between the above two and generally do not settle. Nearly 65 percent of the colloids are organic and fast perishing so they are the vital factor for treatment and disposal of wastewater.

Total solids are the sum of the suspended and dissolved solids. The average domestic wastewater has approximately 50% organic and another 50% inorganic solids, and about two-thirds are dissolved and one-third exists in suspension. The level of total solids in wastewater is in the range of 350–1200 mg L^{-1} and has a chemical oxygen demand (COD) of 250–1000 mg L^{-1} (Warwick et al., 2013). Treatment of this water is required to reduce the content of total solids, COD, and biochemical oxygen demand (BOD) and other impurities and pathogens to the nontoxic level as set by the environmental authorities.

12.2.3 Nutrients

The nutrients present in wastewater are basically nitrogen and phosphorus. They are useful for plants but higher concentration leads to the depletion of water quality parameters. So, they need to be regulated carefully.

12.2.3.1 Phosphorus

The main sources of phosphorus in municipal wastewater are the excreta and detergents containing wastewater released from households. Phosphorus is present in surface water in various forms of compounds. It is an essential element of all living creatures. Phosphates are roughly 63% of the dissolved solids in wastewater and supports algal growth

(Parsons and Smith, April 2008). In natural ecosystem, the phosphorus concentration in water is balanced. When phosphorus is present in higher concentration, it promotes algal growth and reduces the dissolved oxygen level of water.

More than 95% of phosphorus is found as inorganic phosphates and the household discharges is the chief source in densely populated regions. The phosphorus found in the excretion as undigested mineral calcium phosphates. The domestic sources vary from 75–85% of total phosphorous. Urbanization and industrial development change the proportion of phosphorous in wastewater and the concentration varies between 7–15 mg/L (Kumar et al., 1998).

12.2.3.2 Nitrogen

Nitrogen mixes with water by the discharges of municipal, industrial, and agriculture wastewater. Ammonia, nitrite, nitrate, and organic nitrogen are the different forms of nitrogen. Organic nitrogen is decomposed into ammonia, which helps in bacterial growth and also oxidizes to some extent to nitrite and nitrate. Finally, nitrate is converted to gaseous nitrogen and is released (Sotirakou et al., 1999). The fresh municipal wastewater contains nearly 60% organic nitrogen and 40% in ammonia form, but biodegradation enhances the ammonia content in the decayed wastewater. The residual water from animal farming contains high quantity of ammonia nitrogen. Nitrogen in domestic wastewater generates from feces and urine (Vinnerås et al., 2003).

Nitrogen is mainly found as urea (80%), ammonia (7%), and creatine (6%) and others are free amino acids or shorter peptides (Guyton, 1992). The enzyme transforms the urea into ammonia and carbon dioxide. Pharmaceuticals and their metabolites are also released through urine. 50% of the fecal nitrogen is water-soluble. Concentration of heavy metals in urine is low and they are found in excreta. Pathogens like, bacteria, viruses and parasites, hormones, and pharmaceuticals also exist in feces.

12.2.3.3 Nitrogen present in municipal wastewater treatment plants (WWTPS)

Nitrogen exists in -3 oxidation state in ammonia whereas in nitrate, it is +5, activities of living organism changes from one oxidation state to another. The most common forms of nitrogen in wastewaters are organic, ammonium and nitrate nitrogen which requires treatment.

Removal of all forms of nitrogen can be attained economically by biological processes. Bacterial decomposition converts organic nitrogen to the ammonium form. Biological treatments also promote bacterial growth. The remaining assimilated nitrogen can be removed from the system or wasted as biological sludge. Free ammonia in the range of 0.1–10 mg-NH_3/L can poison fish. Since nitrates can lead to methemoglobinemia (blue baby syndrome) and gastric carcinoma, their concentrations are also strictly restricted.

12.2.4 Effects of phosphorus and nitrogen on environment

The nitrogen and phosphorus enriched water bodies cause massive growth of algae and plants as they act as fertilizers. They accumulate organic matters and gradually

degrades the water quality (Camargo et al., 2016). But, this growth is limited in natural water bodies. Eutrophication is caused by the excessive release of these nutrients in municipal waste water (Von Sperling and de Lemos Chernicharo, 2005, Wei et al., 2008). Continuous inflow of ammonia is the root of following complications,

1. Hydrophyte and algae will grow in large numbers and cover the water surface
2. Then they will disturb in breathing of aquatic animals
3. Toxins will be produced and that will be leading to the fish poisoning, odour etc.

The intensive animal farming also poses animal waste disposal problem and ultimately leads to eutrophication (Yoshida et al., 2008). It is a serious environmental concern in the developed countries.

The presence of nitrogen in a wastewater is also not desirable as the nitrate ion is a potential public health hazard. In order to minimize the environmental problems, nitrogen removal from the wastewaters is essential. Biological methods of nitrogen removal are widely accepted. Removal of ammonium nitrogen under aerobic conditions is well established, however its removal under anaerobic conditions is in developing stage.

12.2.5 Pathogens

Humans and animals excrete pathogen through their stool and when mixes with water, causes various diseases. Some common disease causing pathogens are listed in Table 12.1. Entero viruses cause ailments of the center nervous system, skin, and heart. The hepatitis A virus is particularly virulent. The symptoms of the

Table 12.1 List of common pathogens present in faeces.

Pathogen Group	Diseases caused
Virus	
Adenoviruses	Respiratory, eye infections
Caliciviruses	Diarrhea
Hepatitis A virus	Infection hepatitis
Polio viruses	Aseptic meningitis, poliomyelitis
Echoviruses	Aseptic meningitis, diarrhea, respiratory, eye infections
Bacterium	
Salmonella typhi	Typhoid fever
Vibrio cholerae	Cholera
Salmonella paratyphi	Gastroenteritis
Protozoan	
Giardia lamblia	Diarrhea
Entamoeba histolytica	Amoebic dysentery

diseases are loss of appetite, fatigue, nausea, and pain. Bacteria are microscopic single-cells plants capable of self-reproduction. The human feces contain the following groups of bacteria: enterobateria, enterococci, lactobacilli, clostridia, bacterioides, bifidobacteria, and eudacteria E. coli. For many bacterial infections of the intestines, the major symptom is diarrhea. The most serious waterborne bacterial diseases are typhoid fever caused by salmonella typhicholera (Vibrio cholera), and bacillary dysentery. Kazmi et al. (Kazmi et al., 2008) investigated for total and fecal coilform elimination from municipal wastewater in the northern parts of India by activated sludge process. The total coilform is due to the presence of bacretial pathogen and fecal coilform is combination of bacterial pathogen and enteric viruses. Though the activated sludge process could remove both of them significantly but was unfit for irrigation. Further study revealed that the total solid content, suspended solids, BOD, and coilform were interlinked and the removal of suspended solids were related with the level of pathogen and it can serve as a standard for the coilforms. They suggested that extended aeration with high retention time was better for high level of suspended solid bearing wastewater (Kazmi et al., 2008). Pant and Mittal studied the pathogenicity of treated water from a upflow anaerobic sludge blanket (UASB) based sewage treatment plant near Delhi and found that the presence of pathogens were much higher than the prescribed limits. They monitored the existence of Salmonella, Shigella, and Vibrio pathogens and found that they were originated from human sources. Their density in treated water was 4.5×10^5 MPN/100 ml which was much higher than the prescribed limit of 1000 MPN/100 ml (Pant and Mittal, 2007).

12.3 Wastewater treatment

It is understood that the stale water requites treatment for the environmental protection and reuse of the scare resource. Physical, chemical, thermal, and biological methods are utilized to purify the sewage and to eliminate the contaminants to make it reusable. The methods are applied separately or in combination of two or three together.

12.3.1 Physical treatment

The physical treatment is importantly filtration of solid-liquid mixture. Wastewater is allowed to pass through screens to arrest the bigger sized objects like, leaves, plastics, and other impurities. A number of physical operations, such as flow equalization, sedimentation, flotation, filtration, etc. are carried out in series to remove the contaminants and make the water clean. Soil filters can eliminate organic pollutants, phosphorus, and microorganisms to some extent (Li et al., 2009). Ward (2000) used only physical separation methods to treat municipal wastewater and was able to reduce biochemical oxygen demand and turbidity (Ward, 2000). Researchers tried ultrafiltration, nanofiltration methods also to treat the grey water.

12.3.2 Chemical treatment

Chemical treatments are carried out basically to disinfect the wastewater and are done in combination of physical and biological processes. Chemical precipitation, adsorption, disinfection, dechlorination electrocoagulation, coagulation, and photo catalytic oxidation are some of the processes applied to municipal waste water to make it reusable. In this process, chemicals from outside source are added to react with the toxic elements or to disinfect and then to eliminate by physical separation techniques. Researchers attempted coagulation and magnetic ion exchange resin process for grey water management. Coagulation with aluminum salt helped to reduce the chemical and bio-chemical oxygen demand and turbidity (Pidou et al., 2008). Combination of coagulation, sand filter and granular activated carbon, and advanced oxidation processes were applied successfully by water process scientists (Šostar-Turk et al., 2005, Parsons, 2004). Chemical treatment alone can deal with low strength water.

12.3.3 Thermal treatment

This treatment is applied primarily to sterilize the drinking water from the infecting pathogens and to produce high quality water. It is often used to disinfect the sludge from the organic contaminants and also drying up the sludge to reduce the volume.

12.3.4 Bioremediation

Biological processes are less harmful as compared to the physical and chemical processes to the environment and almost no sludge is produced. Here, naturally occurring materials, such as microorganisms, particularly bacteria, algae, and fungi are applied to break down the colloidal and carbonaceous organic mattes into various gases into the cell tissues. It is cheap and environmental friendly process. The robust growth of the microorganisms in natural biological medium helps the process without much outside intervention. Biological processes are often employed along with physical and chemical processes, for effective reduction of the organic content (biochemical oxygen demand, total organic carbon, or chemical oxygen demand) and nutrient content (N and P) of wastewater. Different natural biological methods, such as such as constructed wetland, sand filters, land treatment, and waste stabilization ponds are in common applications. In aquatic treatment different plants such as water hyacinth, duckweed, pond weed, and hydrilla plays the role for the treatment of wastewater.

The technique includes aerobic processes, anoxic processes, anaerobic processes, combined process, and pond processes. Rotating biological contractor (RBC), sequencing batch reactor (SBR), UASB, and membrane bioreactor (MBR) are some of the methods applied by water researchers for grey water treatment. The practices are helpful to reach the target. Sometimes a combination of biological process along with physical or chemical methods yield the better result (Elmitwalli and Otterpohl, 2007, Hernandez-Ramirez and Holmes, 2008). Complex membrane bioreactor reactor was achieved in combination with an aerobic tank, an anoxic tank and a sealed

membrane tank by Liu et al. for superb waste water management (Liu et al., 2005, Nolde, 2000). The biological processes may be broadly divided into two categories, aerobic, and anaerobic treatment.

12.3.4.1 Aerobic treatment

This is a conventional method for treatment of municipal wastewater. In this method oxygen through air is used continuously to breakdown the organic matter, reduce pathogens, and alter the nutrients (P and N) from the wastewater. The aerobic bacteria decompose the solids in presence of air and compared to the conventional septic tanks, it is more effective method for faster decaying of organic solids and pathogens. The treated water is pure and regeneration of microbial are mostly omitted and make the water suitable for storage for a longer time without occurrence of odor. However, this method is mostly suitable for low strength wastewater. Though this is a widely used method, but large quantity of sludge is produced and operational cost is high. These drawbacks are directing people towards anaerobic treatments.

12.3.4.2 Anaerobic treatment

Considerable amount of research have been carried out for sewage treatment in anaerobic method since 1980. This treatment facility requires less initial investment, less operating cost as compared to the aerobic process, and also produces less sludge. In this technique, no air is supplied from outside. Controlled anaerobic conversions of the organic pollutants produce carbon dioxide and methane in absence of air. Anaerobic treatment processes can handle very high loading rates (10 to 20 times of conventional activated sludge treatment) and less retention time. Moreover, the methane produced in the process can be utilized as energy source (bio gas). Anaerobic treatment of domestic wastewater is cost-effective and the investment has a normal pay-back period of 2 years. This method provides a potential solution for municipal wastewater treatment in a reliable and sustainable way. In anaerobic digestion process, a colony of bacteria decomposes natural polymers, proteins, lipids, etc. This process is especially active in warm climate and very helpful for removal of organic pollutants.

Anaerobic lagoons, UASB reactors, RBC, anaerobic filter, FBR, SBR, hybrid systems, and expanded granular sludge bed systems (EGSB) are some examples of anaerobic treatment methods. Among these, UASB reactors are very popular. The reactor works excellent for removal of organic impurities and total suspended solids but not so effective in case of pathogens and nutrients (Cavalcanti et al., 2001). The UASB digester is discussed in detail below.

12.3.5 Up flow anaerobic sludge blanket (UASB) reactors

Low initial cost, smaller amount of space requirement, higher quantity of organic pollutant removal capacity with lower amount of sludge generation and less operational cost, etc. are making these reactors popular nowadays (Mungray et al., 2010). In this reactor, the influent liquid at the bottom of the reactor is evenly distributed and then allowed to pass through the reactor filled with the biological sludge. When

the wastewater comes in intimate contact with the sludge, the toxic organic pollutants and the suspended solids are retained in the sludge bed. The clear water passes out. Special care are taken to trap the carried over solid particle by allowing suitable settling time, so that clear water comes out from the top of the reactor. In the reactor, mechanical agitation is not allowed much, so that the sludge settling is not disturbed. Moreover, the anaerobic sludge is immobilized to exhibit granulation properties. The anaerobic microbes are self-immobilized in the granules and the performance of the UASB depends highly on the properties of granulation. Due to high performance, over 900 reactors are in operation so far worldwide (Lettinga and Hulshoff Pol., 1991, Yu et al., 2002). A review of performances of some UASB based waste treatment plants are presented in Table 12.2. It may be seen from Table 12.2 that average BOD, COD and TSS removal was 50–75% , 52–74%, and 51–75% respectively.

12.4 Post-treatment options

The anaerobic digesters are excellent in removal of organic pollutants but the nitrogen, phosphorous, and pathogens are not completely removed. So, the water coming out from these reactor, often require further treatment to comply to the standard discharging norms for all the water quality parameters set by the environmental regulatory authorities (Table 12.3). After the post treatment, the water becomes fit for reuse in agricultural field or may be suitable for discharging in to the surface water bodies. A good number of studies are available to measure the pathogenicity of the discharge water from the UASB reactors. Pant and Mittal conducted a study in 2007 to monitor the presence of pathogens, viz., Salmonella, Shigella, and Vibrio in the treated effluent of a Delhipbased UASB reactors. The pathogens were present at a higher percentage than the prescribed limits. The performance of the plant was low as compared to the activated sludge plants in terms of pathogen removal. Post treatments were required to make the water safe (Pant and Mittal, 2007). A good number of choices are available for the post treatment of the outflow water from the UASB digester (Cavalcanti et al., 2001, Tawfi k et al., 2006) and are listed in Table 12.4.

12.4.1 Polishing ponds

Effluents from anaerobic treatment are further treated in polishing ponds for up gradation of its quality and maintain the required standard. This method is applied for reduction of TSS and organic matters, thereby increases the hygienic quality and makes the water clean. It depletes the pathogen. The main advantages of polishing ponds are that it can remove the pathogen and make the water useable for irrigation purpose. It removes the odor also. The performance of the pond is measured by the two indicators, viz., helminthes eggs and fecal coli forms. The final water quality is a function of retention time. It works better in combination up-flow anaerobic sludge blanket reactors (UASB). TSS, E-coli, and ammonia can effectively be removed within in a time span of 1 week. The water can safely be used for agriculture purpose (Keller et al., 2004).

Table 12.2 Performance of some UASB treatment Plants.

Location of the plant	BOD_5, mg/L			COD, mg/L			TSS, mg/L			Operating Temp, °C	Reference
	In	Out	% Removal	In	Out	% Removal	In	Out	% Removal		
India	214	53	75%	563	146	74%	418	105	75%	20–30	(Draaijer et al., 1992)
Colombia	160	46	71% (average)	380	70	52.5% (average)	240	96	60%	24	(Schellinkhout and Osorio, 1994)
India	484	184	62% (average)	1183	509	57% (average)	1000	450	55% (average)	18–32	(Haskoning 1996, Tare et al., 1997)
Brazil	313	85	73%	549	137	75%	196	96	51%	30.8	(Kato et al., 2003)
India	398	197	50%	838	402	52%	846	372	56%	-	(Tare et al., 2003)

Table 12.3 Effluent discharge standards in India (35).

Parameters	Standard (mg L^{-1})		
	Inland surface water	Public sewers	Land for irrigations
Suspended solids , Max	100	600	200
pH value	5.5 – 9.0	5.5 – 9.0	5.5–9.0
Temperature °C, max	40	45	–
Oil and Grease	10	20	10
N as Ammonical nitrogen, max	50	50	–
N as Total Kjeldahl nitrogen, max	100	—	–
Free ammonia, max	5	—	–
P as Dissolved phosphates, max.	5.0	-	-
BOD_5 at 20° C), max	30	350	100
COD, max	250	–	–
Pathogens (MPN/100 ml)	10,000		

12.4.2 Overland flow system

It is one of the cost effective and excellent land treatment facilities to achieve the required water quality. It requires minimum efforts of operation and maintenance. Wastewater is allowed to flow at a controlled rate over the impermeable soil with slope covered with grass. The hydraulic loading is several inches of liquid per week and is more cost effective than slow rate process to maintain the same water quality. Perennial grass on the top soil is the necessary component for treatment and acts as a filter to eliminate the nutrients and withholding and transforming the organic matters.

Table 12.4 Remedial actions available after UASB reactor.

Method for post treatment	Reference
Polishing ponds	(Pant and Mittal, 2007, Sato et al., 2006, Mahmoud, 2002, Seghezzo et al., 1998)
Over land flow process	(Chernicharo, 2006, Chernicharo et al., 2001)
Submerged aerated bio filter	(Goncalves et al., 1999)
Trickling Filter	(Chernicharo and Nascimento, 2001)
Aerated Filter	(Chernicharo and Machado, 1998)
Dissolved Air Floatation	(Reali et al., 2001, Penetra et al., 1999, Manjunath et al., 2000)
Activated Sludge Process	(Tawfi k et al., 2008)
Constructed Wetland	(El-Khateeb et al., 2009, Wendland et al., 2006, Kivaisi, 2001)
Aerated Lagoons	(Nameche and Vasel, 1998)
Down flow hanging Sponge	(Gasi et al., 1991, Uemura et al., 2002, Tandukar et al., 2007, Tandukar et al., 2006, Tawfi k et al., 2006, Farooq and Al-Yousef, 1993)

Organic materials and solids are eradicated by biological oxidation, sedimentation, and filtration. While the wastewater flows down the inclined field, it is collected in the ditches and finally mixes with the surface water. In this method, the evaporation or deep percolation loss of water is very less (Von Sperling and de Lemos Chernicharo, 2005). In combination with UASB, the overland flow system removes the helminthes eggs efficiently to a final count of 0.2 eggs per liter in the treated water. The water quality upgrades after this post treatment.

12.4.3 Submerged aerated bio filter

A submerged aerated bio filter is a post treatment facility of UASB reactors. Some porous material is filled in a tank and sewage water and air flows through it. The porous medium goes under the water by the hydraulic flow. The bio filters are three-phase reactor in which the mechanical support and the microorganisms present in form of biofilm are considered as solid phase while the effluent liquid and air and bio gases produced are the as the other two phases.

A team of researchers demonstrated that UASB in combination with submerged aerated bio-filter systems can sustain stable operational conditions regardless influent load disparity and reuse the aerobic sludge generated from the bio filter (Lesjean and Gnirss, 2006).

12.4.4 Trickling filter

It is another potential wastewater treatment facility in which a tank is filled with highly permeable materials, such as rock, sand etc., and the effluent water allows to down flow in form of drops or jets. This allows bacterial growth in form of bio films over the packed materials in the tank. When the dirty water passes over the bio film, the microorganisms grown over the bio film comes in contact with the organic matters in water and digested. This association of UASB and trickling filter is a simple treatment process with low operational and low energy cost (Chernicharo and Nascimento, 2001).

12.4.5 Anaerobic filter

Anaerobic filters are getting popularity over the aerobic digesters for treatment of municipal wastewater as they produce fewer residues. The anaerobic microorganisms grow with in the filter and live without oxygen. They can take care of both high and low strength wastewater. The use of anaerobic filters in association with UASB reactors are exercised in bigger cities nowadays (Cavalcanti et al., 2001).When the sewage is fed to the filter the particulate solids are retained in the filter bed and bio films form on the packing and helps in accumulation of the residual organic solids. This method consumes less power and has low running cost.

12.4.6 Dissolved air flotation

This is a new compact and high quality technique for management of effluents from anaerobic digester by batch floatation technique. It can manage chemical oxygen

demand, total suspended solids and phosphorous very efficiently, but other components, like nitrogen, ammonia, and pathogen removal is insignificant (Penetra et al., 1999, Manjunath et al., 2000).

12.4.7 Activated sludge process

This is a widely used and highly efficient method to clean up the industrial as well as municipal wastewater. Flocculation is carried out by aeration through the primary treated sewage. This depletes the organic content effectively and reduces nutrients and the chemical oxygen demand of the effluent.

12.4.8 Aerated lagoons

It is a simple and efficient method for sewage and industrial wastewater treatment. Here, oxygen is supplied to the sewage by mechanical means in addition to the oxygen produced by the algae. It is in between the oxidation pond and the activated sludge process. Power and land requirement is not much and minimum civil works are required.

12.4.9 Down flow hanging Sponge

This type of reactor is used for the post treatment of UASB effluent in aerobic condition to meet up the standard wastewater discharge norms. The method was invented in Japan by a group of researchers (Uemura et al., 2002). The polyurethane foam cubes are applied to arrest the BOD and microorganisms present in water. The retention time was low. Some researchers commented that oxygen from outside was not required as the air coming in with the effluent water was sufficient for oxidation and BOD removal. Though the process has similarity with trickling filter, but the performance is very high and 90% of BOD could be removed (Cavalcanti et al., 2001).

12.4.10 Bio filter

Bio filters in combination with UASB digesters perform well for domestic sewage treatment. The biomass that grows on the filter media is very effective in elimination of organic pollutants. This bio film oxidizes the organics and uses this as a source of energy and carbon for the reproduction of microbes. The technique is capable of reducing the quantum of organic, microorganisms, taste, and odor of the waste water. Diverse nature of microbes grows and performs differently in different working conditions and thus affects the performance of the bio filters and it is difficult to generalize its activity. It can be applied for both primary and secondary treatment of wastewater. When the amount of wastewater is small, treatment can be accomplished in a single tank and can be applied on site foe domestic or industrial applications (Chaudhary et al., 2003). The functioning of some bio filters of different sizes is presented in Table 12.5. It may be seen from the Table 12.5 that the

Table 12.5 Functioning of bio filters of different sizes.

Bio filter size, m	Primary treated Sewage (mg/L)				Final Outflow (mg/L)				Reference
	Alkalinity	Ammonia Nitrogen	BOD_5	Suspended Solid	Alkalinity	Ammonia Nitrogen	BOD_5	Suspended Solid	
16	142	19.1	108	84	9	<2.2	11	36	(Cleasby et al., 1984)
26	300	22.5	136	118	120	<2.3	6.3	20	
6	165	23.5	146	126	79	14.6	24	45	
22	240	15.7	72	77	100	<2.0	7.2	17.5	
102 x 16.8	171	17.4	130	102	73	<2.5	14	30	

Table 12.6 Comparison of biological processes for wastewater treatment.

Treatment method	COD (mg L^{-1}) In Out	BOD (mg L^{-1}) In Out	Total Nitrogen (mg L^{-1}) In Out	Total Phosphorus (mg L^{-1}) In Out	References
Sedimentation +RBC+ UV disinfection	100–430 -	50–250 <5	5–10 -	0.2–0.6 -	[23]
FBR+UV disinfection	113–633 -	70–300 <5	- -	- -	[23]
MBR	130–322 18	99–221 <5	- -	- -	[22]
MBR	493 24	- -	21 10	7.4 3.5	[28]
MBR	109 15	59 4	15.2 5.7	1.6 1.3	[29]
UASB	681 469.9	- -	27.1 20.6	9.9 7.5	[20]
SBR	827 100	- -	29.9 26.5	8.5 5.8	[21]

bio filter is very effective in removing alkalinity, BOD_5 and ammonia-N. Average removal efficiency was nearly 65–75% for all the parameters for strong water.

12.5 Comparison of various biological treatment processes

Various UASB and their post-treatment unit effluent concentrations are presented in Table 12.6 for some important parameters like COD, BOD, total Nitrogen, total Phosphorous and their average removal efficiency. It is clear from Table 12.6 that almost all the effluents follow the discharge standards limits. Post treatment steps are used to satisfy the standard discharge limits in surface waters. After the post treatment steps at every combination, all the parameters are below the standard limits for discharging except pathogens which is slightly higher at almost everywhere. For pathogen exclusion, often UASB digester in combination with polishing pond found effective. About 98% fecal coliform was eliminated in UASB combined with down flow hanging sponge reactor. In UASB-Activated sludge combined reactor, 94–95% total and fecal coliform could be taken away.

12.6 Sand filter for the post treatment

This is the last treatment process where the secondary water is converted in to portable water. And here normally various type membrane separation and sand filtration is use. Sand filters are very effective for cost reduction compared to the membrane. It may be used for pre-treatment or post treatment purpose. Biological slow sand filters are very efficient in removing nitrogen, microorganisms present in water. The various types of slow sand filters are listed in Table 12.7.

Table 12.7 Slow sand filtration.

Wasre water type	Effective size of sand (mm)	Flow rate (L/h)	Filtration rate (m/h)	Turbidity removal%	Suspended solid removal%	COD removal%	BOD removal%	Bacteria TC&FC removal%	Reference
	0.32	0.3		97				99	(Cleasby et al., 1984)
	0.29							97	
Secondery effluents	0.3				90		65	97	
	0.6								
	0.23						86	96	
UASB effluent	0.43	1.0	0.14	91.6	89.1	77	85	99.95	(Tyagi et al., 2009)
		1.5	1.9						
		2.0	0.26						
Municipal	1–2		0.25						(Zheng et al., 2009)
Domestic	0.1–0.3		0.1–0.3						
Secondary chloride effluent	0.31					50–67	79–92	90	(Farooq and Al-Yousef, 1993)
	0.56								
Waste water	0.3		0.15–0.38		21.8–43.4	33.4–40.4	76.5–83.4		(Nakhla and Farooq, 2003)
	0.5				49.6–71	11.7–35	33.4–65.4		

12.7 Conclusion

Biological treatment has proved its efficiency in treatment of domestic as well as industrial wastewater. Both aerobic and anaerobic digesters are useful after primary sedimentation process. UASB digester is widely used for sewage treatment due to its reliability, cost effectiveness and diverse advantages. However, UASB reactor alone cannot eliminate organics, pathogen and coliforms to the desired levels. To achieve the wastewater discharge standards, post treatment after UASB digester is required. Many options are available for post treatment. UASB followed by aerobic biological treatment is very effective method to remove organics, nitrogen, phosphorous and pathogens.

However, there is still demand for simple, cost-effective technology for sewage treatment in developing countries which would deploy less sophisticated equipment, less land requirement, maintenance free and low capital and operational cost. A combination UASB and post operative treatment, such as trickling filter, activated sludge method or use of bio filter is often found suitable. Considering all factors, bioremediation is becoming a popular process because of its simplicity, cost-effectiveness, efficiency, ecofriendliness, and reusability.

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CHAPTER

13 Detection and removal of pathogenic bacteria from wastewater using various nanoparticles

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13.1 Presence of different contaminants in wastewater

Human activity generates vast amount of contaminated water or wastewater. It includes substances such as human excreta, food scraps, chemicals, microbes, oils, detergents, etc. It also includes rain runoff water containing harmful leaching from washes of roads, irrigation fields, roofs, and buildings and takes into water bodies. The dilution of sewage by rain runoff has only minor impact on the wastewater (Elliott, 2003). The type of contaminant present in wastewater is dependent upon the point and non-point sources of wastewater. Point sources contribute directly whereas non-point sources contribute by slow diffusion or with the help of other carrier sources. Point source contamination occurs by an identified source, which controls the flow and helps us in knowing the major contaminants in it. The effect of this type of contaminant is local to the point of discharge such as thermal plants wastewater contamination, oils and chemicals spills, etc. In non-point sources such as groundwater, the contaminants cannot be traced to a single point, and it is rather more diffused type. Groundwater though, looks clean and clear as the ground itself filters out the particulate matter but natural and human-induced chemicals contaminate groundwater (Elliott and Hemingway, 2002, Tran et al., 2019).

The wastewater of industrial, domestic, and municipal origin pollutes the environment. A large number of contaminants are detected in wastewater treatment plants (Stuart et al., 2014). They are primarily originated from household, pharmaceutical,

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cosmetic productions and so on. Even after treatment, various contaminants are present in the effluent in different concentrations ranging from nanograms to several hundred micrograms per liter (Li et al., 2018). Examples of contaminants in wastewater are estrogens, quaternary ammonium compounds, and chlorinated organic compounds (Ting and Praveena, 2017, Liu et al., 2015, Zhang et al., 2015, Krzmarzick and Novak, 2014). A monomer of melamine resin which acts as a cross-linker called hexamethoxymethylmelamine (HMMM) is a contaminant in wastewater. The presence of the monomer in municipal wastewater is not known to many despite its extensive use in different fields (Alhelou et al., 2019). Coatings and plastics for automobiles, cans and coils use HMMM (Rink, 2008). The contaminants in wastewater also damage the groundwater quality through surface run-off as well as leakage from sewage treatment plants. Influents and effluents of wastewater are considered as the main sources of Contaminants of Emerging Concern (CECs) across the globe (Benotti et al., 2009, Lapworth et al., 2012). Carbamazepine, nicotine and estrogenic compounds along with their metabolites may also pose as contaminants of wastewater (Ekpeghere et al., 2018). The environment and human health are greatly affected by the presence of these toxic compounds in wastewater along with quality of aquatic environment (Li et al., 2015 Sep, Padhye et al., 2014, Clara et al., 2005). Microplastics found in the cosmetic products leach to wastewater and cause great loss to the ecosystems (Prata, 2018). In wastewater treatment plants, most of the contaminating microplastics are taken out, but a fraction of it remains in the solid part that may act as the potential pollutants of terrestrial ecosystems when employed as fertilizer. However, some also continue to remain in the final sewage contaminating aquatic ecosystems. The contamination of microplastic can be minimized by source reduction (Prata, 2018).

13.2 Pathogenic bacterial component in wastewater

Wastewater of different sources comprises pathogenic microorganisms of bacteria, fungi, virus, or protozoa type. The wastewater discharged from hospitals is very hazardous to public health and ecological balance since it contains radioactive, chemical, pharmaceutical waste and pathogenic bacteria including antibiotic-resistant bacteria (Moges et al., 2014). The wastes of pharmaceutical industries are major contributor of antibiotic resistant bacteria (ARB) and antibiotic resistance genes (ARGs) (Ezeuko et al., 2021). The wastewater treatment plants (WWTPs) and their effluents contain ARB/ARGs due to inadequate treatment of sewage, agricultural, hospitals and pharmaceuticals wastes (Fig. 13.1). As wastewater has high nutrient load, pathogens can thrive there very successfully increasing risk of infection. Further, wastewater carries toxins as byproducts of the pathogenic bacteria. Endotoxins are a portion of outer membrane of Gram-negative bacteria. Response to endotoxin varies with dose, site, route, and rapid release in the blood system. The low dose of endotoxins can cause serious effects such as alteration in body temperature, metabolism, hematopoiesis, immune, and endocrine systems. The toxins go through biomagnification and gets

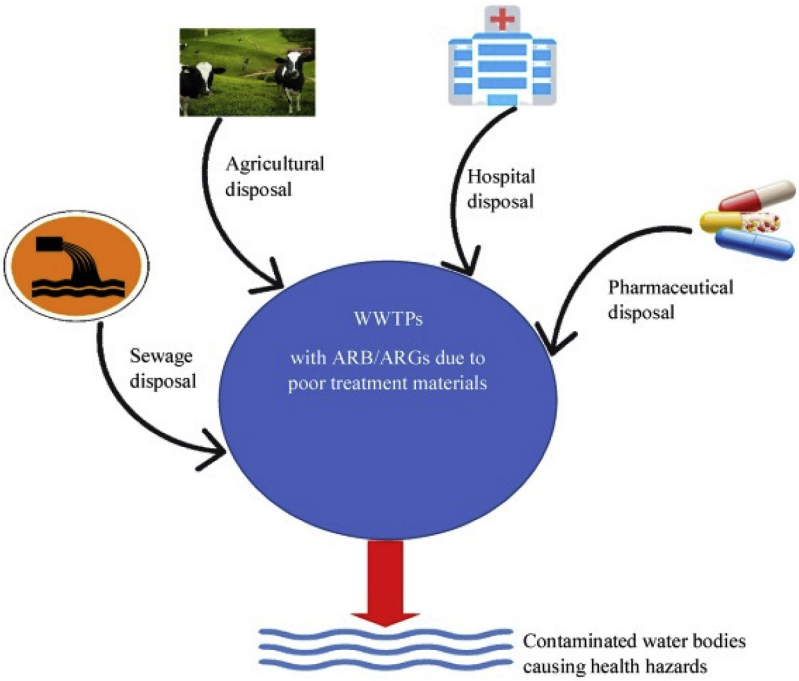

FIG. 13.1 Health hazards due to contaminated water bodies with antibiotic-resistant bacteria/genes.

(Figure adapted, with permission, from Ezeuko et al., 2021 © 2021 Elsevier Ltd.)

accumulated in higher tropic levels. The dairy industry wastewater is rich in nutrient and hence support growth of microorganisms. Casein forms sludge supporting anaerobic growth of bacteria. Lactose present in the wastewater supports growth of filamentous bacteria known as sewage fungus, which indicates higher level of lactose in the environment (Kolev Slavov, 2017). Similarly, other food processing industries discharge nutrient-rich effluent like from brewery industries.

Pathogenic bacterial components are predominant in wastewater and may result in severe health and environmental hazard (Cyprowski et al., 2018). Wastewater includes bacterial species acting as pathogens like *Escherichia coli*, *Enterobacter cloacae*, *Enterococcus faecalis*, *Klebsiella pneumoniae, Salmonella*, *Shigella*, and *Pseudomonas aeruginosa,* which can cause several systemic infections in people with poor immunity (Cyprowski et al., 2018, Cyprowski et al., 2005, Gerardi and Zimmerman, 2005). A study showed that 18 species of bacteria belong to the genera *Longilinea*, *Georgenia*, *Desulfuromonas*, *Arcobacter* and *Desulforhabdus*occur in the sewage system (Liu et al., 2015). A variety of pathogenic bacterial species are also found in domestic wastewater belonging to the genera *Pseudomonas* and *Lactococcus*. Pharmaceutical wastewater, on the other hand, consists of bacterial communities belonging to the phylum *Synergistetes* (Zhao et al., 2019). The workers of wastewater treatment plants are often exposed to

disease-causing bacteria like *Acinetobacter lwoffii* and *Micrococcus luteus* (Bruni et al., 2020). These opportunistic bacteria cause nosocomial infections in people with weak immunity and cause neonatal sepsis. A group of bacteria belonging to genus *Clostridium* are found in wastewater which can be used as indicators of water pollution (Pillai et al., 1996). The *Clostridium* is causative agents of botulism and tetanus. Few species from *Peptostreptococcus*, *Bifidobacterium.* and *Propionibacterium* genera are abundant in municipal wastewater and act as good indicators of fecal contamination (Ballesté and Blanch, 2011, Wéry et al., 2010). A species *Actinomyces israelii*, found in wastewater is the causative agent of infections in oral, thoracic as well as abdominal cavities (Mabeza and Macfarlane, 2003). *Clostridium perfringens* present in wastewater is another type of pathogenic bacterial component which accounts for the myonecrosis of connective tissues (Stevens and Bryant, 2002). Wastewater remains contaminated even after routine treatment which results in serious damage to human health as well as the environment. Highly efficient detection system with specificity for these harmful microbes is needed. The nanomaterial enabled biosensors are very efficient for the detection of microbes present in wastewater. The biosensors have three major components: nanomaterial, microbe recognition elements, and signal transduction material for monitoring the interactions (Vikesland and Wigginton, 2010) (Fig. 13.2).

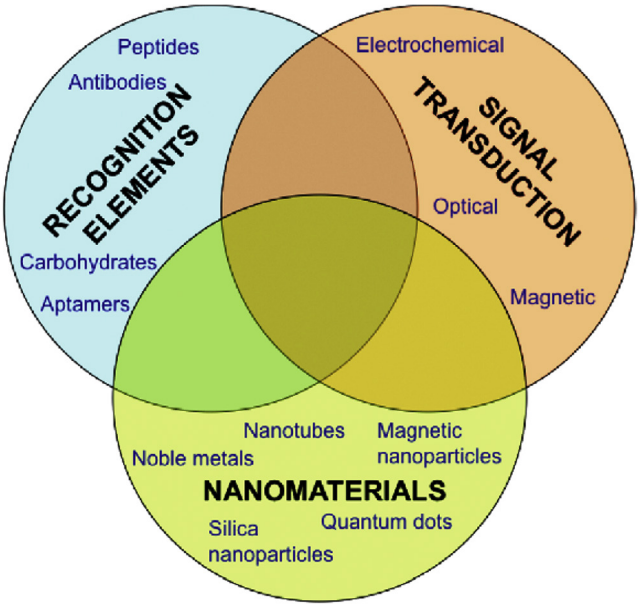

FIG. 13.2 Major components of nanomaterial enabled pathogen detection system.

(Figure adapted, with permission, from Vikesland and Wigginton, 2010 © 2010 American Chemical Society)

13.3 Detection of pathogenic bacteria using different nanoparticles

13.3.1 Nanomaterial enabled with antibodies

Pathogenic microorganisms are plenty around us. Foodborne pathogens and hospital-acquired nosocomial infection are sources of bacterial outbreak. They must be swiftly detected and eradicated. The traditional detection methods are time-consuming and laborious. To overcome this, biomolecule based detection techniques are devised for detection of pathogenic bacteria from water and wastewater. This nanomaterial enabled techniques has advanced to a great extent. The use of nanomaterial enabled biosensors combined with antibodies are beneficial than the traditional assays for detection. In the detection process, biosensors employ biomolecules for recognition which have high binding affinity for bacterial cell surface epitopes (Abdel-Hamid et al., 1999, Campbell and Mutharasan, 2008, Cui et al., 2006, Dou et al., 1997). Nanomaterials enabled with antibodies are extensively used in detecting pathogenic microorganisms. The use of sensitive and immensely selective antibodies is preferred to interfuse with nanomaterial (Ni et al., 1999, Kalele et al., 2006). The process depends on three kinds of antibodies, monoclonal, polyclonal and the engineered fragment antibodies. The monoclonal antibodies arise from identical cell lines and possess monovalent affinity which suggests that they bind to a single epitope on the antigen. On the other hand, polyclonal antibodies arise from different lineages and possess polyvalent binding affinity, i.e. bind to several epitopes on the antigen. The use of polyclonal antibodies is advantageous to some extent as they are resistant to variation in pH and salt concentrations. They are also cheaper than monoclonal antibodies. However, monoclonal antibodies have less probability of cross-reacting than polyclonal antibodies whereas polyclonal antibodies have high chances of non-specific binding (Iqbal et al., 2000, Deshpande, 2012) The engineered fragments of antibodies can also be used for pathogen detection as the specificity of antibodies is kept intact. Disadvantages of the use of nanomaterial enabled with antibodies are chances of nonspecific binding, need to establish physiological pH and temperature, the high sensitivity of the antibodies towards the chemicals present in water, the expenditure on the monoclonal antibody production as well as the short shelf-life period (Jayasena, 1999).

Silver nanoshells are prepared by a chemical process to detect *E. coli* present in water. Silver nanoshells were mixed with antibodies and the shells dispersed in water. The amino groups present in the antibodies help them in conjugating with the silver nanoshells. The nanomaterial interfused with antibodies were centrifuged and then dispersed in water again so that it helps in removing any unbound antibodies, which can be further used for the detection of *E. coli* (Kalele et al., 2006). *Salmonella* contamination in food can be detected using magnetic nanoparticles (MNPs) and TiO_2 nanocrystals (TNs). *Salmonella* causes mild to fatal foodborne disease. The MNPs allows rapid extraction of target bacterium when kept under external magnetic field. TNs in this experiment are tagged with optical nanoprobe used for

spectroscopic detection. The *salmonella* is kept in buffer or milk matrix and is separated using an external magnetic by selectively Antibody immobilized NP based captured (Joo et al., 2012). Improved cytometric process developed by combination of two different colored dyes antibody conjugated RuBpy doped fluorescent silica nanoparticles which appear Red and SYBR Green-I, which color the nucleus green used for the detection of *Mycobacterium tuberculosis*. The RuBpy doped silica NPs are highly luminescent. They label the bacterial cells bright red. The nucleic acid stain SYBR Green-I nullifying the false positive. This method is very sensitive and can assay the organism within a short span of two hours (Qin et al., 2008). The Zhao et al. had focused on three foodborne pathogens *Shigella flexneri, Salmonella typhimurium and E. coli O*157:H7. Magnetic microbeads and quantum dot (QD) capture for fluorescence label the bacterium with fluorescent tag. QDs give out different emission peaks when excited by single wavelength. Also, applying magnetic bead coating can enrich the target bacteria from the samples. Sandwich complexes are formed between bead cell complex and QD-antibody conjugate, then different emission peaks determined and target bacteria are quantified (Zhao et al., 2009). Thus the higher specificity of antibodies for a particular organism makes it more potent for detection. The nanotechnology and antibodies make amazing biosensors for microbial detection.

13.3.2 Nanomaterial enabled with aptamers

Similar to nanomaterial conjugated antibodies, nanomaterial enabled with aptamers are efficient for microbial detection. The aptamers are deoxyribonucleic acid (DNA) or ribonucleic acid (RNA) oligonucleotides which are mainly single-stranded. They are highly selective for binding to target (Arbabi-Ghahroudi et al., 2005). The aptamers can be a beneficial alternative to the antibodies used with the nanomaterial (Reinemann and Strehlitz, 2014), their three-dimensional configuration helps in specifically bind to target organisms when conjugated with nanomaterial. Aptamers offer special features such as small size, flexible structures, small molecule recognition and almost no batch to batch variation. Aptamers can be engineered towards wide variety of targets ranging from protein, drugs, and organic molecules to whole cells and is synthesized with high reproducibility and in unlimited quantities using standard procedures (Vikesland and Wigginton, 2010, Urmann et al., 2017). Also, there is no use of animals or cell lines during production of aptamers (Tombelli et al., 2007). The fluorescence intensity before and after quenching is used to monitor the concentration of targets. Since the aptamers are produced *in vitro*, it can be easily conjugated with nonmaterial for any kind of target pathogen (Vikesland and Wigginton, 2010). One of the greatest drawbacks linked to the use of nanomaterial enabled with aptamers is that their susceptibility to nuclease attack. This is resolved by employment of highly stable aptamers, mirror-image nucleotides, which are stable enough against the nuclease activity. Mirror-image nucleotides can be produced with the unnatural enantiomer L-ribose or L-2'-deoxyribose (Mairal et al., 2008, Klußmann et al., 1996). They also effectively bind to the target organism due to molecular symmetry.

Another way of using nanoparticle-aptamer is the detection of lipopolysaccharide (LPS) present on the outer membrane as in case of is *E. coli*. Ethanolamine is a common compound of core polysaccharide of LPS. Inprobe-1, gold nanoparticle (AuNP) conjugated with ethanolamine specific aptamer to determine the presence of LPS. AuNP is conjugated with *E.coli* Q111:B4 specific aptamer which can recognize LPS of this strain (Zhu et al., 2019). Other studies have shown the development of nanomaterial like quantum dots conjugated with aptamers for the detection of *Bacillus thuringiensis* and *Campylobacter jejuni* (Ikanovic et al., 2007, Bruno et al., 2009). The advancement owing to the use of nanomaterial enabled with aptamers has far-reaching impacts so far. But there is still a huge scope for developing it further to get promising outcomes in the future.

13.3.3 Nanomaterials enabled with carbohydrates

Carbohydrates are one of the most abundant biomolecules. They take part in vital cellular functions like cell growth, cellular modifications, cell- communication, signal transduction etc. Thus, any abnormality in the expression of carbohydrates signifies the association of disease with that organism (Yuzwa et al., 2012, Dube and Bertozzi, 2005). Bacteria, virus, fungi, etc., often target their host through the carbohydrates present in the outer layer of the cell as an anchoring agent to infect. Thus, anchoring mechanisms can be exploited for detection of pathogens. Many pathogens recognize and bind to specific carbohydrate in the glycocalyx that can be exploited for microbial detection. Due to these interactions, carbohydrates may be used as receptors for the detection of pathogenic microorganisms (Haseley, 2002). Carbohydrates do not lose their activity upon changes in temperature or pH, because they do not denature, thus advantageous for detection. Also, carbohydrates have broad affinity and specificity for variety of microorganisms and their proteins (Haseley, 2002). Thus, it would enable classification of a wide range of organisms in wastewater samples (Vikesland and Wigginton, 2010, El-Boubbou et al., 2007).

Magnetic-glyco nanoparticles are employed for detection of pathogens. In an experiment, pathogenic *E. coli* ORN178 strain is detected using magnetic-glyco-nanoparticles (MGNPs) (El-Boubbou et al., 2007). Lectins, carbohydrate binding proteins, are oligomeric molecule with multiple glycon-binding sites. Also, fimbriae or pili of bacteria facilitate the adhesion to glycosylated surface of the host. Glycosylated NPs and Glyco-MNPs can be applied for detection of bacteria (El-Boubbou et al., 2007, Liu et al., 2009). Glycosylated gold NPs is used for exploiting the carbohydrate lectin interactions. The demonstration was based on the aggregation of glycosylated gold NPs, which are polymer- stabilized, in response to unlabeled proteins. Rechards et al. tested immobilization of seven sugars and measured their binding to six distinct proteins each with eight different concentrations. They observed the colorimetric changes specifically associated with the aggregation of gold NPs (Richards et al., 2016). Bogdan et al. worked on lectin recognition with carbohydrate coated lanthanide-doped upconverting NPs. They investigated both Ln NPs functionalized with carbohydrates as well as with Poly amidoamine dendrimers. These were applied for the detection of both

P. aeruginosa as well as breast cancer cells (Bogdan et al., 2010). Carbohydrates associated NP derived biosensors are effective for the rapid detection of bacteria, fungus and toxins. They act as biosensors employed in medical and research purposes.

13.4 Conclusion

Microorganisms such as pathogenic bacteria cause variety of water and foodborne diseases even at low concentrations. Despite stringent regulation and water treatment processes, outbreaks of waterborne diseases occur regularly. Colony culture and counting, polymerase chain reaction, and enzyme-linked immune-sorbent assay are the existing strategies based on which bacterial detection are made. Nanomaterial-enabled detection is a promising strategy to monitor pathogen.

Abbreviations

AuNP	Gold nanoparticle
CBM	Carbamazepine
CEC	Contaminants of Emerging Concern
HTP	Human waste treatment plants
HMMM	Hexamethoxymethylmelamine
MNP	Magnetic nanoparticles
NCT	Nicotine
NP	Nanoparticle
QD	Quantum dot

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CHAPTER

14

Application of TiO_2 photocatalysts hybridized with carbonaceous for degradation of pharmaceuticals

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14.1 Introduction

In the past decades, scientific research has been responsible for the discovery and production of several substances. It is estimated that about 300 new materials are synthesized each year (Lee and Park, 2013). These compounds over time present chemical chains that are increasingly complex and difficult to break. This makes their removal difficult when these substances come into contact with the environment, causing increasing impacts that concern society. One of the biggest exposure channels is water bodies, through domestic wastewater, hospital discharge, improper disposal by the manufacturer, sewage treatment plants, and water treatment plants. The control and monitoring of wastewater pollution have been a challenge, as water quality endangers the health of humans and animals.

The water quality of rivers and lakes has improved with the implantation of municipal wastewater treatment plants (MWWTP). Traditional treatment methods can comply with legislation regarding acceptable concentrations of carbon, nitrogen, phosphorus, pathogens, etc. (Arfanis et al., 2017). However, a variety of substances have harmful activities to the environment in minimal concentrations, in the order of nanograms. These compounds are known as micropollutants and come from pharmaceutical products, pesticides, personal care products (PCP), hormones, endocrine

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disrupting compounds (EDC), microconstituents, cyanotoxins, herbicides, disinfection by-products, etc. As for these substances, MWWTP is still inefficient, both due to the complexity of the molecules in question and the inhibitory action on the microorganisms of the activated sludge used in biological treatment. As a result, worrying concentrations of micropollutants are found in water bodies around the world.

As they are compounds that have not been monitored for some decades, these biologically active recalcitrant contaminants are also called emerging contaminants (EC), recently gaining recognition as significant water pollutants. However, they are toxic substances and do not have specific legislation, also to being highly persistent in conventional water and sewage treatments (Salomão et al., 2019).

Although there are no legal discharge limits for micropollutants, some regulations have been published. In the European Union, Directive 2008/105/EC began to establish strategies to combat the contamination of the environment by emerging contaminants. Initially, a set of 33 priority substances was selected that required greater attention due to their high risk (Ebele et al., 2017). Five years later, the European Union Directive 2013/39/EU increased the list by adding another 12 substances. In the first quarter of 2015 (two years since the last Directive), the list of harmful ECs to be monitored continued to grow with the addition of antibiotics and hormones (Barbosa et al., 2016). Besides, the Directive 39/2013/EU implemented a watch list as a guideline of substances for monitoring (Sousa et al., 2018).

The Environment Agency (EA) of England and Wales also showed concern when they ranked the most dangerous EC based on traditional risk assessment procedures, persistence, bioaccumulation, and toxicity (Ebele et al., 2017). All these measures show the eminent concern with micropollutants, causing structural changes in MWWTP in an attempt to cover the removal of a greater number of aquatic pollutants. Currently, it is still necessary to develop modern detection technologies appropriate for monitoring and controlling these compounds. It is estimated that more than two thousand ECs were found in surface waters after conventional treatment (Sodré et al., 2010; Yoon et al., 2010). Also, it is in wastewater treatment plants that the highest concentration of these pollutants is found.

14.2 Pharmaceuticals

In the past few years, the variety of EC present in the water available in nature has increased, partly due to the advance in analytical detection techniques, measuring increasingly low concentrations in water bodies. Among the large number of EC that may be present in water resources, pharmaceutical residues in surface and groundwater have been a major environmental concern.

Pharmaceutical products are defined as prescription, over-the-counter drugs, and veterinary therapies used to prevent or treat human and animal diseases (Ebele et al., 2017). The pharmaceuticals of most concern when in contact with the environment may have estrogenic effects on living organisms, which have altered the pattern of hormonal metabolism and interfere with normal endocrine functions (Likodimos et al., 2010).

Another concern is the arrival of residual antibiotics in surface waters leads to increased resistance to antibiotics in pathogenic and non-pathogenic microorganisms (Abdel-Maksoud et al., 2018). Antibiotics can be percolated from the soil surface to deeper layers and groundwater, which extends its impact not only to surface waters (Bilal et al., 2020).

According to some studies, pharmaceutical products can bioaccumulate in living organisms such as algae, fish and mollusks (de Solla et al., 2016). Oxazepam has been found to persist in aquatic environments for more than four decades in its active form (Klaminder et al., 2015). An additional concern concerns synergistic interactions between pharmaceutical or PCP. These interactions between two or more inert drugs cause significant toxic effects, even at minimal concentrations (Cleuvers, 2003).

As stated by statistics, there are more than 250 different antibiotic entities registered for treatment in human and veterinary medicine (Ahmed et al., 2015). Besides, discoveries of new pharmaceutical products result in the exponential addition of pollutants to the vast number of existing chemical compounds that are brought into the environment. It is estimated that approximately half of the pharmaceutical wastewaters generated throughout the world are being discarded without appropriate treatment (Vijaya Bhaskar Reddy et al., 2019). Since the use of these pharmaceutical products cannot be controlled or eliminated, due to the population growth, new treatment measures are pointed out as assistants in the processes of removing contaminants in MWWTP.

The route of contact between pharmaceuticals and the environment can come from residues from the pharmaceutical industry, hospitals, and veterinary medicines. Moreover, unused or expired pharmaceutical products are discarded directly into municipal wastewater or deposited in landfills, overloading MWWTP that are unable to completely remove these compounds, inducing pharmaceutical waste to reach the water surface and even filter into groundwater (Wang et al., 2019).

14.3 Advanced oxidative processes (AOP)

Since conventional treatments do not guarantee safe removal of EC, new techniques have been devised to fill this gap. Among them are the advanced oxidative processes (AOP), which has studied, with good results, removing recalcitrant compounds, even in low concentrations and whose synergy has been explored both among them and in combination with conventional treatments, producing gradually better performances (Miklos et al., 2018).

Several scientific works present AOP as the best technique to mineralize resistant organic pollutants (Bourgin et al., 2017; Gassie and Englehardt, 2019; Xiang et al., 2016). A great advantage of these techniques is the rapid oxidation of pollutants to harmless final products, through homogeneous and/or heterogeneous processes. Furthermore, AOP can degrade levels of undetectable contaminants, but which can present a risk to human health (Kanakaraju et al., 2018). During AOP there is no

phase transfer of the pollutant, besides, the entire process can be operated at ambient pressure and temperature and is efficient for a wide range of contaminants and concentrations, besides to requiring little maintenance and operational requirements (Mustafa et al., 2014).

AOP are based on the formation of reactive oxygen species (ROS) in the presence of water (Eq. 14.1). Most of the hydroxyl radical (•OH) stand out, which has an oxidative power of 2.8 eV, inferior only to the fluorine element (3.03 eV). These oxidizing agents attack the chemical bonds of organic molecules, promoting their degradation into simpler compounds. At the end of the process, partial degradation (Eq. 14.2) or complete mineralization (Eq. 14.3) can be achieved, where there are only carbon dioxide and inorganic ions as final products (Lavand and Malghe, 2018).

$$H_2O \rightarrow \bullet OH + H^+ + e^- \tag{14.1}$$

$$R \rightarrow RO + e^- \tag{14.2}$$

$$R \rightarrow CO_2 + H_2O + ions \tag{14.3}$$

There are two routes of action for the attack of radicals to pollutants within the electrolytic cell: direct and indirect oxidation. Indirect oxidation, and organic molecules are degraded on the anode surface by electron transfer, that is, it depends fundamentally on the diffusion of the organics in solution to the electrode. The laws that rule over this process are the transfer of mass (between the substrate and the anode) and the transfer of electrons on the electrode surface. In the case of indirect oxidation, oxidizing agents are formed in the solution by the process of chemical adsorption (chemisorption) and physical adsorption (physisorption), which will also promote degradation (Garcia-Segura et al., 2018; Martínez-Huitle and Panizza, 2018).

AOP are an ecological alternative to solve the problem of water contamination by EC. They can be used both before and after biodegradation. In the first case, AOP oxidizes complex molecules to simpler chain intermediates, this facilitates the action of microorganisms in the next treatment. In the second case, AOP acts to remove residual contaminants that have not been completely degraded by biological processes (Gimeno et al., 2016).

Different AOP can be used in the process of degradation or mineralization of organic compounds (Table 14.1). Among the AOP include the ozonation, Fenton, photo-Fenton, photocatalysis, electrochemistry, photolysis, sonolysis, etc. processes. Photocatalysis is one of the most promising technologies for the treatment of wastewater contaminated with EC (Abdel-Maksoud et al., 2018). However, one of the major disadvantages of using AOP is energy consumption (Gimeno et al., 2016), so it is important to develop "green technology" and environmentally friendly. Photocatalysis is a technique that uses semiconductor materials to generate unstable and non-selective radical species during light activation. Given this, photocatalysts sensitive to sunlight have been developed; this reduces the energy limitation and favors its implantation on larger scales.

Table 14.1 Examples of types and classes of advanced oxidative processes.

Advanced Oxidation Process				
Ozonation	**UV irradiation**	**Electrochemistry**	**Catalysis**	**Physical processes**
O_3	UV/H_2O_2	BDD	Fenton	Electron beam
O_3/H_2O_2	UV/O_3	SnO_2	Photo-Fenton	Ultrasound
O_3/catalysis	UV/SO_4	PbO_2	UV/catalysis	Plasma
O_3/photolysis	UV/Cl_2	TiO_2	Photocatalysis	Microwave

14.3.1 Photocatalysis

Photocatalysis applied to wastewater treatment is a heterogeneous catalytic process that uses semiconductor metal oxides, such as TiO_2, ZnO, CdS, WO_3, ZnS, SnO_2, SiO_2, Nb_2O_3, etc. These oxides are photosensitive solids, that is, when under irradiation of light at a certain wavelength they can promote the passage of electrons from the valence band (VB) to the conduction band (CB), generating energized "holes." These electrons and holes migrate to the surface of the photocatalyst and react in the presence of water to form hydroxyl radicals (Nasirian et al., 2018). Similarly, free electrons react with oxygen and other molecules dissolved in the solution, forming oxidizing agents.

During the photocatalytic reaction •OH reacts with the organic pollutant oxidizing its molecule to form an aldehyde (Eq. 14.4), afterwards the reaction continues to form carboxylic acid (Eq. 14.5) and, finally, results in carbon dioxide, water and some inorganic ions (Eq. 14.6) after a series of parallel reactions. When all reaction steps are completed, mineralization of the organic contaminant is achieved.

$$R + OH\bullet \rightarrow RCHO \tag{14.4}$$

$$RCHO + OH\bullet \rightarrow RCHOOH \tag{14.5}$$

$$RCHOOH + OH\bullet \rightarrow CO_2 + H_2O + 2H^+ + ions \tag{14.6}$$

Among the most used photocatalysts, titanium dioxide, or titania (TiO_2) stands out for its low cost, flexibility, ease of production, chemical stability, insolubility in water, availability, low toxicity and high photocatalytic efficiency (Devi and Kavitha, 2016; Peng et al., 2018; Qi et al., 2016). In general, TiO_2 can be found in nature in the crystalline rutile (tetragonal), anatase (tetragonal) and brookite (orthorhombic) phases, with anatase being its most photoactive form (De Angelis et al., 2014), as a result of high electronic mobility, low dielectric constant and lower volumetric density than other forms of TiO_2.

However, the band gap of about 3.2 eV for anatase allows the material to absorb only ultraviolet light, which corresponds to 4 to 5% of the sunlight spectrum (Dewil, 2017; Wu et al., 2013). Another worrying factor is the rapid recombination of the photogenerated electron-hole pairs, which favors the photocatalytic reaction on the

surface of the photocatalyst (Liu et al., 2016). The recombination time of TiO_2-generated charge carriers is around 10^{-9} s, while the chemical reaction time for TiO_2 and the adsorbed pollutants is in the range of 10^{-8} to 10^{-3} s (Zhou et al., 2011). When recombination occurs, the excited electron returns to the valence band without reacting with the species adsorbed by the photocatalyst, dissipating the energy as light or heat (Pelaez et al., 2012).

To overcome these problems, new ways of producing photocatalysts with high energy efficiency are being sought. The significant factors that affect photocatalysis are light conditions, the presence of oxidants, pH, and surface modification (Zhao et al., 2018). The latter is being used as an alternative to solve the deficit of energy efficiency, through different techniques such as metal loading, metal ion doping, dye sensitization, composite semiconductors, anion doping, and metal and metal ion implantation (De Silva et al., 2018).

Another problem is in the morphology used in the photocatalytic treatment, as normally TiO_2 is in the form of nanoparticles suspended in effluents. This means that after the water purification process, it is necessary to separate the TiO_2 powder so as not to lose the material and avoid contamination with the solid, which can pose a threat to aquatic life (Arfanis et al., 2017). Usually, this separation process is done with the aid of filters, increasing the costs of photocatalytic treatment and may even make its application on a large scale unfeasible (Abdel-Maksoud et al., 2018).

The deposition of noble metals on the surface of the photocatalyst proved to be an effective method to reduce the energy gap for photo-excitation and, simultaneously, to reduce the photogenerated recombination rate of the electron-vacancy pair. These metals function as electron traps, thus generating the Schottky barrier (Murcia, 2020). This doping has shown positive results regarding the application of solar energy since it reduces the band gap of the catalyst and increases the lifetime of photogenerated charge carriers (Pelaez et al., 2012).

However, these metallic dopants can function as recombination centers, reducing photostability, and preventing the photocatalytic reaction from happening. For this to not happen, it is necessary to accurately dose the amount of the dopant so as not to disadvantage photocatalytic activity (Chung et al., 2015). Besides, there are complications regarding corrosion, high costs, and difficulties in active-site engineering (Reddy et al., 2018). As for nonmetallic dopants, the recombination between holes and electrons is considerably reduced. Moreover, their impurity states are near the valence band edge, but they do not act as charge carriers, and their role as recombination centers might be reduced (Dong et al., 2015).

Among nonmetallic materials, carbon (C) has attracted attention as a dopant of photocatalysts and can either replace oxygen sites on the semiconductor surface or occupy interstitial spaces in the material, depending on the amount of and doping reaction conditions (Di Valentin et al., 2005). According to some studies, carbon can considerably increase the absorption of visible light from the photocatalyst (Wu et al., 2013), increasing its efficiency and improving the pollutant degradation capacity by up to five times compared to other dopants (Sakthivel and Kisch, 2003).

14.4 Carbonaceous TiO_2 doping

The synthesis route for doping TiO_2 nanoparticles with carbon has great influence to achieve a high photocatalytic performance of the material produced. However, many conventional methodologies result in the aggregation of carbon species, limiting its use as a photocatalyst (Quan et al., 2014). Among the most used techniques are the sol-gel method, which allows the introduction of dopants into the crystalline matrix of TiO_2 and directly affects photoreactivity, charge carrier recombination rates, and interfacial electron transfer rates (Sannino, 2020); and the chemical vapor deposition (CVD) technique, which allows the mass production of nanoparticles or thin films by controlling relevant factors such as composition, crystal structure, purity and particle size (Kuo et al., 2007). Through these methods it is possible to replace the oxygen present in the TiO_2 network with carbon, another mechanism occurs simultaneously by depositing carbon on the surface of the TiO_2 crystals (Khalid et al., 2017).

The subsequent process of carbonization or heat treatment of carbon-doped TiO_2 (C– TiO_2) modifies the structure of the photocatalyst electronic band, narrowing the band gap (Fig. 14.1). The carbonization temperature directly influences the doping level, since the incomplete calcination process of complex residual species containing carbon results in narrowing of large bandgaps (Liu et al., 2017).

Other methods have also been incorporated into the synthesis of carbon-doped photocatalysts, microwave digestion is an example. In their work, Surenjan et al. (2017), prepared C–TiO_2 nanoparticles from titanium oxy acetyl acetate and using glucose as a carbon source. As an answer, he obtained a crystal in the anatase phase with a high concentration of carbon on the surface. Even with the presence of graphitic carbon on the TiO_2 surface, there was significant absorption of visible light, capable of removing 99% of an effluent contaminated with carbamazepine and diclofenac.

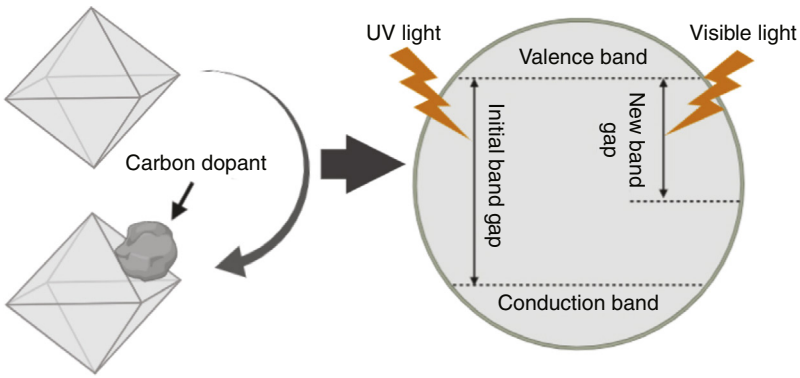

FIG. 14.1 Effect of carbon doping on narrowing the semiconductor band gap.

Cordero-García et al. (2016) made a study about the influence of carbon doping in a heterojunction between WO_3 and TiO_2 (WO_3/TiO_2–C), since doping with non-metals favor the photocatalytic performance of mixed oxides (Daous et al., 2014). It was observed that the synergy between C and WO_3 allowed a greater performance in sunlight, the same occurs with the anatase phase of TiO_2. There was no significant difference between the percentage of final degradation of diclofenac in the presence of pure TiO_2 and WO_3/TiO_2–C (82.4%), however, there was an increase in the degradation kinetics by the carbon-doped hybrid oxide (Cordero- García et al., 2016).

Further to its use in hybridized oxides in the degradation of diclofenac, carbon has also been applied together with other ions, resulting in a hybrid doping of TiO_2 to solve the contamination of this same effluent. In a work by Ramandi et al. (2017), for example, he used the most recurrent non-metallic ions in semiconductor doping (Hu et al., 2010; N. Li et al., 2014; Ratova et al., 2018) to synthesize the tridoped TiO_2 with ions of carbon (C), nitrogen (N) and sulfur (S) by a simple sonochemical methodology of low frequency (20 kHz) and room temperature. The C–N–S tri doped TiO_2 nanoparticles showed mineralization of 100% of the pharmaceutical in 180 minutes of reaction time, under solar irradiation (Ramandi et al., 2017).

14.5 Graphene–TiO_2

Graphene is a two-dimensional material that corresponds to a monolayer of graphite or even a few layers of that material overlapping. Because it has excellent physical-chemical properties (high surface area, high conductivity, high mechanical and thermal resistance, ease of functionalization, mass production, excellent mobility of the cargo conveyor, etc.), graphene has been the subject of studies in the manufacture photocatalysts (X. Li et al., 2014; Shao et al., 2010). The use of semiconductor materials with a photocatalytic application under visible light has been reported in the literature (Zhou et al., 2016). In graphene structures there is a narrow distance between carbon atoms, such an arrangement promotes electrons and holes like similar mass-free charge carriers, leading to electronic overlap (Adly et al., 2019).

When combined with TiO_2, graphene enhances photocatalytic activity under visible light, this is due to a redshift of the band edge and a significant reduction in the band interval of the graphene-TiO_2 compound, resulting in greater absorption of visible light. and improvement in the transport of photogenerated electrons on the graphene surface (Xiang and Yu, 2013). Further, due to its high capacity for adsorption of organic molecules, graphene serves as an enhancer of photocatalytic activity, facilitating contact between pollutants and the surface of the photocatalyst (Kamat, 2011).

Graphene can function as two-dimensional support to increase the photocatalyst's surface area, which can facilitate the adsorption of contaminants to be degraded. However, the contact between the metal oxide nanoparticle and the graphene sheet is minimal, reducing the interaction between the materials and impairing the electron transfer for the photocatalytic reaction (Xiang and Yu, 2013). To overcome this

problem, technologies for the synthesis of graphene oxide (GO) nanoparticles were developed, with a self-assembled core-hull structure with high photocatalytic efficiency (Kim et al., 2012). In general, GO is synthesized by the Brodie, Staudenmaier, or Hummers method, or by some variation of these methods. These methods have in common the fact that they involve the oxidation of graphite at various levels (Zhu et al., 2010).

Graphene oxide is formed by a graphite oxide monolayer, which arouses great interest in the area of photocatalysis. One of the causes of this interest is that the GO has a large number of functional groups containing oxygen, which can serve as anchorage centers for molecules and favorable nucleation sites for active species or precursors (Sheshmani and Nayebi, 2019). The junction between graphene oxide and TiO_2 (GO–TiO_2) causes an advantage both in reducing the band gap and in the adsorption capacity resulting from graphene, which facilitates the contact of pollutants with the surface of the photocatalyst.

The synthesis of hydrogels/airgels carbon–TiO_2 is a good alternative for lower costs and ease of production (Zhang et al., 2013). It is a 3D structure of graphene networks impregnated with TiO_2, highly hydrophobic, and facilitate photocatalyst recycling (Qiu et al., 2014). The major disadvantage of this material is the high-temperature conditions required during the synthesis. There are two possible synthetic routes for the production of GO–TiO_2 hydrogels/airgel, the in-situ technique uses precursors for the formation of TiO_2 nanoparticles, while the ex-situ technique appropriates TiO_2 nanoparticles already synthesized for the incorporation of graphene oxide. Nawaz et al. (2017) conducted a study in which he applied the in-situ and ex-situ techniques to produce 3D GO–TiO_2 structures. As a result of the high degree of TiO_2 aggregation, it resulted in less interaction with the GO, disabling the formation of a hydrogel in the *in situ* case. On the other hand, the synthesis of the ex-situ airgel showed high adsorption and photodegradation efficiency almost twice as high as pure TiO_2. At the end of 90 min, more than 99% of carbamazepine was removed at an initial concentration of 10 mg L^{-1} (Nawaz et al., 2017).

A study by Bhatia et al. (2017), showed the influences of different operational parameters on the photocatalytic degradation of atenolol using GO–TiO_2. It was observed that the increase in the concentration of the photocatalyst increases the availability of active sites in the solution; however, in very high concentrations there is an increase in excess particles, which are not fully illuminated due to agglomeration (Estahbanati et al., 2017). In the same work it is also shown that the intensity of light favors photocatalytic activity since it increases the number of photons that can affect the active sites, producing a greater amount of hydroxyl radicals (•OH) and superoxides ($O2^{\bullet-}$) (Fig. 14.2), providing the degradation of 72% of atenolol (1.5 g L^{-1}) in 60 min of experiment with GO–TiO_2, well above the removal achieved with commercial TiO_2 (56%) and complete mineralization in 7 h using sunlight (Bhatia et al., 2017).

Pastrana-Martínez et al. (2012) observed that high temperatures (350 °C) in the heat treatment of GO–TiO_2 cause unwanted effects due to excess GO on the surface of TiO_2 and the disruption of the GO–TiO_2 binding. In the experiments carried out

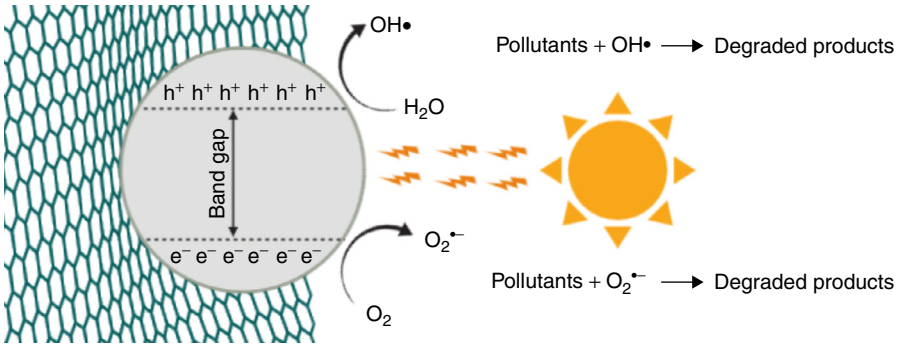

FIG. 14.2 Schematic of photocatalytic degradation of pollutants by the action of oxidizing radicals produced in GO–TiO_2 composite.

it was possible in 60 min degraded almost completely to diphenhydramine solution (100 mg L^{-1}) under visible light. Amalraj Appavoo et al. (2014) managed to further reduce the time to remove carbamazepine in their study using response surface methodology (RSM) to optimize the experimental conditions of GO–TiO_2 photocatalysis. Their results show the total removal of carbamazepine (168 μg L^{-1}) in just 5 min under the irradiation of a UV-A lamp (1.35 mW cm^{-2}) and a catalyst load of 25.14 mg L^{-1} (Amalraj Appavoo et al., 2014).

Yang et al. (2019) point out GO–TiO_2 as an efficient activator of persulfate, capable of producing large amounts of sulfate radicals ($SO_4^{\bullet-}$) when present in solution, besides to hydroxyl radicals. In a solution containing micropollutants such as bisphenol A, phenol, acetaminophen, and sulfamethoxazole, the authors analyzed photodegradation using GO–TiO_2 under visible light. The $SO_4^{\bullet-}$ and •OH root systems were observed as the main degradation pathways of the system, with the removal of 80% of Total Organic Carbon (TOC) in just 12 min (Yang et al., 2019). In a similar study, Chen et al. (2019) analyzed the influence of peroxodisulfate (PDS) as an electron acceptor to accelerate the photocatalytic activity of GO–TiO_2 on the degradation of diclofenac using light-emitting diode (LED) as the visible light irradiation source. The results indicated that the PDS functioned as a promoter of the electron-hole pair separation and the generation of additional ROS, capable of degrading 100% of diclofenac after 30 min (Chen et al., 2019).

Karaolia et al. (2018) tested the GO–TiO_2 nanoparticles in real effluents after treatment in membrane bioreactor and analyzed the photodegradation under solar irradiation of different antibiotics (sulfamethoxazole, erythromycin, and clarithromycin) and bacteria with high biological resistance (Escherichia coli) simultaneously. The results showed that in 60 min there was superior degradation of GO–TiO_2 (above 80%) to erythromycin and clarithromycin compared to commercial TiO_2 P25, which was slightly more efficient at removing sulfamethoxazole (Karaolia et al., 2018).

Hybridization between semiconductors with excellent photocatalytic properties has also shown good results in the degradation of recalcitrant pollutants

(Brooms et al., 2018). Among the options, the TiO_2–ZnO junction offers improved photocatalytic activity over separate systems due to an extended light absorption range and an effective charge transfer from ZnO to TiO_2, increasing a lifetime of the charge carriers and enhancing the interfacial charge transfer from photocatalyst to adsorbed substrates (Benton et al., 2016; Jonidi-Jafari et al., 2015). In the study by Bilgin Simsek et al. (2018), GO was used as an immobilizer of TiO_2–ZnO, to increase the adsorption power of organic contaminants, moreover to optimizing the stability of the photocatalyst and reducing particle agglomeration. Synergy was observed between metal oxides in the production of oxidizing radicals, resulting in a degradation of 97.8% of ibuprofen and 87.7% of flurbiprofen under visible light in acidic pH solutions after 180 min of reaction time (Bilgin Simsek et al., 2018).

Modifications on the surface of nanostructured composites based on GO can give new attractive characteristics to the photocatalyst. The deposition of magnetic nanoparticles allows the reuse of the semiconductor after the reaction through exposure to a magnetic field (Lin et al., 2012), without the need for more complex and time-consuming separation treatments. However, direct contact between TiO_2 and magnetic iron oxide impairs photoreactivity concerning pure TiO_2. This is because the photogenerated electrons migrate quickly into the lower-lying conduction band of magnetite and the holes transferred to the upper lying valence of this iron oxide, causing a high electron-hole recombination rate. This passage of electrons also causes a reduction in iron oxide, causing the loss of magnetism (Yao et al., 2015).

To solve this problem, techniques have emerged to add an intermediate layer of silica, isolating the passage of electrons between the elements on the semiconductor surface (Wang et al., 2012). The addition of GO to the surface of the magnetic TiO_2 maintains its recyclable character and enhances its photoactivity (Cheng et al., 2015; Tang et al., 2013). In their study using magnetic GO–TiO_2 nanoparticles, Linley et al. (2014) were able to remove caffeine (1250 ng L^{-1}) and carbamazepine (1180 ng L^{-1}) at concentrations below the detection limit employed (109 ng L^{-1}). The reactions showed higher kinetics than those found with commercial TiO_2 (P25).

Another way to facilitate the recovery of a photocatalyst suspended in water is by immobilizing semiconductors on strategic surfaces such as glass, fibers, and membranes for example (Almeida et al., 2016; Malakootian et al., 2020; Nair and Jagadeesh, 2017). The immobilization of photocatalysts in membranes allows their use in full-scale, as it allows the use of larger areas for the dispersion of photoactive nanoparticles. The poly (vinylidene fluoride) (PVDF) membrane has been identified as a potential immobilizer due to characteristics such as open structure, the large availability of pore sites (100–500 nm), thermal stability, mechanical strength and relative chemical inertness (Dzinun et al., 2015).

The double-layer configuration is seen as a way to enhance the application in the treatment of effluents, as it works as a barrier for pollutants and having the photocatalyst supported instead of suspended (Dzinun et al., 2017). In the study by Li et al. (2019), the retention of pharmaceutical products in commercial ceramic membranes (90 mm diameter, 2.5 mm thickness, TAMI Industries, Nyons, France) modified by GO–TiO_2, also to antifouling properties that facilitate contact between

the photocatalyst and the pollutant increasing the degradation efficiency. However, similar studies were not found in the use of GO–TiO_2 membranes in the removal of effluents contaminated by pharmaceuticals.

In the work of Lin et al. (2017a), the authors made a comparison between the photocatalytic activity of TiO_2 with different doping (Fe^{3+} and GO) immobilized in optical fiber by polymer assisted hydrothermal deposition method (PAHD), testing the materials obtained in the degradation of carbamazepine, ibuprofen, and sulfamethoxazole. Optical fiber allows for light irradiance distribution, improving the efficiency of light use in large-scale reactors (Lin et al., 2017b). This study shows that despite the greater decrease in the band gap through doping with Fe^{3+} (2.4 eV) to doping with GO (2.85 eV), which results in greater photoactivity in the visible spectrum, the GO–TiO_2 showed greater activity in the removal of pharmaceuticals, due to reduced recombination rate of photoexcited electrons-hole pairs (Lin et al., 2017a).

14.6 Carbon Nanotubes–TiO_2

Carbon nanotubes (CNT) are tubular nanometric structures (about 100 nm in diameter) formed by one or more concentric layers of graphite-like, with easy connection with other specific nanoparticles and molecules (Wang et al., 2018). According to the number of layers (Fig. 14.3), the CNT can be categorized into single-walled carbon nanotubes (SWCNT), composed of a single sheet of graphene folded into a cylinder, and the multiwalled carbon nanotubes (MWCNT), with multiple layers of graphene sheets (Anzar et al., 2020).

Distinctive optical properties, high surface area, high-quality active sites, specific mechanical, physical, chemical, electroconductive, and field-emitting properties stand out among the characteristics of CNT (Jiang et al., 2011; Peining et al., 2011; Zouzelka et al., 2016). For this reason, there is a growing interest in incorporating CNTs in metal oxides to improve their photocatalytic properties (Shaban et al., 2018). The CNT-TiO_2 junction causes the transfer of photogenerated charge carriers from

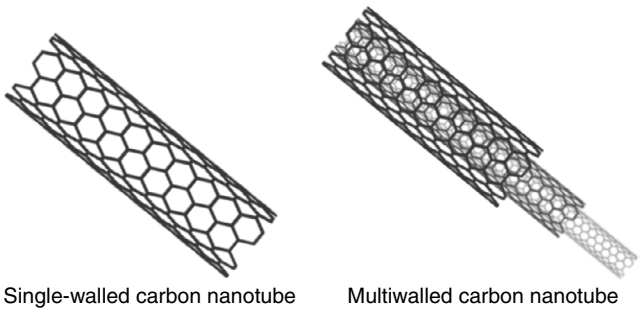

FIG. 14.3 Schematic representation of single walled carbon nanotube (SWCNT) and multiwalled carbon nanotube (MWCNT).

TiO_2 to CNT, decreasing the recombination of electron-hole pairs; this increases the photocatalytic activity of the composite and, consequently, increases the absorption in the visible light range (Tarigh et al., 2015). Moreover, CNT serves as a dispersing bed in reducing the agglomeration of TiO_2 nanoparticles (Bagheri et al., 2017).

A scientific work developed by Czech and Tyszczuk-Rotko (2018), silicon oxide (SiO_2) was used to control the crystallization of TiO_2 through the sol-gel method. The multiwalled CNT was added to the photocatalyst to perform tests for the degradation of acetaminophen under visible light, reducing the band gap from 3.22 to 2.82 eV. CNT–TiO_2–SiO_2 demonstrated high photoactivity in the removal of approximately 81.6% of acetaminophen in 60 min, using a single pollutant matrix (Czech and Tyszczuk-Rotko, 2018). The following year, the same authors published a similar study of acetaminophen degradation under visible light in the presence of caffeine. Surprisingly, the maximum observed removal of acetaminophen with the addition of caffeine was approximately 52% in 60 min. In the experiments, only 30% of the organic load was removed. These results, according to the authors, make it impossible to apply CNT–TiO_2–SiO_2 under visible light for the degradation of the two drugs tested simultaneously, since the application of additional materials (photocatalyst) and procedures from an ecological and economical point of view (Czech and Tyszczuk-Rotko, 2019).

The metal/non-metal-TiO_2 combination has also been investigated. Payan et al. (2019) produced photocatalysts made of single-walled CNT functionalized with Cu–TiO_2 in different stages (sol-gel and hydrothermal). The use of copper as a dopant is common due to the low associated cost, capable of reducing the rate of electron-hole pair recombination and the band gap of TiO_2 (Kavitha et al., 2016). CNT–Cu–TiO_2 was evaluated in the photodecontamination of sulfamethazine under natural solar irradiation. The experiments demonstrated after 135 min of solar irradiation, the total elimination of sulfamethazine (Payan et al., 2019).

Using a similar synthesis methodology, Isari et al. (2020) recently developed the ternary nanocomposite with N–Cu co-doped TiO_2 immobilized on single-walled CNT (CNT–N–Cu–TiO_2). However, besides to photocatalysis under visible light (Xe lamps, 200 W), ultrasound waves were applied to remove sulfamethoxazole (60 mg L^{-1}). During the degradation, the total degradation of the effluent pharmaceutical was found after 60 min, while there was a 45% reduction in TOC, which characterizes the formation of intermediate organic compounds that were not completely degraded by the radicals generated during the reaction (Isari et al., 2020).

Most photocatalytic and drug removal tests in general use favorable conditions for their performance, usually in simple matrices with individual contaminants in concentrations much higher than those found in real environments (Awfa et al., 2018). In a more recent study, Awfa et al. (2019) conducted drug degradation experiments in the presence of background natural organic matter (NOM), a very common matrix in water treatment plants. Besides, the entire process was done under solar irradiation and inherently magnetic particles present in pristine CNT (Ateia et al., 2017) were used to immobilize TiO_2, to propose an economical technique on a reusable material. In response, a regenerable photocatalytic composite was obtained.

Although carbamazepine did not show a significant removal rate, the concentration of sulfamethoxazole declined by up to 50% in 30 min (Awfa et al., 2019).

Photodegradation studies with CNT–TiO_2 in complex real matrices of pharmaceutical wastewater have also been carried out by Ahmadi et al. (2017). The authors reported the total removal of tetracycline after 100 min and mineralization of 83% of the real pharmaceutical wastewater. Moreover, the photocatalytic efficiency gain was demonstrated by the incorporation of multiwalled CNT in TiO2 nanoparticles, seeing the inferior result in experiments with pure TiO_2 (47%) and CNT (32.5%) (Ahmadi et al., 2017).

The immobilization of photocatalysts in nanofilms has the advantage of facilitating the separation of suspended particles, reducing the secondary pollution generated by these solids. However, they have the disadvantage of reducing the contact between the semiconductor surface and the target pollutant, impairing the efficiency of the photocatalytic process. To get around this problem, some researchers have used nanofibers as support for TiO_2 immobilization (Yar et al., 2017). In this sense, polyacrylonitrile (PAN) nanofibers have great potential due to characteristics such as good electrospinnability and stability, high surface area to volume ratio of the one-dimensional nanofibers and capacity to form macroscopical mats with large continuous surface areas and flexible property, low density and hydrophobic nature (Chou et al., 2013). Electrospinning is considered a versatile and effective approach for the preparation of flexible nanofiber materials with controllable diameter, due to its advantages of ease of control and environmental compatibility (Zhang et al., 2011).

In the work of Mohamed et al. (2018), a photocatalytic composite of CNT–TiO_2 supported on amine-functionalized PAN nanofibers (PAN–NH_2) was used. PAN–CNT–TiO_2–NH_2 was applied to the photodegradation of three pharmaceutical products under the irradiation of a 40-watt UV-A lamp (315–400 nm). Complete degradation of ibuprofen, naproxen, and cetirizine was observed at 120, 40, and 25 min, respectively (Mohamed et al., 2018). In a similar study, Uheida et al. (2019) used PAN–CNT–TiO_2–NH_2 to degrade the same pollutants under visible light (0.1 W cm^{-2}). With the change in irradiation, the efficiency of the process was halved, with the complete removal of ibuprofen, naproxen, and cetirizine at 210, 90, and 50 min (Uheida et al., 2019). In both cases, the multiwalled CNT increased the degradation efficiency to pure PAN–TiO_2–NH_2, this gain is attributed to the increase in the adsorption of contaminants to the active sites of TiO_2, with an increase in the photocatalytic efficiency in the acid medium. Since the variation in the rate of degradation between pharmaceuticals can be attributed to different levels of affinity between pharmaceuticals and the binding sites on the catalyst.

14.7 Activated carbono-TiO_2

Activated carbon (AC) is a material derived from biomass with high adsorption capacity, has desirable characteristics such as high chemical stability, high surface area and porosity, resistance to corrosion and low cost (Nelson et al., 2016). This

porous solid is made by carbonizing and then activating a rich in carbon material. The AC is basically a group of materials with greater internal surface area and porosity (generally from 900 to 1200 $m^2\ g^{-1}$), this complex pore structure is classified into three groups according to its size: micropores (<1nm), mesopores (1–25 nm) and macropores (> 25 nm) (NR Khalid et al., 2017).

The good conductivity of the AC also generates interest in the area of photocatalysis, as it can facilitate the transfer of electrons and maintain stability during the photocatalytic reaction process (Jiang et al., 2018). The porosity of CA leads to high pollutant adsorption on the catalyst surface, as it favors the transfer of the adsorbed molecules to the TiO_2 surface, increasing the decomposition efficiency of the organic pollutant. Furthermore, the AC helps to preserve the characteristics of the photocatalyst after the photocatalytic process, enabling the reuse of the material after several cycles (Velasco et al., 2014; Velo-Gala et al., 2017). Therefore, AC can be used as a potential immobilizer, providing synergistic effects by creating an interface between TiO_2 particles and activated carbon.

In a study developed by Gar Alalm et al. (2016), evaluated the photocatalytic activity of TiO_2 immobilized on activated carbon (AC–TiO_2) for degradation of different pharmaceutical products. Amoxicillin and ampicillin were completely degraded after 120 and 180 min, respectively under solar irradiation, while the highest rates of removal by pure TiO_2 for these pharmaceuticals were 89 and 83%. As for diclofenac and paracetamol, there were removals of 85 and 70% in 180 min, respectively, under the same conditions (Gar Alalm et al., 2016). The different degradation values are explained by the different affinity of the compounds for the photocatalyst binding sites. The authors also reported the cost-benefit gain of immobilization with AC, experiments with pure TiO_2 did not reach complete degradation with total costs of 3.29 € m^{-3}, while the composite AC–TiO_2 generated a total cost of 3.19 € m^{-3} (Gar Alalm et al., 2016).

In a recent study, Kakavandi et al. (2019) produced using the TiO_2 nanoparticles on magnetic activated carbon (MAC) impregnation method. The MAC–TiO_2 composite showed desirable characteristics in the removal of tetracycline via sonophotocatalysis as easy recovery, due to the presence of magnetic particles (Fe_3O_4), avoiding the waste of the photocatalyst and the generation of secondary pollution by it. Moreover, degradation efficiency was enhanced by increased adsorption to MAC–TiO_2 and synergy between TiO_2 and Fe_3O_4, which contributes to additional generation of radicals and oxidizing species. The increase in the concentration of these reactive oxygen species (ROS) was also observed with the use of ultrasonic irradiation, through the phenomenon of cavitation, additionally responsible for cleaning the surface of MAC–TiO_2 (Kakavandi et al., 2019), maintaining the exposure of active sites over the reaction time. The results showed a 93% degradation of tetracycline (20 mg L^{-1}) after 180 min. The time for total removal drops to 60 min with the addition (1.0 mM) of chemical oxidants including peroxide hydrogen (H_2O_2), peroxymonosulfate (HSO_5^-), persulfate ($S_2O_8^{2-}$) and periodate (IO_4^-) (Kakavandi et al., 2019).

In the study by Peñas-Garzón et al. (2020), different catalysts of AC–TiO_2 heterostructures were used for degradation under simulated solar light of three

pharmaceuticals including acetaminophen, ibuprofen and antipyrine. The photocatalyst produced by the sol-gel method showed the worst degradation rate for the three contaminants, with only 50% for acetaminophen and much lower rates for the others. This result was probably due to the higher crystal and particle size and lower surface area of this heterostructure (Peñas-Garzón et al., 2020). The AC–TiO_2 produced by the microwave method showed a final degradation similar to that produced by the solvothermal method, with complete removal of acetaminophen and ibuprofen after 360 and 180 min, respectively. However, for antipyrine no complete degradation was achieved up to 360 min in any of the cases studied (Peñas-Garzón et al., 2020).

14.8 Concluding remarks and future challenges

With the increasing discharge of pharmaceutical products in the environment, mainly in water bodies and the increase in the environmental requirements of regulatory bodies, it is essential for scientific studies to propose alternatives to solve this problem, mainly due to the harmful activity of these micropollutants in very low concentrations. In this respect, the use of carbonaceous species hybridized with TiO_2 has shown a great contribution in the treatment of these contaminants, complementing the traditional methods of treatment made in MWWTP. At this point, there is still a lack of research in the literature that involves the coupling of advanced oxidative processes, especially photocatalytic processes, upstream or downstream of water and sewage treatment plants. In the case of TiO_2 composites combined with carbon, there are few studies in the literature that involve them with other AOP either.

Photocatalysts hybridized with carbon species can reduce the bandgap and increase the absorption of the visible spectrum, in addition to preventing electron-hole recombination and facilitating the transport of the pollutant to the active sites of the catalyst through the adsorption forces of activated carbon, graphene, oxide graphene, nanotubes, among others. The incorporation of these carbon-containing species also helps to reduce costs associated with energy consumption using solar irradiation. With the addition of cheap materials like Fe and Cu, it is possible to enhance the photocatalytic activity of the composite and, depending on the immobilization, facilitate the recovery and reuse of this material, avoiding secondary pollution and enabling its use on larger scales. However, to the best of our knowledge, there is still no work with semiconductors immobilized in carbon applied on industrial scales.

It is important to highlight that there is a need to carry out tests using the technologies described in this work in real effluents, with and/or without prior treatment. To evaluate the performance of photocatalysts against complex and multicomponent matrices, not only with pharmaceuticals, but also with other impurities (organic or inorganic) commonly found in real effluents. Such experiments could highlight the problem of the agglomeration of nanoparticles of GO–TiO_2 in aqueous phase, which reduce the exposure of the active sites of the photocatalyst. Solutions with immobilization on different materials or application of ultrasound could be used to overcome this deficiency.

Future research can be carried out to develop new techniques and more efficient semiconductor materials, with good selectivity for EC and extended reuse time. With these measures, it will be possible to apply photocatalytic processes on industrial scales to treat pharmaceutical effluents. We hope that this work helps to understand what has already been developed and inspire new applications of TiO_2 hybridized with carbonaceous in the degradation of pollutants.

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CHAPTER

15

Moving bed biofilm reactor- (MBBR-) based advanced wastewater treatment technology for the removal of emerging contaminants

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15.1 Introduction

In the past few decades, the application of biofilm systems in wastewater treatment has increased significantly due to its effectiveness on, both, the economic and environmental parameters (Asri et al., 2020). As compared to the free cells system, the biofilm-based systems have several merits including a reduced hydraulic retention time (HRT), reusability of biomass, enhanced performance stability, and less space-requirement in the wastewater treatment (Sonwani et al., 2019; Zhao et al., 2019). The microbial culture in the form of biofilms tends to be more diverse as compared to the conventional activated sludge process and hence allows to degrade a wide range of contaminants such as pharmaceuticals, pesticides, dyes, and aromatic hydrocarbons (Zhang et al., 2020). In this direction, the biofilm-based reactors such as a packed bed bioreactor (PBBR), rotating biological contactor (RBC), fluidized bed bioreactor (FBBR or FBR), and moving bed biofilm reactor (MBBR) have been investigated to remove a wide range of contaminants from the industrial and municipal wastewaters (Safwat, 2018; Sonwani et al., 2020; Swain et al., 2020). Amongst these bioreactors, a MBBR has emerged as a promising substitute to remove the contaminants from wastewater (Derakhshan et al., 2018b; Leyva-Díaz et al., 2013). The MBBR technology exploits the natural ability of microorganisms (e.g. bacteria, fungi, and algae) to adhere to the surfaces of carriers (or support media) and grow as biofilms, either as pure or mixed cultures. The wastewater flows in direct contact with the developed biofilm and allows to exchange of substrate, nutrients, and products between the biofilm and bulk liquid (Melo, 2003).

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After its development in the 1980s, thousands of research and review articles on the MBBR have been published over worldwide in last few decades and reported it a simple, flexible, and compact technology for wastewater treatment (Derakhshan et al., 2018c). Previously, the MBBR technology has been widely and effectively applied to remove the various contaminants such as pesticides, pharmaceuticals, industrial chemicals, dye, and aromatic hydrocarbons from the industrial or municipal wastewater (Derakhshan et al., 2018c; Safwat, 2018; Swain et al., 2020). Recently, the MBBR was used to remove the Congo red dye using polyurethane foam-polypropylene (PUF-PP) immobilized *Bacillus* sp. MH587030.1 (Sonwani et al., 2020). They found that the MBBR was able to remove more than 95% of Congo red dye up to 50 mg/L of the initial concentration of dye. Similarly, Derakhshan et al. (2018d) also reported that the atrazine was successfully removed in the MBBR under nitrate-reducing conditions.

The performance of bioreactor is mainly related to the properties and characteristics (e.g. surface area, surface morphology, pore structure, density, hydrophobicity, and microbial adhesion capacity) of carriers on which the biofilm is developed or formed (Asri et al., 2018). The carriers made of polyurethane foam (PUF), polyethylene (PE), porous ceramics, polyvinyl alcohol (PVA), polypropylene (PP), and high-density polyethylene (HDPE) have been used in the MBBR to remove the contaminants from wastewater (Derakhshan et al., 2018e; Sonwani et al., 2019; Tang et al., 2017). The operational parameters such as pH, temperature, HRT, carrier filling ratio, and organic lading rate also affect the performance of the MBBR process. It has been reported that the novel modified carriers, such as PUF-PP and LDPE-PP, are more effective in terms of removal efficiency and elimination capacity as compare to the conventional carriers (i.e. PP) (Sonwani et al., 2019). Therefore, the knowledge of carrier characteristics and their properties and optimum operational parameters is necessary to obtain the highest performance of the MBBR.

In this chapter, the fundamental of moving bed biofilm reactor (MBBR), different biofilm carriers and their characteristics, and the effect of operational parameters are systematically summarized. An overview of the MBBR reactor used for the treatment of emerging contaminants (ECs) and persistent organic contaminants (POCs) from industrial and municipal wastewater is also discussed. In addition, the mathematical models employed in the literature for evaluating the kinetics of substrate degradation are summarized.

15.2 Overview of the moving bed biofilm reactor (MBBR)

The moving bed biofilm reactor (MBBR) is a biofilm-based technology for the treatment of contaminants present in the wastewater and presently employed in more than 50 countries. This technology was initially developed in Norway in the late 1980s (Diaz et al., 2019). Fundamentally, the MBBR technology is based on the merger of the conventional activated sludge process (ASP) and a fluidized bed bioreactor (FBBR) (Nur et al., 2018). In MBBR, the biofilm developed on plastic elements

(called carrier) is kept moving inside the bioreactor either by aeration or mechanical stirrers. Based on the application, the MBBR may be used either aerobic or anaerobic or anoxic approach. In the earlier case (aerobic), the movement of carriers is caused by aeration and agitation, whereas in later case (anaerobic and anoxic), the carriers are kept in moving by mechanical mixing (Asri et al., 2018). A schematic diagram of the MBBR is shown in Fig. 15.1.

Initially, when there are no biofilms developed on the carriers, they float on the water surface because their densities are lower than water. As the biofilm starts to grow onto carriers, they become heavier than water and tend to settle. However, they are made suspended in the bioreactor either by aeration or agitation. The wastewater supplied into bioreactor comes into a direct contact with the developed biofilm on carriers, and the exchange of substrate, nutrients, and products between the biofilm and bulk liquid begins (Melo, 2003). A controlled biofilm development is possible in the MBBR due to high shear stress from the wastewater and carrier circulation which also help in the diffusion of substrate and nutrients through biofilm (Asri et al., 2018; Nur et al., 2018). The merits of MBBR over a conventional ASP and other biofilm-based processes include a less clogging, effective mass transfer, elimination of sludge recirculation, and low HRT (Biase et al., 2019; Díaz et al., 2019). Additionally, the amount of biomass (mg/L) can be increased with increasing carrier filling ratio to accelerate the rate of biodegradation. However, a continuous mixing of the carrier (either by aeration or agitation) may raise the demand of energy resulting into high processing cost.

In order to further enhance the performance of the MBBR, it can be integrated with a membrane bioreactor (MBR) or settling tank (ST) (Rodriguez-sanchez et al.,

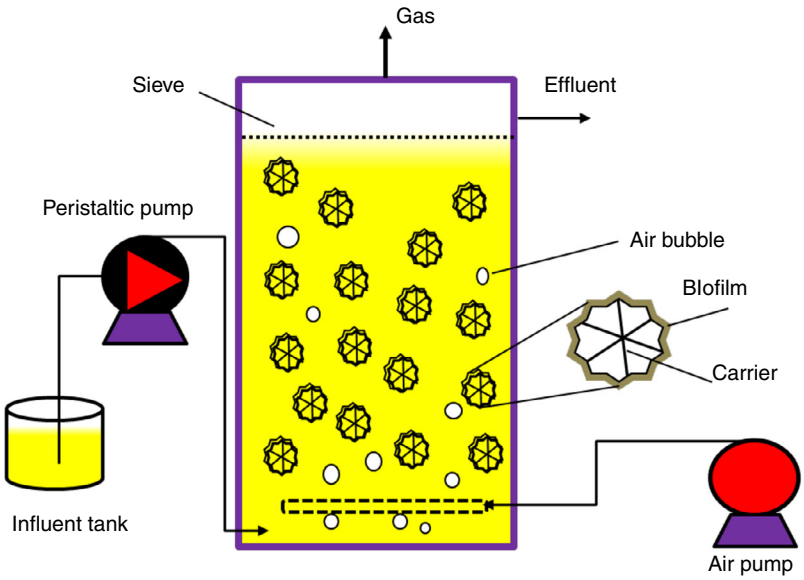

FIG. 15.1 Schematic diagram of a moving bed biofilm reactor.

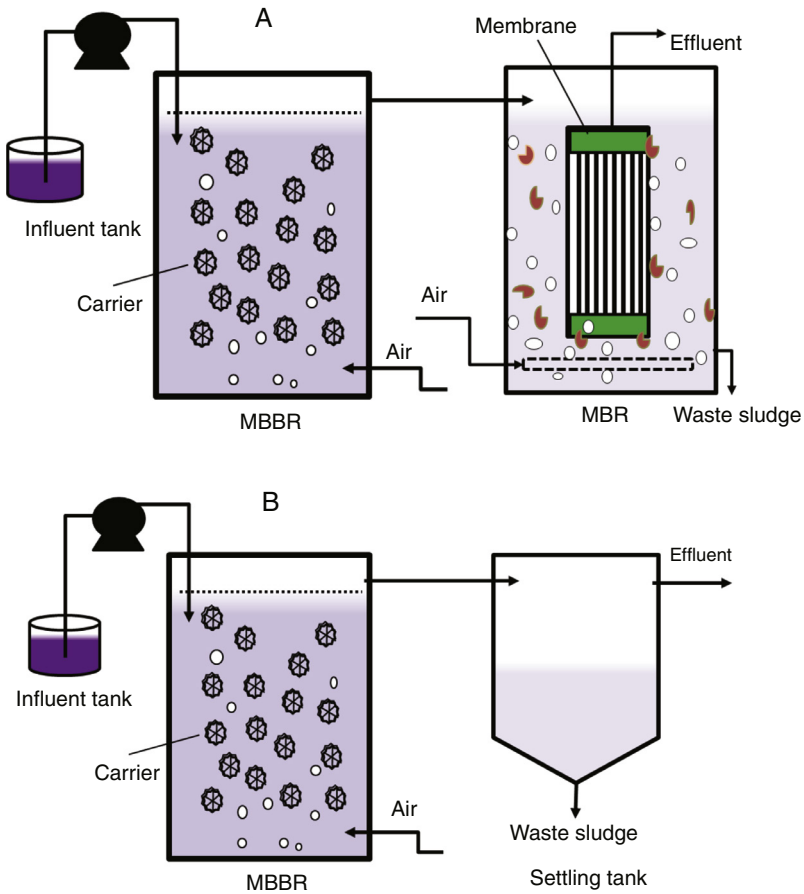

FIG. 15.2 Schematic diagram of an integrated bioreactor.

(A) Integrated moving bed biofilm reactor-membrane bioreactor; (B) Integrated moving bed biofilm reactor-settling tank.

2017; Jiang et al., 2018). The earlier is known as an integrated MBBR-MBR system whereas later is considered as an integrated MBBR-settling tank (Fu et al., 2017; Rodriguez-sanchez et al., 2017). The schematic diagram of an integrated bioreactor is shown in Fig. 15.2.

15.3 Operating benchmarks of the MBBR

There are several parameters that need to be optimized before the operation of a MBBR. They include the characteristics of the MBBR carriers, biofilm, carrier filling fraction or ratio, aeration system, and flow configuration.

15.3.1 Carriers characteristics

The characteristic of carriers plays an important role in the formation of biofilm, and therefore in the removal of contaminants from wastewater in the MBBR systems. The carriers used in MBBRs usually have a density between 0.93-1.0 g/cm^3. These carriers have diameters and heights in the range of 5-10 mm, and may also have small fins on the outer surface and internal cross-member that divide each carrier into four or six sectors (Nur et al., 2018; Sonwani et al., 2019). The size of the carrier may vary according to the application and organic loading rate. The specific surface area, porosity, and shape also affects the performance of MBBR (Nur et al., 2018). A good carrier should have the following characteristic; high porosity to get optimum diffusion of the substrate, large specific surface area for more biofilm formation, high mechanical strength, inert, and should be reusable (Marc A. Demeter et al., 2017; Nur et al., 2018).

Based on the nature of the carriers, these are broadly classified as inert organic and inorganic carriers. The inorganic carriers are generally made of porous ceramics, zeolite, and volcanic rock, whereas the organic carriers include polyester, polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC), low-density polyethylene (LDPE), polyurethane foam (PUF), based carriers (Zhao et al., 2019). The inorganic carriers exhibit an excellent mechanical strength and high chemical resistant, whereas the slow biofilm development, poor permeability, and clogging are the drawback of such carriers. In the last few decades, considerable efforts have been given on the development of inert organic carriers such PP, LDPE-PP, polyester, PUF-PP, and other material, which is likely to overcome the drawback associated with inorganic carriers. Table 15.1 summarizes the specification carriers that are used to remove the contaminants from wastewater.

Recently, Swain et al. (2020) claimed that modified carrier based on PUF-PP in the MBBR was effective in removing the pollutants in terms of ammonia (91%) and phenol (92%) from wastewater. They reported that the original PP carrier combined with PUF (PUF-PP carrier) enhanced performance of the MBBR, which was probably due to the high porosity of PUF for the immobilization of microbial culture. In another work, Derakhshan et al. (2018b) used Raschig rings in the MBBR to remove the pesticide from wastewater, and they reported the removal of 74.8% of atrazine and 99.2% of COD.

15.3.2 Biofilm formation

Biofilm plays a key role in biofilm type rector to breakdown the pollutant present in wastewater. “Biofilm” is the biomass or cells of microorganisms that attached and embedded on the surface of solid matrix or carriers (Rittmann, 2018). The formation of biofilm takes place with the following phases; adsorption of macromolecules and nutrients to the carrier surface, initial cell transport, adhesion, and irreversible attachment (Kowalski et al., 2019; Zhu et al., 2015). A schematic diagram of nutrient diffusion through the developed biofilm into carriers is shown in Fig. 15.3. The growth of microbial biofilm starts onto the surface of carriers or solid matrix (both loose

Table 15.1 Summary of the biofilm carriers used in the MBBR systems in the literature to remove the wide range of contaminants from wastewater.

Configuration	MBBR volume (L)	Pollutants	Carriers specification			Materials	Media filling ratio (%)	Removal efficiency (%)	Reference
			Carriers	Density (g/cm^3)	Specific surface area (m^2/m^3)				
Aerobic MBBR	2.0	Phenol, Ammonia	Modified AnoxKaldnes K3	0.93	550	PUF-PP	40	Phenol: 92 Ammonia:91	Swain et al (2020)
Aerobic MBBR	12	Sulfadiazine, Ibuprofen, Carbamazepine	Cubic polyurethane sponges	0.028	-	Polyurethane	20	Sulfadiazine: 61 Ibuprofen:75 Carbamazepine: 28	Zhang et al. (2020)
Aerobic MBBR	2.0	Congo red dye	Modified AnoxKaldnes K3	0.93	550	PUF-PP	45	95	Sonwani et al. (2020)
Anaerobic-Anoxic MBBR	52	Organic matter, Nutrient	AnoxKaldness-K3	0.93	500	_	30	COD: 95 TN: 96 TP: 94	Almomani & Bohsale (2020)
Aerobic MBBR	3.0	Organic and Total ammonia nitrogen	Al Andalus	-	850	Polyethylene	70	COD: 76 TAN: 46	Safwat (2018)
Aerobic MBBR	2.0	Naphthalene	Modified AnoxKaldnes K3	0.93	550	PP, LDPE-PP, and PUF-PP	40	COD: 90	Sonwani et al.(2019)

Table 15.1 Summary of the biofilm carriers used in the MBBR systems in the literature to remove the wide range of contaminants from wastewater. *Continued*

Configuration	MBBR volume (L)	Pollutants	Carriers specification			Materials	Media filling ratio (%)	Removal efficiency (%)	Reference
			Carriers	Density (g/cm^3)	Specific surface area (m^2/m^3)				
Anaerobic MBBR	15	Atrazine	Raschig rings	0.98	410	_	60	Atrazine: 74.8 COD: 99.2	Derakhshan et al. (2018)
Aerobic MBBR	223	Ammonia	AnoxKaldnes K5	0.95	800	Polyethylene	60	Ammonia: 22.8	Young et al. (2017)
Aerobic MBBR	12	Nitrogen	Cubic polyurethane sponge	0.028	-	Polyurethane	30	Total nitrogen: 86	Zhang et al., 2016
Aerobic MBBR	3.0	Pharmaceutical	AnoxKaldnes K5	0.95	800	Polyethylene	50	20%	Casas et al. (2015)
MBBR-MBR	40	Micropollutants in wastewater	Sponge cubes	0.028	-	Polyurethane	-	DOC: 94.7±0.5 NH4-N: 84.9±4.5 TN: 45.2±8.8	Luo et al. (2015)
Aerobic MBBR	6.0	Nitrogen, Phosphorus	Cubic shaped polyurethane foam	0.025	1120	Polyurethane	30	TN: 51 TP: 10	Feng et al. (2012)
Aerobic MBBR	15	Atrazine, carbon, nutrients	Raschig rings	0.98	410	-	50	Atrazine: 83 COD: 90 Nutrients:>85	Derakhshan et al. (2018)

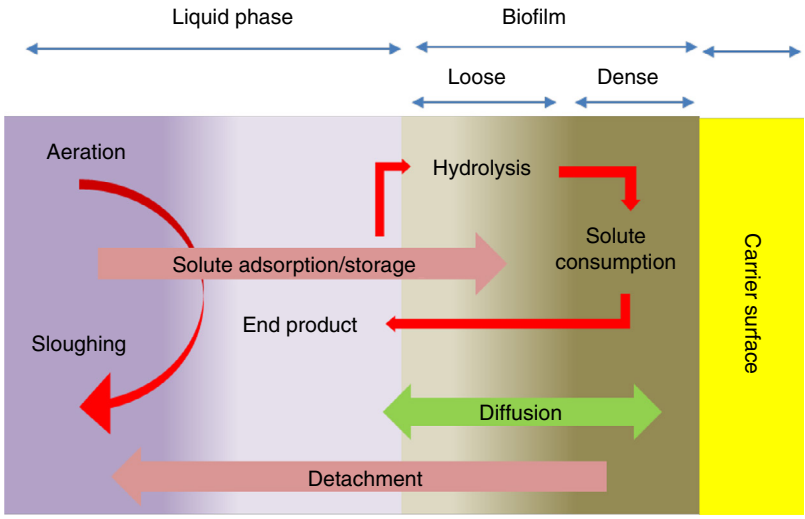

FIG. 15.3 Schematic diagram of nutrient diffusion through the developed biofilm into carriers.

and dense) through the formation of microcolonies and extracellular polymeric substances (EPS) production (Biase et al., 2019; Qureshi, 2009). The hydrolysis and diffusion of nutrients between liquid portion and biofilm occurred. After completion of metabolism, the end products are released back from biofilm to liquid phase.

The thickness of biofilm may vary from 10 μm to 1 mm, and it depends on the characteristic of carriers, inlet loading rate of pollutants, flow pattern, and the configuration of system (Mudliar et al., 2010). In addition, the carrier materials, HRT, rheological, and adhesive properties of a biofilm can also affect the growth of biofilm (Garrett et al., 2008; Nur et al., 2018; Partovinia and Rasekh, 2018). In this direction, Escudie et al. (2010) reported that the high shear force tends to the formation of thin, dense, and active biofilm under turbulent conditions. In contrast, the formation of fluffy and scattered biofilm takes place under laminar conations, which may be easily removed off during operation. The activity increases with increasing biofilm thickness up to a certain level (called active thickness). Beyond this thickness, the diffusion of substrate and nutrients becomes a limiting factor, hence the performance of the MBBR system adversely affected (Mudliar et al., 2010). The performance of the biofilm reactor was adversely affected because of the external and internal mass transfer resistance (Banerjee and Ghoshal, 2016).

15.3.3 Carrier filling fraction

The performance of the MBBR system is significantly affected by the carrier filling fraction (or ratio). The carrier filling fraction is referred to the ratio of volume occupied by carriers to the total volume of the MBBR. An increased carriers filling

fraction in the MBBR offers an enhanced available surface area for the biofilm formation (Adabju, 2013). The amount of carrier filling fraction in a MBBR mainly depends on the carriers characteristic, composition and loading rate of wastewater, and size and configuration of bioreactor. Generally, the carrier filling fraction of 20 to 70% is recommended in the MBBR for the treatment of municipal and industrial wastewater (Nur et al., 2018; Sonwani et al., 2020; Zhang et al., 2016).

The previous studies suggested that the performance of MBBR is adversely affected by filling the MBBR with carrier volume more than 70% because it leads to inadequate movement of carriers inside the bioreactor (Nur et al., 2018). Zhang et al. (2016) studied the effect of carriers filling fraction on the performance of MBBR containing cubic-shaped polyurethane sponges (15 × 15 × 15 mm) as carrier for the treatment of synthetic domestic wastewater. In their study, the total nitrogen removal of 77.2, 85.5%, and 86.7% were obtained with 10%, 20%, and 30%, respectively, of the carrier filling fraction. The effect of carrier filling fraction (in the range of 10 to 60%) for the biodegradation of Congo red dye was evaluated in the MBBR by Sonwani et al. (2020). They found that the dye removal efficiency improved as the carrier filling fraction was increased up to 45%, however, no further improvement in the removal efficiency was observed beyond that level of carrier filling fraction.

15.3.4 Aeration and mechanical mixing system

The main objective of aeration and mechanical mixing in MBBRs is to evenly distribute the biofilm carriers throughout the reactor to ensure proper mixing (Nur et al., 2018). Generally, the aeration and mechanical mixing are used in the aerobic MBBR, and a mechanical mixing is applied in the anaerobic MBBR. For aeration, the low-pressure air is passed through a grid of diffusers, which is attached at the bottom of the MBBR. The diffusers are generally made of stainless-steal or stone. The coarse-bubble diffusers are being less affected by scaling and fouling and preferred over fine-bubble diffusers (Mcquarriev and Boltz, 2010). However, the effective oxygen transfer efficiency (OTE) might be obtained using fine-bubble diffusers at the cost of scaling and fouling. Quan et al. (2012) used an MBBR (6.0 L) for the treatment of synthetic wastewater using polyurethane foam as carriers at 5 L/min rate of aeration with 30% of carriers. The mechanical mixing is used to agitate the bulk liquid along with the uniform distribution of biofilm carriers. Generally, the blade type impeller (with three blades in each impeller) is used to avoid the damage of biofilm developed into carriers (Mcquarriev and Boltz, 2010).

15.4 Effect of operating parameters

The operating parameters such as temperature, pH, inlet flow rate, and pollutant concentration affect the performance of a MBBR system (Sonwani et al., 2019). In order to maximize the performance of a scale-able MBBR system, the following operating parameters must be optimized.

15.4.1 Effect of organic loading rate

The performance of a MBBR system can be optimized by maintaining a suitable inlet organic loading rate which, in turn, can cause an effective interaction between the microbes and contaminants (Escude et al., 2010). It has been reported that a very high organic loading rate could reduce the interaction between the contaminants and microbes, resulting into a sluggish growth of microbes (Derakhshan et al., 2018e). Further, a high organic loading rate corresponds to a high substrate concentration which could cause substrate inhibition and toxicity towards the microbes, and finally result into a subdued performance of the bioreactor (Geed et al., 2017; Kureel et al., 2017). Therefore, the inlet organic loading rate in bioreactors must be monitored and optimized during the operation to avoid overloading and inappropriate/ineffective interactions.

Yadav et al. (2015) and (Geed et al. (2017) reported that the substrate biodegradation mechanism in a bioreactor changes from mass transfer control to bio-reaction control as the inlet loading rate is increased. The point of interaction between substrate removal efficiency and elimination capacity curve may be considered as an approximate operating loading range. Sonwani et al. (2020) studied the biodegradation of Congo red dye (of concentration 50 mg/L) at various inlet loading rates in a MBBR system and found that the performance of bioreactor enhanced up to the substrate loading rate of 80 mg/L.day, however, the performance of bioreactor reduced beyond that loading rate. The optimum operating range was obtained to be in the range of 60 to 72.3 mg/L•day of the inlet loading rate to yield a maximum removal of dye. In another work, Geed et al. (2017) studied the biodegradation of Malathion at deferent flow rates (in the range of 5.0-30 mL/h), and reported a window of the inlet loading rate as 144 to 165 mg/L.day for the optimum performance of a bioreactor.

15.4.2 Effect of hydraulic retention time

The hydraulic retention time (HRT) is a measure of the average duration of time that a soluble contaminant or compound remains in the bioreactor. It has a direct impact on the design, performance, and economic viability of a process (Metcalf and Eddy, 2003). It is calculated by dividing the volume of bioreactor by the inlet flow rate. The volume of the bioreactor and its compactness is directly related to the HRT (Almomani and Bohsale, 2020). Generally, bioreactors are designed to allow short HRT, which lowers the capital cost by reducing size of the bioreactor (Curtis, 2003). According to Derakhshan et al. (2018e), the minimum time required by a bioreactor to reach its favourable performance is referred as suitable HRT. The biodegradation of contaminants is the result of the interaction between microbes and contaminants. A short HRT could lead a less interaction, which lowers the performance of bioreactors (Banerjee and Ghoshal, 2016). Whereas, a long HRT increases the contact time between the contaminants and microorganisms, which favours the biodegradation of pollutants (Derakhshan et al., 2018a). However, a long HRT raises the size of a bioreactor and, therefore, fix the operating costs. Qaderi et al (2018) studied the

biodegradation of petroleum wastewater in the serial MBBRs. According to them, the microorganisms get sufficient time, at long HRT, to adopt for the wastewater environment and produce the suitable enzymes for the biodegradation.

15.4.3 Effect of temperature

The metabolic activity of microorganisms, and hence their performance towards biodegradation, is adversely affected with the temperature of the MBBR system. The temperature of the medium is responsible for controlling the nature and extent of microbial growth on carriers, degradation of substrate, internal and external diffusion of the substrate through biofilm, bioavailability, and solubility (El-naas et al., 2014). For example, the solubility of aromatic hydrocarbons increases with temperature and therefore enhances the bioavailability (Ghosal et al., 2016). According to Nur et al. (2018), the temperature affects the strength of hydrogen bonds and corresponding growth and thickness of the biofilm onto carrier or support matrix.

The previous works supported that the biodegradation potential of microbes increases with the temperature up to a certain level (Geed et al., 2017; Kureel et al., 2017). Therefore in order to achieve an optimum performance of the MBBR system, a suitable temperature range must be maintained. Most of the bacterial species could grow in the region of 20-45°C (El-naas et al., 2014). The effect of temperature (25-45°C) on the biodegradation of Chlorpyrifos was studied in a continuous biofilm reactor by Yadav et al. (2014). In their work, the maximum removal of Chlorpyrifos was obtained at 37°C. Kureel et al. (2017) examined the effect of temperature (25-43°C) against the biodegradation of benzene in a PBBR. They found that the optimum removal of benzene was achieved under 37°C.

15.4.4 Effect of pH

The variation of pH of the solution has a significant influence on the microbial growth and enzyme activity (Li et al., 2019). The microorganisms needed a suitable pH to produce the enzymes, which is responsible for the biodegradation of pollutants. The variation of pH either acidic or alkaline can change the ionic activity of the enzyme, and subsequently, their biodegradation efficacy for the pollutants (Lin et al., 2010). Therefore, it is very a serious concern to monitor and regulate the pH to accomplish an optimized growth of the microorganisms and biodegradation of the pollutants (Al-Hawash et al., 2018). Generally, the optimum growth of microorganisms has been found between 6.0 to 8.0 pH (Li et al., 2019; Lin et al., 2010). Rajamanickam et al. (2017) examined the effect of pH (in the range of 4.0 to 9.0) against the biodegradation of toluene by using mixed microbial consortia. The maximum toluene biodegradation rate was achieved at pH 6.85, whereas the lower biodegradation rate was obtained at acidic or strong alkaline conditions. Recently, Swain et al. (2020) have informed that the optimum removal of phenol was observed at pH of 6.5, and both the acidic and alkaline nature impeded the microbial growth and hence, hampered the biodegradation of phenol.

15.5 Mathematical models used in kinetics evaluation of the MBBRs

The mathematical models are helpful in predicting the performance of bioreactor, relation amongst different process variable (such as volume, HRT, influent and effluent concentration), design and scale-up the biological process from laboratory to industrial scale (Brink et al., 2017; Derakhshan et al., 2018a). Conventionally, the first-order, second-order, and modified Stover Kincannon models have been tested to evaluate the kinetics of various substrates degradation in the MBBRs (Ahmadi et al., 2015; Swain et al., 2020).

15.5.1 First-order kinetic model

In a complete mixed bioreactor, the change of substrate concentration can be expressed using the first-order equation as follows (Brink et al., 2017; Derakhshan et al., 2018e).

$$\frac{dS_F}{dt} = \frac{Q.S_O}{V} - \frac{Q.S_F}{V} - k.X.S_F \tag{15.1}$$

At the steady state, the substrate change (dS_F/dt) within the bioreactor is insignificant and Eq. (15.1) can be simplified as

$$\frac{(S_O - S_F)}{HRT} = k.X.S_F = k_1.S_F \tag{15.2}$$

Where S_O and S_F are the initial and effluent concentrations of substrate (mg/L), respectively. Q is the inlet flow rate of influent (L/h), V represents the working volume of the bioreactor (L), HRT is the hydraulic retention time (h) which is the ratio of bioreactor volume to inlet flow rate of influent, X the active bacterial concentration (mg VSS/L), k is the first-order kinetic constant (L/mgVSS.hr) and k_1 is the lumped first-order kinetic constant (1/h). The value of k_1 can be obtained from the slope of Eq. (15.2).

15.5.2 Second-order kinetic model (Grau model)

The change of substrate concentration based on the second-order substrate biodegradation in a bioreactor can be can be given as following (Brink et al., 2017; Swain et al., 2020).

$$\frac{dS_F}{dt} = \frac{Q.S_O}{V} - \frac{Q.S_F}{V} - k.X.\left(\frac{S_F}{SO}\right)^2 \tag{15.3}$$

Further, Eq. (15.3) is integrated to obtain a linearized Eq. (15.4).

$$\frac{S_O.HRT}{(S_O - S_F)} = HRT + \frac{S_O}{k_2} \tag{15.4}$$

Where k_2 is the lumped second-order rate constant (L/mg VSS. h). The term (S_O-S_F/S_O) is the substrate removal efficiency and can be represented as E. Furthermore, the term (S_O/k_2) can be donated as a constant (a) and the final Eq. (15.5) can be obtained as follows

$$\frac{HRT}{E} = b.HRT + a \tag{15.5}$$

Where a and b are the second-order kinetic constants.

15.5.3 Modified Stover-Kincannon model

A conventional Stover-Kincannon model (Eq. 15.6) was applied to evaluate the substrate removal rate in the RBC bioreactors (Sonwani et al., 2019).

$$\frac{dS}{dt} = \frac{Q.(S_O - S_F)}{V} = \frac{U_{\max}\left(\frac{Q.S_O}{A}\right)}{K_B + \left(\frac{Q.S_O}{A}\right)} \tag{15.6}$$

Where S_0 and S_F represent the influent and effluent concentrations of substrate (mg/L), V is the working volume of the bioreactor, Q is the inlet flow rate of influent (L/h). K_B, $U_{\max}$, and A are the saturation constant (mg/L.day), maximum substrate removal rate (mg/L.day), and film surface area (m^2), respectively.

For the case of a MBBR, the Eq. (15.6) was modified by replacing the area of biofilm (A) with the working volume of bioreactor (V), and the model is now referred as modified Stover-Kincannon model (Eq. 15.7) (Brink et al., 2017).

$$\frac{dS}{dt} = \frac{Q.(S_O - S_F)}{V} = \frac{U_{\max}\left(\frac{Q.S_O}{V}\right)}{K_B + \left(\frac{Q.S_O}{V}\right)} \tag{15.7}$$

Further, Eq. (15.7) is linearized and expressed in Eq. (15.8).

$$\frac{V}{Q.(S_O - S_F)} = \frac{K_B.V}{U_{\max}.Q.S_O} + \frac{1}{U_{\max}} \tag{15.8}$$

This modified Kincannon-Stover kinetic model has been used extensively for evaluating the kinetics of substrate removal rate in the MBBRs. Further, the substrate mass balance can be calculated using the following equation.

$$QS_O = QS_F + V\left(\frac{dS}{dt}\right) \tag{15.9}$$

Table 15.2 Profile of kinetic constants evaluated by modified Kincannon-Stover model in moving bed biofilm reactor.

Pollutants	K_B, (g/L.day)	U_{max} (g/L.day)	R^2	References
Diethyl phthalate	37.10	32.57	0.99	Ahmadi et al. (2015)
Diallyl phthalate	47.83	41.15	0.98	
Phenol	11.14	20.12	0.99	Brink et al. (2017)
Atrazine	0.012	0.007	0.93	Derakhshan et al. (2018b)
Atrazine	0.338	1.716	0.98	Derakhshan et al. (2018c)
Naphthalene	0.769	0.874	0.99	Sonwani et al. (2019)
Congo red dye	0.263	0.253	0.99	Sonwani et al. (2020)

The combination of Eqs. (15.7) and (15.9) yields the following result (Eq. 15.10)

$$QS_O = QS_F + \frac{U_{\max}\left(\frac{QS_O}{V}\right)}{K_B + \left(\frac{QS_O}{V}\right)} \times V \tag{15.10}$$

Finally, Eq. (15.10) can be used to predict the outlet concentration of dye (Eq. 15.11) and the required volume of a MBBR (Eq. 15.12).

$$S_F = S_O - \frac{U_{\max} S_O}{K_B + \left(\frac{QS_O}{V}\right)} \tag{15.11}$$

$$V = \frac{QS_O}{\left(\frac{U_{\max} S_O}{S_O - S_F}\right) - K_B} \tag{15.12}$$

A summary of kinetic constants obtained by the modified Kincannon-Stover model for the biodegradation of various pollutants in the moving bed biofilm reactor is given in Table 15.2.

15.6 Recent applications of MBBRs in the wastewater treatment

15.6.1 Treatment of the emerging contaminants in MBBRs

In the last few years, the presence of emerging contaminants (ECs) in water bodies has become a new environmental concern to the researchers due to their associated threats and impacts to both aquatic life and human health (Sutherland and Ralph, 2019). The ECs can be defined as the synthetic chemical substances that have no current

regulation, and they could be exhibiting potential risks to the human health or environment (Zhang et al., 2020). The substance such as artificial sweeteners, pesticides, pharmaceuticals, personal care products (PCPs), flame retardants, plasticizers, illicit drugs, endocrine-disrupting compounds (EDCs), and other several industrial chemicals are considered as ECs (Sutherland and Ralph, 2019). Amongst these ECs, the pesticides and pharmaceuticals have received a large visibility as they are highly persistent to the environment and have toxic and carcinogenic effect on the human health (Derakhshan et al., 2018a; Zhang et al., 2020). Therefore, these contaminants must be removed or treated before discharging them into the environment. In this section, the MBBR technology used to remove ECs from wastewater has been briefly discussed.

Recently, the pharmaceuticals and personal care products (PPCPs) namely, sulfadiazine, ibuprofen, and carbamazepine were treated in four lab-scale MBBR bioreactors (Zhang et al., 2020). A polyurethane sponge-based material was used as carrier in the bioreactor. The results indicated that the removal efficiencies of sulfadiazine, ibuprofen, and carbamazepine were obtained as 61.1 ± 8.8%, 74.9 ± 8.8%, and 28.3 ± 7.4%, respectively. Further, the performance of bioreactors was found to be adversely affected when the concentration of PPCPs. was exceeded. The performance of a MBBR was also evaluated during the treatment of wastewater containing a pesticide such as atrazine (Derakhshan et al., 2018a). The process variables, atrazine concentration (1.0-10 mg/L) and HRT (6.0-24 h), were optimized using the response surface methodology (RSM). The maximum atrazine removal efficiency of 83.57% was obtained with 10 mg/L of atrazine concentration and 24 h of HRT. The effect of salinity (NaCl) on the performance of a MBBR was also examined. It was reported that a high concentration of NaCl (40 mg/L or higher) inhibited the atrazine removal efficiency. The kinetics of substrate removal rate was examined by employing the modified Kincannon-Stover kinetic model. The kinetic constants K_B (g/L.day) and $U_{\max}$ (g/L.day) were estimated as 0.338 and 1.716, respectively. In another study, the pharmaceutical wastewater contaminated with clindamycin was treated in a MBBR with 40% of AnoxKaldnes™ K5 carriers (Ooi et al., 2017). They also found the MBBR very effective in the treatment of clindamycin, and reported clindamycin sulfoxide as the main intermediate product. Similarly, Casas et al. (2015) studied the biodegradation of a pharmaceuticals wastewater containing X-ray contrast media, b-blockers, analgesics and antibiotics, and other compounds in the three MBBRs in series. The experiments were performed in both the batch and continuous modes. The pharmaceutical removal rates were found to be higher in the batch mode as compared to the continuous mode.

15.6.2 Treatment of the persistent organic contaminants in MBBRs

The industries such as petroleum refinery, petrochemicals, textile, pulp and paper, and leather discharged enormous amount of wastewater containing various organic pollutants (e.g., mono and polycyclic aromatic hydrocarbons (MAHs and PAHs), dyes, surfactant, solvents, etc.) (Bharti et al., 2019; Zheng et al., 2016; Derakhshan et al., 2018e). Among these pollutants, the PAHs have been underscored as highly

hazardous and persistent organic contaminants by the international environmental legislations (Sakulthaew et al., 2014; Sonwani et al., 2018). The health and environmental threats of the PAHs has been well reported in the literature as they cause toxic, carcinogenic, and mutagenic effects to human health and the ecosystem (Lang et al., 2016; Pugazhendi et al., 2017). The MBBR technology has also been tested in the literature to remove various such contaminants in a cost-effective manner (Qaderi et al., 2018). Sonwani et al., 2019 used three types of carriers namely PP, LDPE-PP, and PUF-PP in a lab-scale MBBR for the removal of PAH (i.e., naphthalene). The process parameters namely, pH (5.0-9.0) and HRT (1.0-5.0) were optimized using the RSM tool, and optimum pH and HRT were found to be 7.0 and 5.0, respectively. The MBBR filled with PUF-PP showed the highest removal efficiency of naphthalene ~90.2%) as compared to the MBBR filled with PP (72.4%) or LDPE-PP (84.4%). Qaderi et al., 2018 used two MBBRs in series for the treatment of petroleum wastewater. The "Bee Cell 2000" media made of HDPE with a density of 0.96 g/cm^3 was used as carriers in the MBBR. The process variables including HRT (11.2-34.7 h), total petroleum hydrocarbon (164.7-585.2 mg/L), and media filling fraction (28.1-61.8%) were optimized using the RSM. The petroleum hydrocarbon removal efficiency increased with increasing the HRT and carriers filling ration, whereas the petroleum hydrocarbon concentration showed a negative effect on the removal efficiency. The maximum removal efficiency of 97% was obtained at the optimum condition with HRT of 23 h, petroleum hydrocarbon of 164.7 mg/L, and the media filling ratio of 45%. Oberoi and Philip, (2017) have used the MBBR for the treatment of AHCs and phenolic compounds. They reported that the removal efficiencies of AHCs and phenolic compounds were achieved to be 90 and 85%, respectively, at HRT of 24 h and OLR of 2.45 kg/m^3.day. In addition, the removal efficiencies were reduced with increasing the organic loading rate. In another work, a MBBR packed with Peenox^{TM} carriers was used to treat the PAHs contaminated wastewater, and the suitability and effectiveness of the MBBR was again endorsed for the treatment of PAHs (Demeter et al., 2017).

15.7 Conclusions

This chapter highlighted an overview on the MBBR technology and its operating benchmarks for the effective abatement of ECs and POCs present in the wastewater. A large number of MBBRs have been successfully used in the literature for the abatement of a wide range of contaminants. The previous studies suggested that the highest performance of the MBBR could be achieved by operating the bioreactor at optimum processes conditions. A MBBR technology is acknowledged as a fitting candidate for the removal of emerging contaminants because of many merits (such as effective mass transfer, less clogging, no need of sludge recirculation, low HRT, and straightforward and ecofriendly approach). Although, the amount of biomass (mg/L) can be increased by increasing the carrier filling ratio in the bioreactor, the continuous mixing of the high load of carriers could be highly energy intensive at large scale.

The recent integration of a MBBR with the advanced MBR (a hybrid MBBR-MBR) is an emerging field and could be a promising candidate for further optimizing the wastewater treatment technology.

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Further readings

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CHAPTER

16 An application of bionanotechnology in removal of emerging contaminants from pharmaceutical waste

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16.1 Introduction

As population growth increases, requirements of medicines and health care products also increase to recover from or prevent illness and diseases. This enhances and promotes production of different pharmaceutical and medical product as well. Waste that is generated from pharmaceutical industries or health care centers are sometimes released in to environment without treatment due to lack of proper techniques or treatment methods. This poses many problems as the half life of pharmaceutically active compounds is different for different molecules. Pharmaceutical waste is a material having prescribed utilized or unutilized out dated expired medicines and products related to personal care (Shannon & Woolridge, 2011). Products which are disposed after research in clinical laboratory are also sometimes also known as pharmaceutical waste. According to data released by World Health Organization (WHO), 2018 about 85% waste is general or nonhazardous and 15% is hazardous which may be infectious, radioactive or toxic.

Sources of pharmaceutical waste are research laboratories, hospitals, autopsy center, nursing home, blood bank, testing laboratories of animals and birds, and mortuary. Hospital generate 0.5 kg of hazardous waste is generated by developed countries, while approximately 0.2 kg of waste is generated in developing countries per bad per day. There are different types of waste— (1) infectious wastes, (2) pathological wastes, (3) sharpe wastes, (4) chemical wastes, (5) pharmaceutical wastes, (6) cytotoxic wastes, (7) radioactive wastes, and (7) general wastes.

Pharmaceutical waste water has different characteristics based on their origin and discharge. Waste water discharged from pharmacy company which synthesize medicines, is with low amount of nutrition, not easily degradable by microflora and with risk

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towards natural microbes. Waste water released from biopharmaceutical sources has complex nutritional composition and sulphate concentration high too (Guo et al., 2017).

Pharmaceutical waste water mainly consists of antibiotics, pharmaceutically active compounds, various hormones, organic compounds, which may be volatile (Carballa et al., 2008). Some compounds are present in waste water with high concentration due to their regular worldwide usage. For example, caffeine residues were detected with high concentration in sewage (Gao et al., 2016). Macrolides were also detected with high concentration in sewage as they are mostly excreted in their unmetabolized form of 60% (Le-Minh et al., 2010). Active pharmaceutical compounds are mostly polar and have molecular weight from 200 Da to 1000 Da (Pal, 2018).

Burning of pharmaceutical waste in open condition results in release of furans, dioxins, and particulate matter. Result of unintentionally released waste in environment lead to development of drug resistance and release of chemical or microbial hazardous which affects health of workers, patients, doctors, public, or other living beings (Guo et al., 2017). Active pharmaceutical compounds can prove pathogenic indirectly as various microbes can naturally cultivate on these compounds. Some pharmaceutical compounds are able to interfere with normal regulatory process in living organisms, even when they are presence with very minute concentration (Ankley et al., 2007). Antibiotics used as animal feed supplement or in agricultural sector are anthropogenic as they are excreted or released back to the environment without metabolization (Kurwadkar et al., 2015). Some studies indicate the presence of endocrine disrupting pharmaceutical compound in tap or drinking water (Hughes et al., 2013). On earlier time between 1970 to 1990, pharmaceutical compounds were detected in aqueous bodies (Patel et al., 2019).

16.2 Methods for treatment of pharmaceutical waste water

Different physical and biological methods are used for treatment of emerging pharmaceutical waste containing water. Autoclaving of physical method include sterilization at high temperature. It is useful for degradation of antibiotics present in waste water, as antibiotics are mostly sensitive for denaturation towards high temperature (Hossain et al., 2011). Advanced oxidation process utilizes oxidizing agents like UV light, ozonation, ultrasonication, and electrolysis. Advanced oxidation process is efficient in removal of personal care products and drugs like carbamazepine (Pal, 2018). Used precipitation method for pollutants removal shows better removal efficiency of COD than coagulation. Different flocculants are generally used for removal of phosphate from waste like CaOH and $FeCl_3$. Ion exchange and adsorption are other physicochemical methods used for treatment (Cheng et al., 2007). After coagulation sedimentation is commonly used which involves separation of waste material based on their density (Guo et al., 2017). Adsorption of pharmaceutical compounds depends on factors like pH and functional groups of adsorptive material and compounds. Electro coagulation applied electric current and coagulating agents

having hydroxyl group which provides flocks formation through good surface area (Pal, 2018). Activated carbon is used for physical and chemical adsorption of wastes. Activated carbon has porous structure and high surface area. Oxidation at supercritical water condition involves reaction between pharmaceutical waste and dissolved oxygen of water. This method is advantageous as it does not produce secondary pollution (Guo et al., 2017).

Biological methods utilizes microbes to remediate or degrade pharmaceutical wastes in to less toxic or nontoxic compounds. Vermicomposting utilizes digestion of solid waste by worms. Vermicomposting of herbal pharmaceutical compounds through *E. foetida* results in stable and odorless end product (Singh & Suthar, 2012). Anaerobic digestion and co digestion are used for degradation of pharmaceutically active compounds like diclofenac and atenolol (Pal, 2018). Wetlands which are constructed artificially can solve the problem of mixing of pharmaceutical waste water with other sewage or waste water. Activated sludge is effective for removal of 68% tetracycline and 67% doxycycline (Karthikeyan & Meyer, 2006). Bio augmentation involves either addition of microbes to an activated sludge or extraction of specific type of pharmaceutical pollutant from waste water to treat it with microbes. Biotransformation used for treatment of pharmaceutical waste water involves modification or conversion of pollutant compounds (Pal, 2018; Patel et al., 2021).

Pharmaceutical waste removal through membrane involves microfiltration, ultra filtration, reverse osmosis and electro dialysis. In microfiltration, ultrafiltration and reverse osmosis pressure difference is the main factor for process operation. In electro dialysis electric current is used for waste removal. Membrane bioreactor have advantages of high sludge retention time, parameter controlling facility and high waste water volume accommodation capacity. Membrane bioreactor has more than 95% COD removal capacity. Each of these techniques has some limitations. For example, sedimentation requires large quantity of chemicals. Ion exchange requires replacement of column due to blockage problem. Autoclaving and solvent extraction consumes high costing as well as energy. Waste water treated with adsorption process needs further treatment and effluent is discharged untreated, it will cause another problem of toxicity (Pal, 2018). Modifications and variation of these conventional treatment methods can eliminate various limitations.

16.3 Different nanomaterials and treatment of pharmaceutical waste water

Nanotechnology is nowadays used for treatment of different waste water or waste or pollutant material, having developed manometer sized materials. Nano sized compounds have dimension generally less than 100 nm (Amin et al., 2014). Nanoadsorbents, nanocatalyst, nanomembranes, nanoparticles, and hybrid nanomembranes were developed for decontamination and removal of pharmaceutically emerging active compound from waste water (Fig. 16.1).

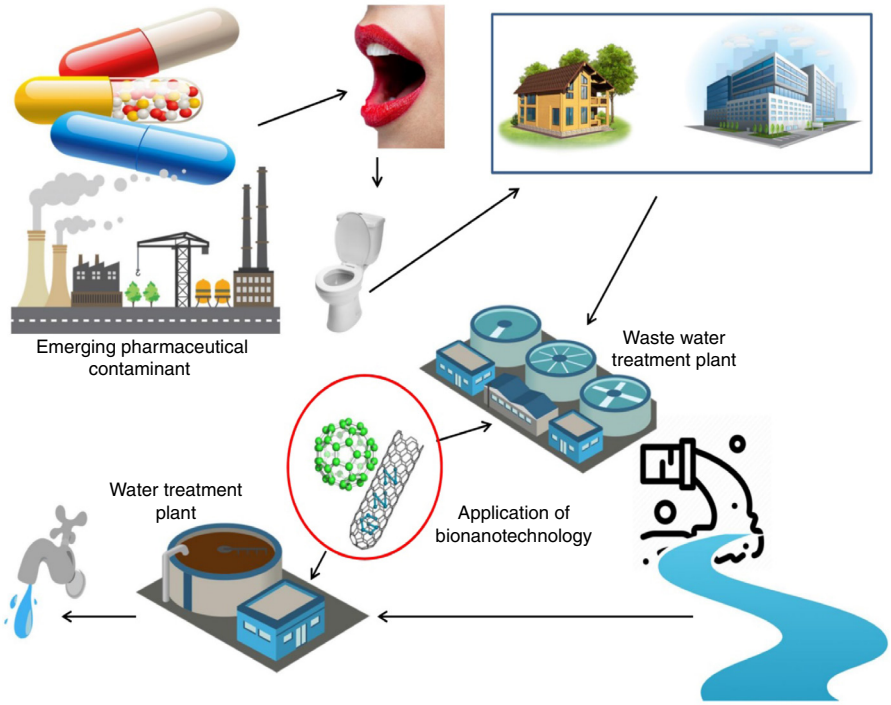

FIG.16.1 Overview on application of bionanotechnology to remove emerging pharmaceutical contaminant.

16.3.1 Nanofilter membrane bioreactor

With comparison of other technologies used in waste water treatment membrane bioreactors having advantages of easy and controlled operating conditions, less energy consumption and production of good quality of effluent which can be released in environment. Influent or feed is passed through inlet in to MBR, it is filtered out in two way passage. One flow is passed through membrane known as permeate and flow doesn't pass out from membrane is known as retardant or rejected. Nanomembrane bioreactor contains membranes having pore size in nanoscale. Sometimes these membranes have different type of configurations like nanoribbons, nanotubes and nanofibres (Lin et al., 2014; Patel et al., 2020).

Zaviska et al., 2013 (Zaviska et al., 2013) developed membrane bioreactor of nanofiltration having a new type of ceramic material membrane to investigate treatment of ciprofloxacin and cyclophosphamide. Results indicate that TSS and COD removal was efficient with retention of small fraction of these two pharmaceutical compounds.

Total 27 pharmaceutical active compounds were studied through pilot scale stainless steel membrane bioreactor having constant temperature and flow rate of

air 630 L/min. comparative study for these compounds was carried out using only membrane bioreactor (MBR) and with combination of nanofiltration membrane bioreactor (NF MBR) and reverse osmosis membrane bioreactor (RO MBR). Use of only membrane bioreactor was with limitations for removal of biologically persistence and hydrophilic organic compounds, which was overcome by NF MBR and RO MBR. Carbamazepine, metoprolol, norfloxacin, and enorfloxacin removal rates were lower with only MBR, while it was increased when combined with NF system. Below the detection limit total 13 pharmaceutical compounds could be eliminated by NF MBR with 95% removal efficiency. Membrane charge, molecular weight of pharmaceutical compounds present in waste water, charge of compounds and hydrophobicity are affecting parameters of NF MBR (Wang et al., 2018; Patel et al., 2021).

Wei et al., 2018 (Wei et al., 2018) studied rejection capacity of 6 different pharmaceutical compounds using membrane of hollow fiber, one having positive charge and another having negative. PEI nanofiltration membrane having Isoelectric point of 8.2 was prepared from polyethyelnimine and trimesoyl chloride, PIP nanofiltration membrane was prepared from piperazine and trimesoyl chloride having isoelectric point of 6.6. Rejection rate for six selected pharmaceutical compounds primidone and carbamazepine which are anti convulsant, sulfamethoxazole an antibiotic, atenolol a beta blocker, sulfadimidine an antibacterial antibiotic and norfloxacin an antibiotic observed by PEI nanofiltration membrane were 85.6, 91.8, 79.9, 98.1, 93.3 and 97.1%, while for for PIP nanofiltration membrane they were 82.2, 85.4, 91.5, 79.1, 87, and 93.3%, respectively. Thus, from this study it can be said that for sulfamethoxazole rejection through PIP nanofiltration membrane is more effective and efficient than PEI nanofiltration membrane. Moreover, from this study it can also be concluded that rejection rate of pharmaceutical waste increases as operating pressure increases due to increased density of membrane selective layer.

As nanofiltration is dependent on pressure gradient for rejection or separation of pharmaceutical waste, following equation can be given for water flux in NF membrane bioreactor (Wei et al., 2018).

$$Jw = -A(\Delta P - \Delta\pi)$$

Where;

Jw = Flux of water

A = Permeability constant of water

ΔP = Pressure difference of hydraulic across the NF membrane

$\Delta\pi$ = Pressure difference of osmosis across the NF membrane

From above equation, it is concluded that water flux across the membrane increases, as operating pressure increases.

$$Js = -B\Delta Cs$$

Where;

Js = Flux of the solute

B = Permeability constant of solute

ΔCs = Concentration difference of solute across the NF membrane

From above equation it can be said that solute flux is dependent on its concentration difference across the NF membrane and not on operating pressure difference.

Kamrani and Akbari, 2018 (Kamrani & Akbari, 2018) studied removal of diphenhydramine and mebeverine rejection using acrylic NF membrane which is modified using chitosan, an antifouling component. Using this modified thin film composite membrane, rejection rate for diphenhydramine was obtained with 97% and for mebeverine it was approximately 98%. Nghiem et al., 2005 (Nghiem et al., 2005) studied retention of sulfamethoxazole, carbamazepine and ibuprofen by two types of NF membrane, one was tight and other was loose. From results it is concluded that size exclusion is the main key factor for rejection of these three pharmaceutical compounds in tight type NF membrane. Good rejection was also observed with negatively charged compounds present in influent.

Foureaux et al., 2019 (Foureaux et al., 2019) gave comparative profiling of NF and RO performance for treatment of drinking surface water containing salinity and pharmaceutical compounds. Detected five compounds fluconazole, prednisone, betamethasone, phenylutazone and metformin removal was considered in this study. NF membranes have better rejection ability of pharmaceuticals due to less fouling and high flux of permeate. Moreover energy consumption was also less in NF membrane compared to RO. From utilized different NF membranes in DK type nanofiltration membrane, rejection rate of fluconazole, phenylutazone and metformin were 99.32, 98.19 and 99.06%, respectively. DK type NF membrane also showed good desalting capacity.

16.3.2 Nanoadsorbants

Nano adsorbants are utilized for removal of different water contaminants. Activated carbon, different nanoparticles, nanotubes of carbon and Graphene are used as nanoadsorbants. Adsorption of pharmaceutical compounds depends on factor coefficient of adsorption Kd. In aqueous environment different factors affect adsorption process like surface area, pH, temperature, resistance of internal diffusion, particle charge and binding energy (Khajeh et al., 2013). Advantage of nanoadsorbents is that they can be further utilized many times after recycling. High surface area can be achieved through small sized particles for efficient removal of emerging pharmaceutical compounds from waste water (Gubin et al., 2005).

Graphene is another different 2 D form of carbon having high potential utility in waste water treatment field. $\pi - \pi$ interaction in graphene is mainly responsible for removal of inorganic and organic pollutants. Ciprofloxacin adsorption is higher in activated graphene having surface area of 512.65 m^2/g compared to chitosan added graphene oxide which has surface area of 388.3 m^2/g (Fanourakis et al., 2020).

Magnetic graphene nanoplatelets have adsorbance capacity of amoxicillin 14.1 mg/g with surface area of 543.2 m^2/g. Ciprofloxacin adsorption was studied using different nanoadsorbant. Oxides of graphene (GO), functionalized GO having noncovalent interaction and composite GO which is magnetically grafted with chitosan, has adsorption capacity of ciprofloxacin 74%, 96.2%, approximately 95% respectively. Adsorption ability of analgesic diclofenac was greater than 80% using hydrogels having reduced GO in 3 D form. Carbamazepine which is anticonvulsant, adsorbed by graphene, nanocomposite of graphene, heteroconjugate complex of

graphene oxide+ Bi^2O^3+TiO^2+$Bi^2Ti^2O^7$ and graphene oxide reduced with TiO^2 with rate of 97%, 100%, greater than 99% and 54% sequentially (Fanourakis et al., 2020).

Sotelo et al., 2012 (Sotelo et al., 2012) studied adsorption efficiency of endocrine disruptor and pharmaceutical compounds by activated carbon, carbon nanotubes having multiple wall and nanofiber of carbon. This study indicated higher adsorption capacity of all three nanoscaled compounds for caffeine, isoproturon, atenolol, and diclofenac. Adsorption of pure compound was higher than the real waste water, which indicates impact of other materials either organic or inorganic on adsorption.

There is some mechanism models proposed for adsorption of compounds on nanomaterial. One is Langmuir model, according to which adsorption is specific and it is monolayer reaction. Adsorption equilibrium of pharmaceutical waste or other wastes compound on nanoscale materials can be given by following equation for Langmuir model (Bushra et al., 2016).

$$C_e / q_e = (1/b)^* (1/K_L) + (1/b)^* (C_e)$$

Where;

C_e = Concentration equilibrium (mg/L)
q_e = Adsorption of sorbent (mg/g)
K_L = Equilibrium constant of Langmuir
b = Capacity of monolayer

Isotherm model of Freundlich is used to study adsorption of pharmaceutical waste when nanoscale surface is heterogeneous and adsorption is multilayered (Adamsom & Gast, 1997). From following equation one can calculate adsorption for multiheterogeneous layer adsorption reaction.

$$\ln q_e = \ln K_f + 1/n \ln C_e$$

Where;

$1/n$ = Intensity of sorption
K_f = Constant of Isotherm for Freund5lich reaction

By increasing or decreasing the concentration of compounds, adsorption mechanisms can be made dependent on either first power of reactant or on second power of reactant. Thus, this alteration of adsorption by modifying compounds concentration or dilution can be calculated using following equations (Adamsom & Gast, 1997).

$$(\text{Pseudo first order kinetics}) \ln(q_e - q_t) = \ln q_e - k_1 t$$

Where;

q_e and q_t = Compounds adsorbed at time t and at equilibrium (mg/g)k_1 = Rate constant of first order (min^{-1})

Pseudo second order kinetics is based on the assumption that chemisorptions are the rate controlling step.

$$t / q_t = 1 / K_2^* q_e^2 + 1 / q_e^* t$$

$$h = K_{2^*} q_e^2$$

Where;

h = Adsorption rate at initial stage (mg/g/min)

K_2 = Pseudo second order rate constant (g/mg/min)

During adsorption equilibrium is established between adsorbent and waste solution used for treatment, this equilibrium can be calculated using given equation (Sadegh et al., 2017).

$$q_e = V(Co - Ce)/m$$

where;

q_e = Equillibrium of adsorption

V = Volume of solution (L)

Co = Adsorbent concentration at initial stage (mmol/g)

Ce = Adsorbent concentration at equillibrium stage (mmol/g)

m = Adsorbent mass (g)

Low surface are of carbon nanotube hinders the adsorption of pharmaceutical wastes. Dry etching treatment of carbon nanotube having single wall and multiple wall enhance adsorption of various antibiotics 2 to 3 times better than previous one. Due to dry etching treatment with potassium hydroxide surface area of single wall carbon naotube increase from 410.7 m^2/g to 652.8 m^2/g and for multiple wall it is increased from 157.3 m^2/g to 422.6 m^2/g (Ji et al., 2010). Kariim et al., 2020 (Kariim et al., 2020) developed multi walled carbon nanotube having nickel ferrite via impregnation process for adsorption of levofloxacin and metronidazole. From study can be concluded that it is pseudo first order kinetic process.

Parashar et al., 2020 (Parashar et al., 2020) studied rejection of oxcarbazepine from waste water using magnetic nanoparticles of iron oxide. Value of Gibbs free energy and enthalpy indicate that adsorption of pharmaceutical compound oxcarbazapine is spontaneous endothermic physical adsorption process. Moreover this study also indicates that adsorption is dependent on temperature, pH, initial oxcarazapine concentration and speed of agitation. From analysis it can also be said that this adsorption process is pseudo second order kinetic reaction.

Whether the reaction of adsorption is spontaneous or not can be determined from enthalpy and Gibbs free energy change (Parashar et al., 2020).

$$\Delta G^\circ = -RT\, ln\, b$$

Where;

ΔG° = Change in Gibbs free energy (kJ/mol)

R = Gas constant (8.314 J/mol K)

T = Absolute temperature of solution (K)

b = Equilibrium constant

$$\Delta H = -R(T_2 T_1)/(T_2 - T_1) ln(b_2/b_1)$$

Where;

ΔH = Standard change in enthalpy (kJ/mol)

16.3.3 Nanocatalyst

Nanocatalyst used for treatment of emerging pharmaceutical waste water may be photo catalyst or electro catalyst. Photo catalyst works on oxidation process by producing reactive oxygen species. Photo catalyst degrades waste material in the presence of light. In this process electrons migrated to conduction band which are originating from valence band. Electron migration is possible due to high energy containing photons. Compounds from which electrons emerge are oxidized and released electrons can react with water molecule or pollutants present in waste water. Photon emission and transfer can be enhanced using diodes and optical fibers. Redox reaction occurs due to nanocatalyst interaction with photon can be given using following equations (Yaqoob et al., 2020).

$$\text{Nanocatalyst} + \text{hn} \rightarrow \text{electron} + \text{hole}$$

$$\text{Electron} + \text{oxygen} \rightarrow \text{superoxide radicals}$$

$$H_2O + \text{hole} \rightarrow OH^- + H^+$$

When nanocatalyst absorbs energy from photon electron hole pair is generated, from which electron combine and interact with oxygen and produce superoxide radicals. Generated hole interact with water and produce hydroxyl ions radical.

Several factors like pH, wavelength and intensity of radiation, pollutant concentration and type, concentration of catalyst and water affect the process of photo catalysis. Mostly TiO_2 and ZnO nanoparticles are used to treat different waste water. There are many advantages of TiO_2 nanoparticles like they are non toxic, have high surface are, it is economically affordable, stable and porosity can be increased according to need (Bonelli et al., 2017). It can remove 68% of chlorhexidine digluconate under the influence of UV light and at alkaline pH condition (Das et al., 2014). Nanocatalyst based on copper and sulphide of metals is prone for photo corrosion (Weng et al., 2019). pH is also an important factor which affects pharmaceutical waste removal. For example with UV radiation degradation of three antibiotics ampicillin, amoxicillin, and cloxicillin was high at pH value of 11 in the presence of TiO_2, while complete degradation was achieved at pH 5. This acidic pH was obtained using hydrogen peroxide (Elmolla & Chaudhuri, 2010).

Another nanocatalyst used for emerging pharmaceutical removal is ZnO. Within three hours it can totally degrade antibiotics ampicillin, amoxicillin and cloxicillin with 23.9% removal of COD (Elmolla & Chaudhuri, 2010). Nanoparticles of ZnS are able for removal of β lactam antibiotics at pH 4.5 (Pouretedal & Hasanali, 2013).

There are mainly two ways by which photocatalyst remove emerging pharmaceutical pollutant compound. One is mineralization and another is degradation. In mineralization pharmaceutical waste is completely converted in to CO_2, H_2O, and other inorganic by product compounds. While in degradation process pharmaceutical wastes are degrade in to many type of degraded products (Umar et al., 2012); (Umar et al., 2013).

El-Maraghy et al., 2020 (El-Maraghy et al., 2020) studied removal of antibiotic levofloxacin using nanoparticles of ZnO, graphen oxide, and both in combination.

Graphen oxide nanoparticles were utilized in the form of sheet of ultrathin size 5nm and ZnO nanoparticles of 17nm with spherical shape structure. Combination of both these structures was able to remove levofloxacin with 99.2% and 99.6% for initial concentration of 50 μg/ml and 400 μg/ml respectively. Removal of levofloxacin is primarily affected by type of nanoparticle. Antibiotic removal efficiency can be calculated using following equation.

$$\text{Percentage of removal} = \left(C' - C\right) / C'^{*} 100$$

Where;

C′ = Initial concentration of antibiotic

C = Concentration of antibiotic after treatment

As every coin has two sides, application and use of nanomaterials for emerging pharmaceutical removal has advantages and limitations too. It is shown that sometimes nanoscale materials have self toxicity. Nanomaterials made up of titanium dioxide and aluminum oxides are more toxic if they have micrometer sized configurations (Wang et al., 2008). Composite nanorod of gold and CTAB are toxic at higher concentration (Takahashi et al., 2006). Above the concentration limit of 15 μg/cm nanotubes having single or multiple wall showed increased toxicity (Taju et al., 2014). But careful used and searching of other new techniques or ways to prevent these harmful effect can make use of nanobiomaterial applicable with less or no disadvantages. For example composite of gold and carbon are nontoxic at lower concentration (Jia et al., 2005).

16.4 Conclusion

To prevent and cure various human and veterinary disease, to control various endemic and epidemic disease production of pharmaceutical compound is necessary. Waste released after production of pharmaceutical compound contains many residues, which are harmful in many ways. These active or degraded pharmaceutical residues enter living organisms body through drinking water, milk, or via food if not properly treated and causes various harmful effects like allergic reaction, side effects, antibiotic resistance or organ failure. Based on study and review it can be outlined that use of bionanomaterial or nanomaterial has been prove effective to treat waste water having novel or traditional pharmaceutical compound. From this study we can conclude that developed NF MBR can efficiently remove various antibiotics from artificial and natural waste water like ciprofloxacin, carbamazepine, norfloxacin and cyclophosphamide. Moreover it can also be concluded from this study, by controlling various parameters of NF MBR one can enhance efficient removal of emerging pharmaceutical waste like pressure gradient, flux rate, temperature, etc. Another type of mechanism for emerging pharmaceutical waste removal is adsorption through activated carbon, carbon nanotube and nanoscale fibers are effective for adsorption of diclofenac and atenolol. Nanoparticles which act as nanocatalyst has also been proved effective for mineralization or degradation of pharmaceutical

pollutant compound. Thus by optimizing various parameters and choosing correction method having less limitations one can use nanobiotechnological tools for efficient removal of emerging pharmaceutical waste from drinking water, municipality water or from other waste water.

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CHAPTER

17

Removal of emerging contaminants in water treatment by an application of nanofiltration and reverse osmosis

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17.1 Introduction

Any unwanted material present in the environment having negative detrimental effect at individual level or at all levels of different spheres is known as contaminant. Contaminants can be natural or manmade based on their source of origin. Contaminants can be solid, liquid or gaseous in their physical form (Ramstorp, 2008). They can be industrial or pharmacological chemicals, biological origin or pathogenic materials and radiological. Based on origin of source they are also classified as point emerging contaminants and diffused one. Origin of pollutants is known and easy for identification in point type while in diffused type origin or source of contaminant is not known. Point source originating contaminants are low volatile and highly soluble. So, they cannot be easily degraded. Example of point source originating pollutants include waste water of industries, municipalities, landfill contaminations, and leakage of septic tanks. Contaminants from various land like agricultural sector and water runoff are examples of diffused type source of origination of contaminants. 80% of marine pollution is due to land surface material run off (Stefanakis & Becker, 2016).

There are some particular types of contaminants which do not found in environmental sphere regularly or previously, but they create and shows their toxic effect when enter to the environment. These types of contaminants are known as emerging contaminants (EC) (Rosenfeld & Feng, 2011). Emerging contaminants are mostly xenobiotics. Emerging contaminants released from different sources, such as various industries, hospital, houses, agricultural sectors, poultry farm, and waste water from treatment plants accumulating in surface water and running off into ground water, fresh water, and marine water with rainfall (Patel et al., 2021). If this type of water contain harmful

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compounds not treated properly, they are accumulated, magnified, and absorbed at different tropic level. Consumption of this contaminated water causes illness to various life forms at pathological risk level (Stefanakis & Becker, 2016).

Emerging contaminants are categorized in to various groups. (1) Personal care products include mosquitoes repellents, fragrance powders, various skin lotions having nitro and polycyclic compounds, benzophenone, camphor, N,N-diethyltoluamide and macrocyclic musks; (2) pharmaceutical products and their intermediates include antibiotics, psychiatric medicines, lipid regulators, antiinflammatory medicines, β blockers, and X ray contrasts having amoxicillin, norfloxacin, chloramphenicol, primidone, diazepam, clofibric acid, etofibrate, diatrizoate, metoprolol etc.; (3) steroids and hormones include estrone and estradiol; (4) perfluoronated compounds (PFCs) further classified as perfluoroctanoic acids (PFOA) and perfluorotoctane sulfonates (PFOs); (5) endocrine disrupting chemical (EDCs), such as nonylphenols, octylphenols and Di(2-ethylhexyl) phthalate (DEHP); (6) Flame retardants such as hexabromocyclododecanes (HBCDs), polybrominated diphenyl ethers (PBDEs), tetrabromo bisphenol A etc.; (7) various agents and industrial additives like EDTA and aromatic sulfonates; (8) surfactants like alkylphenol carboxylates and ethoxylates; (9) antiseptics including chloroxylenol, triclosan and chlorohexidine gluconate (10) Gasoline additives tertiary butyl methyl ether, methanol, tetraethyllead etc. Tetracyclins are used as antibiotic, phthalates are used for plastic manufacturing, and chloroalkanes used as flame retardant are commonly found in environment (Stefanakis & Becker, 2016); (11) biocides used for agricultural plant and crop protection; (12) Toxins released from algae in aqueous environment (Dey et al., 2019); amd (13) various industrial chemicals ex., heavy metals and pesticides like organochlorines (Rosenfeld & Feng, 2011). Caffeine is frequently detected in water as it is required by humans in routine life in form of coffee (Loos et al., 2010). Personal care products and medicinal compounds are emerging contaminants commonly screened out in ground water and surface water (Lapworth et al., 2012).

These emerging contaminants can change balanced metabolic system, microbial population in soil, water or air, affect various organs of humans and also can create pollution in environment at different levels. Toxic or harmful effect of any contaminating material mainly depends on their particular concentration limit, host specificity and their half life time in the environment (Patel et al., 2021). Different contaminants have different host specificity or ligand specificity. Interaction of these contaminants with other compounds or materials in environment or in living body can increase or decrease their harmful effect. Detrimental effects of emerging contaminants can be acute or chronic. Per fluorinated compounds commonly used as fire retardants and lubricant are potentially carcinogenic cause adenomas in rodent animals. PFCs are persistent in environment for very long time. They are also associated with infertility and reproductive malfunction. Gasoline additive group contain more than 500 compounds used to decrease CO_2 emission in environment and to increase fuel quality. Tertiary butyl methyl ether has adverse effects like genotoxcity, hemolytic effect in intravascular region, and renal failure (Hellstern et al., 1990). UV protective sunscreen lotions adversely affect pituitary

endocrine system in humans (Krause et al., 2012). Veterinary antibiotics which are converted in to prototype released in open environment in bioactive form after excretion and negatively affect micro flora of lithosphere, hydrosphere and biosphere (Sarmah et al., 2006). Continuous exposure of antibiotics presents in waste water, in food or supplied as drugs create antibiotic resistance among microbes, which is more harmful and cannot be cured easily (Lei et al., 2015). Arguello-Perez et al. (Arguello-Pérez et al., 2019), studied risk screening associated with five different endocrine system disrupting ECs in five different effluents of waste water released by rural and urban sectors of Jalisco. Toxicity equivalent (TEQ) index calculation indicate that diclofenac, ibuprofen, ketorolac were belongs to toxic category with TEQ value 3 in all five taken samples of waste water. While estradiol was found to be very toxic with TEQ value 18 in two samples of waste water.

Liquid liquid extraction (LLE), solid phase extraction (SPE), high performance liquid chromatography (HPLC), gas chromatography (GC MS), gas chromatography mass spectrometry (GC MS), and liquid chromatography mass spectrometry (LC MS) are various extractive, analytical, and screening methods are available for detection and quantification of various emerging contaminants present in environment (Wenning & Martello, 2014).

From various available waste water treatment techniques, recently nanofiltration and reverse osmosis are widely used.

17.1.1 Nanofiltration

Nanofiltration (NF) technology involves filtration of waste water (WW) such as industrial WW, municipal WW, and other effluent for removal of contaminants of organic compounds and polyvalent cations with the help of membrane having pore size of 0.1 to 10 nm. With such small pore size of membrane NF can efficiently filtered out with pressure input particulate colloids, bacteria, microbes, proteins, polysaccharides, sugar, amino acids, and ions having multivalancy in general (Patel et al., 2020). While ions having mono valancy are selectively rejected or not rejected through NF. Pore size of membrane used in NF is smaller than microfiltration (MF) and ultrafiltration (UF) but larger than the membrane used in reverse osmosis (RO) process (Roy & Warsinger, 2017). Mostly hydrophilic membranes are used for treatment of water in NF, able for removal of charged compounds and uncharged organic compounds too (Nagy, 2018). Membranes used in NF are mostly tubular or spiral with thickness of 150 μm. Material used for membrane is cellulose acetate and applied pressure is generally between 5 to 35 bars (Abdel-Fatah, 2018). Solutes having molecular mass greater than 300 g/mol and which has multivalency are generally retarded or rejected by NF process (Silva, 2018).

Nanofiltration is not as simple as other filtration mechanisms, which are solely dependent on size exclusion principle (Fig. 17.1). Three types of phenomenon take place at the membrane in NF during filtration of waste water and removal of emerging contaminants (1) Diffusion (2) Convection and (3) Electromigration (Roy & Warsinger, 2017).

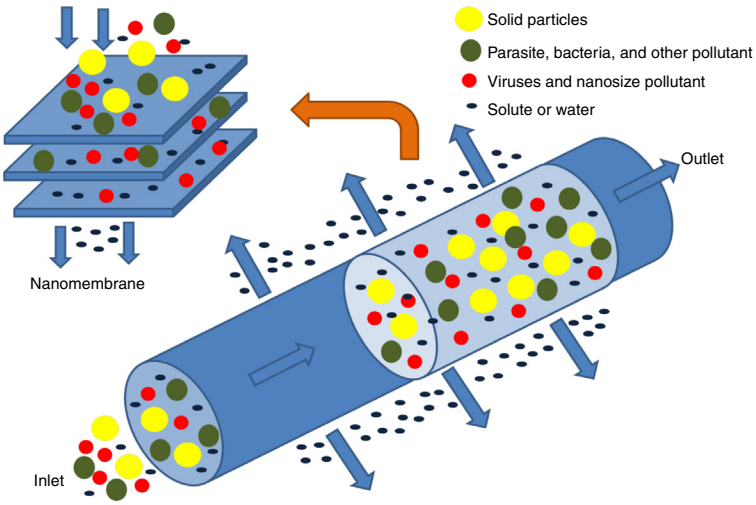

FIG. 17.1 Removal of water contaminant through nanofiltration process.

17.2 Factors affecting performance of nanofiltration

As membrane of NF is charged, separation of emerging contaminants is not only due to their molecular weight cut off, but also due to the osmotic pressure difference across the membrane. As it also based on osmotic pressure difference for purification of waste water, NF is a linking bridge between reverse osmosis and ultrafiltration (Roth et al., 2009). In NF feed or influent was allowed to pass through the membrane and molecules are separated based on their molecular weight cut off too. Molecules having larger size than the pore of the membrane cannot pass out from it and known as retentate, while molecules having smaller size than pores of the membrane will pass through it and known as permeate. More than one factor affect and contribute nanofiltration. They are—(1) Charge of the membrane, (2) concentration polarization, (3) pore size of the membrane (Roth et al., 2009), (4) viscosity of the solvent, (5) pH, (6) temperature, (7) dielectric constant of the membrane (Roy & Warsinger, 2017), (8) level of hydration (Epsztein et al., 2018), (9) flow rate, (10) membrane fouling and, (11) pressure (Mulyanti & Susanto, 2018).

Flux rate (J) is one of the important parameter affecting waste water treatment by nanofiltration. Flux is mainly affected by volume of the permeate and surface size of the membrane. According to Kim et al., 2011 flux can be represented by following equation.

$$\text{Fluxrate of permeate}\left(L/m^{2*}h\right) = \Delta V/A^{*}\Delta t$$

Where;

ΔV = Cumulative volume of permeate (L)

A = Membrane surface size (m^2)

Δt = Time of filtration (h)

Rejection (R) of emerging contaminants can be calculated using an equation given by (Mulyanti & Susanto, 2018).

$$R = 1 - Cp/Cf^{*}100\%$$

Where;

Cp = Concentration of permeate

Cf = Concentration of feed

According to (Abdel-Fatah, 2018) salt passage or permeation can be calculated using following equation.

$$\text{Salt passage} = Cp/Cf^{*}100$$

Some studies indicate that as temperature increase during NF, will decrease viscosity of solution and thus increase flux rate of permeate and also helps in decreasing concentration polarization (Agashichev, 2009). Temperature change in NF also affects diffusion process. If membrane fouling occur than flux rate will be reduced. In this case flux rate will not dependent on temperature variation (Gönder et al., 2011). Higher temperature stimulates decrease of flow rate by denaturing bacterial proteins.

Membrane fouling is an unwanted phenomenon, which decreases the filtration ability of membranes. Fouling is mainly of three types—organic fouling, inorganic fouling, and biological fouling—that occur due to deposition of these materials on membrane, which block pores of the membrane and decrease the flow of filtration of EC. Fouling may be reversible or non reversible. Time is a factor which affects fouling. Fouling also depend on membrane material, characteristics of solutes and operating conditions of NF. Blockage of pores may be partial or complete. Internal blockage of the pores reduces flow of permeate. Gel like layer was formed during fouling on membrane surface due to the precipitations of materials which are mainly organic. At interaction level van der Waals force and acid base mechanism affect the fouling rate by affecting solute and membrane interaction mechanism. Cross flow filtration helps in less fouling or fouling prevention, while dead end type filtration promotes fouling. Foulant identification helps in fouling removal. For example biological foulants can be removed using disinfection, coagulation or microfiltration. Organic foulants can be remove using ion exchange principle or with activated charcoal. Biofilm formation is also a reason for membrane fouling (Silva, 2018). Some studies indicate that pre-treatment of waste water before NF decrease membrane fouling. Coagulation, filtration, and sedimentation is effective as pretreatment step, helps to reduce COD (Hashlamon et al., 2017).

Concentration polarization is dependent on time factor and is reversible. Rejected molecules having larger size than the membrane pores, deposit and accumulated on membrane and creates polarization. Due to this feed flow decrease and produce osmotic pressure (Giorno et al., 1998;de Morais Coutinho et al., 2009).

Flow rate solvent polarity affects the flow rate. Polar solvent has 8 to 10 times higher flow rate than nonpolar in hydrophilic type membrane (Bhanushali et al., 2002). Cross

flow type filtration helps in detachment of membrane surface accumulated material and thus increase flow velocity of feed (Silva, 2018).

As pressure increases in NF system, it will promote dead end type flow of solvent, which causes fouling and retard flow of permeate (Silva, 2018). According to Silva, 2018 (Silva, 2018) relation between pressure gradient across both sides of membrane and flux rate can be given by the following equation.

$$J = 1/\eta R_T^{*} \Delta P$$

$$R_T = R_m + R_a + R_b + R_g + R_{cp}$$

Where;

η = Permeate viscosity
R_T = Total resistance of flow
ΔP = Pressure difference or gradient
R_m = Resistance caused by membrane
R_a = Resistance occur due to adsorption
R_b = Resistance occur due to pores blockage
R_g = Resistance caused by gel layer of membrane
R_{cp} = Resistance produced by concentration polarization

Optimum pH is required as pH change affect protein solubility and precipitation. Precipitation causes membrane fouling. At isolelectric point flux is lower (Silva, 2018).

In NF repulsion of charge takes place due to same charges present on membrane of NF and electrolytes present in feed. Dielectric effect occurs due to dielectric constant differences in membrane of NF and bulk solution. This will lead to difference in charge of polarization and dielectric exclusion (Hussain et al., 2008).

17.3 Nanofiltration with modifications and applications

Organic solvent nanofiltration (OSN) is widely used in refineries and industries for separation of different molecules from organics (Drioli & Giorno, 2010). Tran et al., 2019 (Tran et al., 2019) studied hospital waste water treatment using combination of NF and membrane biofiltration (MBR) in which COD removal was achieved in 3 phases of 94%, 93.3%, and 92.7% with N_2 removal at final efficiency of 83% and Log value of coliforms and *E.coli* removal achieved was also higher. Choi et al., 2002 (Choi et al., 2002) studied treatment of synthetic waste water using NF membrane bioreactor in submerged condition having cellulose acetate filter and influent total organic carbon (TOC) value 91.2 mg/L, after treatment effluent was obtained with TOC value 2.5 mg/L. good quality of water obtained after treatment was obtained by the day of 60 without accumulation of electrolytes.

Some novel technologies are applied nowadays to overcome conventional membrane nanofiltration limitations. Limitation of monovalent ion filtration can be overcome using enhancement of density of membrane surface charge through electric conditions. Charge density of membrane surface increased with the application of

2.5 V from 11.9 mC/m^2 to 73 mC/m^2. Due to this additional external voltage application filtration rate of sodium sulphate was increased from 81.6% to 93%. Sodium chloride filtration was also improved from 53.9% to 82.4% due to increased difference of Gibbs Donnan potential (Zhang et al., 2018).

Modifications in membrane material can also enhance and improve filtration of waste water containing emerging pollutants. Ion filtering effect can be enhanced through fabrication of NF membrane made up of polyamide material on nanotube of carbon which is single layered (SWCNT). This developed very thin film structure is able for filtration of 96.5% sodium sulphate with approximately 40 L/m^2/h/bar of permeability of water (Gao et al., 2019). Another membrane modification involves combination of fabrication of polydopamine containing nanofiltration membrane with nanosheets of molybdenum disulfide having 100% filtration capacity of methylene blue. This fabricated membrane has fouling prevention ability towards serum albumin of bovine and high dye stability (Gao et al., 2019).

Lin et al., 2019 (Lin et al., 2019) studied removal of bromide and bromated from brackish water, from both of them none can be easily removed through traditional water treatment method. Study was carried out at pressure of 0.2, 0.3 and 0.4 MPa and pH range having units of 5, 7 and 9. There was no major change observed with change in pH and ionic strength. As pressure was increased membrane flux was also increased. Moreover this study led to conclusion that bromated can be easily removed through this system rather than bromine.

Soyekwo et al., 2019 (Soyekwo et al., 2019) studied heavy metal removal and degradation of dye using NF membrane having aminophosphate immobilized chain. Polymerised aminophoshpahte acn enhance metal cation immobilization. Added iron in form of Fe^{3+} increase removal of heavy metal more than 98%. Shukla et al., 2018 (Shukla et al., 2018) studied removal efficiency of heavy metal using modified polyphenyl sulfone NF membrane. Modification was carried out using graphene oxide having carboxyl group. Due to this modifications, increased transmembrane pressure and increased concentration of feed, non considerably decreased ability of cation removal, while it has no effect on anion removal efficiency. In this modification based study ions of heavy metal removal rate was observed more than 98%.

Other applications of NF include desalination of processed whey, removals of metals and heavy metals, in industry of leather processing and in salt removal during dye chemical processing, to make concentrated gibberellins after its extraction (Abdel-Fatah, 2018).

17.4 Advantages and limitations of nanofiltration

Every technology has some advantages and limitations. Similar way nanofiltration includes limitations like; NF is more expensive than RO. Energy utilization rate is also higher in NF than MF and UF. Pre-treatment of waste water is sometimes necessary if it is heavily loaded with pollutants to prevent fouling. Soluble substances cannot be filtered out though it. 60% to 150% energy consumption is higher in NF, this costing can be reduced using green energy sources (Abdel-Fatah, 2018).

Advantages of nanofiltration over other methods utilized for emerging contaminant removal includes, chemical free non hazardous method as this method does not involve any type of chemicals for purification of water. NF can efficiently remove divalent ions from hard water to make it potable. NF can remove nearly all viruses from contaminated water. Nanofiltration is useful method for desalting of brackish and salty water. NF also does not require distillation and stirring which reduce costing compared to methods involve distillation for cooling purpose (Abdel-Fatah, 2018).

17.4.1 Reverse osmosis

Limitation of NF which cannot reject monovalent ions and dissolved solutes present in waste water, can be overcome by reverse osmosis (RO). After tertiary treatment step of waste water effluent is linked to RO. It is a pressure driven process as nanofiltration is. It is also known as hyperfiltation method. Reverse osmosis is a process which involves selective membrane that allows only water molecules to pass across membrane and retard passing of ions, organic compounds, pollutants present in water, xenobiotic compounds and suspended solids also. Normal osmosis process contains movement of water from high potential region to lower potential region. While in reverse osmosis water movement is from lower potential region to higher potential region through a selective membrane which retard solutes and does not allow them to pass from membrane. Thus, RO filtered out unwanted contaminants from waste water and make it usable. Reverse osmosis is efficient for removal of pollutants or contaminants present in water having size range of 0.1 to 15 nm with 2000 to 7000 kPa ranged pressure is necessary for RO (Hansen & Cheong, 2019).

Mainly two types of membranes are used in reverse osmosis process (1) cellulose triacetate based membrane (2) thin film composite membrane. Cellulose triacetate membrane has an advantage of tolerance capacity of chlorine but it is highly influences by fouling. Thin film composite type membranes are resistant for fouling having an advantage of 98% emerging contaminant removal ability (El-Dessouky & Ettouney, 2002). Membranes having nanolevel structures, mixed materials and composites have high water flux value and better separation ability of solutes. Membrane made up of ceramic or zeolite materials have benefit of separation of different type of polluted water and organics rejection ability (Nagy, 2018). Hollow fibre configured and spiral wound configured membranes are widely used in RO process. Problem of concentration polarization is low with hollow fibre configured membrane as flow of water of permeate is low (El-Dessouky & Ettouney, 2002).

17.5 Factors affecting reverse osmosis

RO is different in mechanism by other water purification methods, as it is based on osmosis and size exclusion principle. It is affected by several factors such as—(1) fouling, (2) pressure, (3) concentration of solutes (Crittenden & Harza, 2005),

(4) solute's partition coefficient, (5) pH, (6) duration, (7) diffusivity, (8) flux rate, (9) temperature, and (10) concentration of polarization.

According to Nagy, 2018 (Nagy, 2018) osmotic pressure can be calculated using following equation Vant Hoff's.

$$\Pi = \upsilon iRTCi$$

Where;

∏ = Osmotic pressure (Pascal)
υi = Dissociated ion number
R = Gas constant (K mol)
T = Absolute temperature (K)
Ci = Concentration of solute or component i (mol/m^3)

Successful pollutant removal from waste water requires excess external pressure supplementation than osmotic pressure of the feed or influent water to reverse the water flow compared to forward osmosis. As the pressure of influent increases, rate of flux of water also increases. External supplied pressure should be greater than to osmotic pressure for successful reverse osmosis (Saleh & Gupta, 2016).

As with same of nanofiltration fouling also affects RO. Flux rate can be calculated using equation given for NF which is same for RO.

Difference between outer or external given pressure and osmotic pressure (∏) is the main reason for driving of reverse osmosis and treatment of emerging pollutant containing waste water. From following given equation one can measured mass transfer (Hage, 2013).

$$Js\,(\text{solvent mass flux}) = PA(pb - f_R\Pi)$$

Where;

P = Permeability of water through membrane
A = Area of membrane
f_R = Factor of reflaction which is correlated with solute rejection

Solutes which are rejected by reverse osmosis, accumulated on surface of membrane and it is known as concentration polarization. Precipitation of solutes at membrane surface further decrease permeates flux. From following equation one can calculate technical effectiveness of RO (Hage, 2013).

$$E(\text{Enrichment factor}) = V_{Do}/V_{Do} - \Delta V_A$$

Where;

V_{Do} = Volume of initial feed water
ΔV_A = Filtrate volume difference

Temperature is also one of the factors which affect reverse osmosis. Al-Mutaz and Al-Ghunaimi (2001) studied effect of increased temperature of influent or feed water with permeate constant flow. Due to constant flow of permeate and increased influent temperature, energy utilization decreased as external given pressure was

decreased. Following equation can be used for relationship establishment of temperature, osmotic pressure and dissolved solute concentration.

$$\Pi(\text{osmotic pressure})(\text{psi}) = 1.19\left(t + 273\right)^{*} \sum(mi)$$

Where;

t = Temperature (˚C)

∑ (mi) = Total concentration of all solutes present in a solution (molar)

As the temperature of influent increases, viscosity decreased, which in turn increase diffusion and the water flow rate across the membrane. As temperature of feed or influent increases, diffusion rate along with water also increased and this ultimately decrease salt rejection capacity of RO membrane. Effect of temperature change on permeate efflux can be given by following equation (Al-Mutaz & Al-Ghunaimi, 2001).

$$TCF = \exp\left(K^{*}\left(1/273 + t\right) - 1/298\right)$$

Where;

TCP = Correction Factor for temperature

K = Fixed non variable characteristics of a given membrane

t = Temperature of influent (˚C)

Compounds dissolving capacity is also a factor of temperature. Detergents like Sodium dodecyl sulphate (SDS) precipitated at low temperature.

For a given hydraulic pressure difference and osmotic pressure difference water flow rate can be calculated using given equation (Al-Mutaz & Al-Ghunaimi, 2001).

$$Fw = Kw(\Delta P - \Delta\pi)^{*} A/x$$

Where;

Fw = Flow rate of water across the RO membrane

Kw = Coefficient of water permeability through RO membrane

ΔP = Difference of hydraulic pressure across RO membrane

Δπ = Pressure difference due to osmosis across RO membrane

$$Fs = Ks\left(Cf - Cp\right)$$

Where;

Fs = Salt flow rate

Ks = Salt's permeability coefficient across the RO membrane

(Cf-Cp) = Difference of salt concentration across the RO membrane

Cf = Concentration of feed water before RO

Cp = Concentration of permeate water after RO

As concentration of influent increases, water flux across the RO decreases and flux of salt increases. Salts present in permeate water or salinity of RO treated water cab be calculated using given equation (Al-Mutaz & Al-Ghunaimi, 2001).

$$Cp = Fs/Fw$$

Where;

Fw = Water flow rate

Heyde et al., 1975 (Heyde et al., 1975) studied partition coefficient of inorganic component's between cellulose acetate type membrane and water, as distribution of solutes highly influence rejection of pollutants or contaminants present in water. Compounds such as mercuric chloride and auric chloride which are inorganic and unionized were soaked up by membrane. As ionic size or valence capacity of ions increased, coefficient of partition decreased.

RO process is affected by concentration of salts. As concentration of salts in feed water increases, osmotic pressure also increases along with it. In this condition if external applied pressure remains constant, flux rate of water decreases. pH can varyingly affect RO process. Composite membrane having thin film are more stable at pH variation than cellulose acetate. pH has impacts on water flux and rejection of salt also. Solubility of many organic and inorganic salts or compounds are also affected by pH. For example, calcium carbonate dissolves at pH value below 7. Hoang et al. (2010) studied rejection of salt in brackish water over a different range of pH. Larger size ions were retarded by RO stronger than below pH 7. Over different pH range membrane flux was remain mostly stable.

17.6 Applications

Mostly either at large scale or in households it is widely used as it can successfully eliminate all dissolved materials, organic compounds, suspended solids, and pathogenic microbes or other bacteria with 99% efficiency. Efficiency of RO can be measured using following equation (Saleh & Gupta, 2016).

$$\text{Percentage of Rejection}\,(\%) = \left(Cf - Cp\right)/Cf^{*}100$$

Where;

Cf = Solute's molar concentration of feed water

Cp = Solute's molar concentration of feed permeate

Modifications of RO membrane can enhance contamination removal. For example, membrane having low pressure and modified *in situ* using glycidyl methacrylate can efficiently reject boric acid, sodium chloride and other micropollutants (Baransi-Karkaby et al., 2019).

Chung and Kim (2013) studied treatment of water containing wastes by membrane bioreactor, having RO membrane of hollow fibre type with 0.4 μm of pore size. As hydraulic retention time was increased, removal ability of COD by process was also increased. After 24 hrs of HRT COD removal and ammonia removal obtained efficiency was 92.5% and 92.2%.

Membrane bioreactor having RO membrane is also used for treatment of industrial waste water. Flat sheet membrane with pore size of 0.4 μm and with area of

effective surface 0.048 m^2 can efficiently remove total nitrogen, total carbon, COD and TSS with 74, 99.9, 75 and 98%. Treatment study indicate that this process can yield high quality if permeate water (Hosseinzadeh et al., 2013).

Modified composite membrane having thin film can be used for treatment of waste water though RO having high performance. Modified TFC is with having modifications of polyvinyl pyrrolidone which is a macromolecule having hydrophilic characteristic is manufactured using polymerisation at interfacial level and transplanted through radiation. This modification decreased water contact angle with reduction of 93.4% fouling redundancy and 99.5% of salt retardation ability (Liu et al., 2019).

17.7 Advantages and limitations of reverse osmosis

Limitations of RO include that is also removes beneficial salts and ions like magnesium and calcium known as deminaralisation, required for bones development. As it is pressure dependent process, somewhat slower than other purification process.

RO has also some advantages. As high heat or high temperature is not necessary during waste water treatment through RO, product degradation does not take place. There is no chemical change during filtration. So water quality does not compromise. As it does not require additional heat energy, RO can be operated at room temperature without extra heat. This will benefit in the form of low costing (Lazarides & Katsanidis, 2003).

17.8 Conclusion

As water is universal solvent on this earth, its purity, equal distribution, and balancing is one of the most prior need from all. Due to the excess industrial and economical development, water pollution is increased day by day. Microfiltration can eliminate suspended solids and bacteria, while ultrafiltration can filter suspended solids, bacteria, and viruses. Particles or compounds thatare below the virus size cannot be eliminated by microfiltration or ultrafiltration due their limitations of pore size of membrane. So nanofiltration have advantage of removal ability of suspended solids, bacteria, virus and multivalent ions. Thus NF have limitation that it cannot reject monovalents ions as pore size does not allow it. So, this hurdle was removed using reverse osmosis, in which membrane can eliminate suspended solids, bacteria, viruses, monovalent ions, multivalent ions, and only water is allowed to pass through RO membrane. Thus reverse osmosis can be used for removal of most emerging pollutants present in water, with only limitation of it is time consuming and have demineralization property. NF has an advantage of low costing over other method. By combining both NF and RO one can also treat landfill leachates.

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CHAPTER

18 Membrane bioreactor as an advanced wastewater treatment technology

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18.1 Introduction

Membrane bioreactor (MBR) technology connects the biological-activated sludge method and membrane filtration. It has become more prevalent, plentiful, and putative in recent years to treat various wastewaters such as industrial liquid and domestic wastes (Du et al., 2020). In contrast, the conventional activated sludge (CAS) method cannot handle the composition of wastewater or fluctuations of wastewater flow rate. MBR technology is also used in cases where demand for the quality of effluent exceeds CAS capability. Even though its operational and investment expenditures are more than traditional processes', it looks like classical treatment elevation, works in the same way as a conventional process. It can be associated with water price escalation, essential for water recycling and have stricter guidelines on the effluent quality. Membrane bioreactor may become an indispensable advancement for better understanding of evolving pollutants, and their addition in new regulations could be helpful for lawful necessities in wastewater treatment plants (WWTPs) (Radjenović et al., 2008).

The notion for coupling the activated sludge process and membrane separation was initially testified at Rensselaer Polytechnic Institute, Troy, New York, and Dorr-Oliver, Inc. Milford, Connecticut, USA (Hardt et al., 1970). The first MBR installation was prepared by Dorr-Oliver, Inc., with a flat sheet ultrafiltration plate and frame membrane. In 1969, the first application of MBR technology used ultrafiltration membrane to separate activated sludge from the final effluent of a biological wastewater treatment system, and the separated sludge was reprocessed back into the aeration tank (Radjenović et al., 2008). Yamamoto et al. (1989) introduced the usage

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of submerged membranes for the treatment of municipal wastewater that has led to its increased demand in the market. Indeed, MBR is a significant invention for the treatment of wastewater (Le-Clech et al., 2006). It reduces the disadvantages of the traditional ASP, such as large space requirement for liquid-solid separation, secondary purifiers, manufacture of additional sludge, and obstructions with the removal of refractory (Mutamim et al., 2013). Therefore, MBRs have been commonly used for the treatment and recycling of both industrial and municipal wastewater (Chu et al., 2006). The membrane bioreactor is a mixture of physical liquid-solid separation and a traditional biological treatment system using membrane filtration in a single system (Water Environment Federation, 2012).

18.2 Membrane classification

The membrane development is an effective separation method in water and wastewater treatment, becoming progressively economical and loftier than conventional water treatment with established performance. The most extensively operating membrane separation methods are as follows:

1. Microfiltration (MF)
2. Ultrafiltration (UF)
3. Nanofiltration (NF)
4. Reverse Osmosis (RO)
5. Electrodialysis (ED)
6. Electro Deionization (EDI)

The permeate and concentrate are manufactured by the first four methods. The separation ranges for the membranes mentioned above are 100–1000 nm for MF, 5–100 nm for UF, 1–5 nm for NF, and 0.1–1 nm for RO. In the last decade, MBRs have developed an efficient secondary treatment system, while applied membranes remain the same as UF and MF.

Membranes are usually prepared from different ceramic ingredients and plastic, but metallic membranes are also designed as per the requirement. The most commonly used membrane ingredients are polysulfone, charged polysulfone, celluloses, polyamides, and other polymeric ingredients, for instance polyethylsulfone (PES), polyethylene (PE), polyacrylonitrile (PAN), polyvinylidene difluoride (PVDF), and polypropylene (PP). These polymeric ingredients have an anticipated physical and chemical impediment and are also hydrophobic. The hydrophobic membranes are more susceptible to fouling because of maximum interconnections between the foulants and membrane (Judd and Judd, 2008). Therefore, all these commercially available membranes are altered by treatment with plasma, organic chemical reaction, chemical oxidation, or implanting to accomplish more hydrophilic surface. The alteration method generally varies from one membrane to another and depends upon the production of the membrane module.

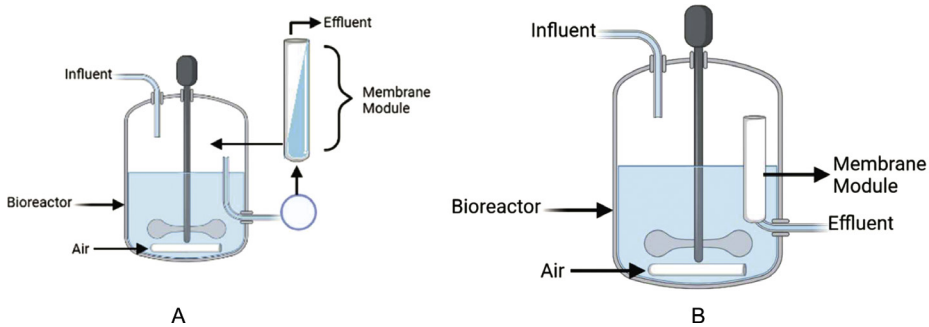

FIG. 18.1 Graphic representation of basic membrane bioreactor arrangements.

(A) MBR with external membrane component and (B) MBR with immersed membrane component.

18.3 Types of membrane bioreactor arrangements

There are two methods to execute membrane separation.

1. External membrane module/pressure-driven filtration in side-stream MBRs (Fig. 18.1A).
2. Immersed membrane module in MBRs (Fig. 18.1B).

The submerged arrangement is more commonly used than the recirculated arrangement since it requires less energy-intensive and gives better cleaning that limits membrane fouling. A suction force is applied to pull the water through the membrane, though the slurry is bound on the membrane surface. On the other hand, a side-stream arrangement is also viable due to recirculated configuration.

The mixed liquor is circulated outside of the reactor to the membrane module, where pressure drives water separation from the slurry. The concentrated slurry with wastewater pumped and reverted to the bioreactor through the membrane module.

The energy utilization is considerably lower for filtration in immersed MBR (Table 18.1). Both alignments require a trim above the surface of the membrane to retard membrane fouling through the ingredients of mingled liquor. Side-stream MBRs impart shear, whereas submerged methods produce aeration in the bioreactor. Shear improvement is vital in reducing membrane fouling and stimulating permeate flux; however, inducing shear also requires energy, which might cause a submerged arrangement. Furthermore, in side-stream MBR module fouling is incredibly distinct due to its advanced permeate flux. Pumping of activated slurry produces shear stress and triggers split-up of microbial flocs, leading to a reduction in particle size (Choi et al., 2002). This might be helpful in the membrane fouling rate significantly.

Table 18.1 Comparison of zenon filtration conditions for tubular and immersed MBRs (modified from Radjenović et al., 2008).

Instrument measurements	Side-stream tubular membrane	Submerged membrane
Model	Permaflow Z-8	ZeeWeed ZW-500
Surface area (m^2)	2	46
Permeate flux ($Lm^{-2}\ h^{-1}$)	50–100	20–50
Pressure (bar)	4	0.2–0.5
Air flow rate ($m^3\ h^{-1}$)		40
Energy for filtration ($kW\ hm^{-3}$)	4–12	0.3–0.6

Table (18.1) represents the filtration conditions in tubular and immersed MBRs (Cote and Thompson, 2000). The arrangements of MBR depend on either planar or cylindrical geometry.

There are five key membrane alignments operating system:

1. Hollow fiber (HF)
2. Spiral wound
3. Plate-and-frame (i.e., flat sheet [FS])
4. Pleated filter cartridge
5. Tubular

Hollow fiber: These membranes are based on the principle of pressure and vacuum, which make a bundle, and the ends of the fibers are wrapped in a sealant block joined with the external housing. The water can move in both directions i.e., from outside to inside and vice versa (Fig. 18.2).

Spiral wound: This arrangement is generally used for the NF and RO methods. The membranes are twisted around the punctured tube over which infiltrate exits.

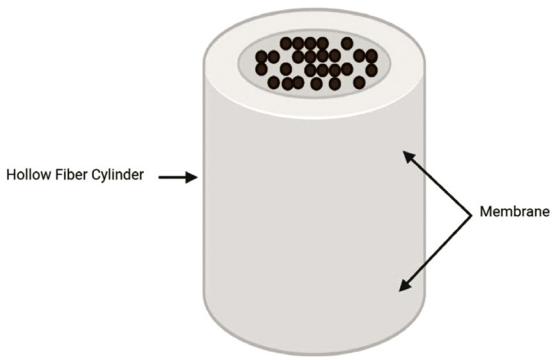

FIG. 18.2 Hollow fiber showing water flow in both directions.

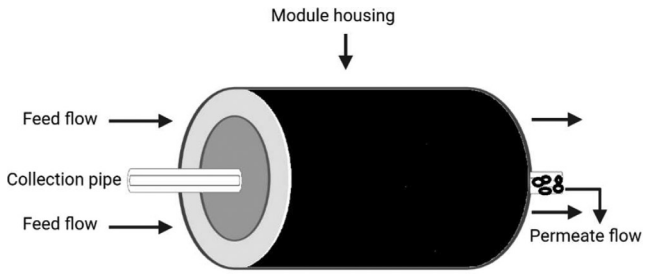

FIG. 18.3 Nanofiltration (NF) and reverse osmosis (RO) method.

These modules are produced in standard dimensions by all key producers, making their production economical and installation more straightforward. Furthermore, various membrane modules can be equipped in parallel or series together in plants with greater dimensions (Fig. 18.3).

Plate-and-frame membrane: This module works under vacuum and comprises FS membranes through separators and/or hold-up membranes. The parts of these sheets are embedded on a plate. The movements of water over the membrane and pervade are accumulated via pipes, originating from the inside of the membrane module.

Pleated filters: It is built with 100% polypropylene cartridge filters comprising of three to four layers of membranes with widespread chemical compatibility. The multilayers membrane structure allows graded filtration, pore sizes and raises the dirt holding capacity of the PP pleated filter cartridge.

18.4 Role of membrane bioreactors

Both biological activity and physical segregation of different pollutants are conjoined to remove domestic and industrial liquid wastes using MBRs. Therefore, MBRs are better quality treated effluent plants than the traditional activated sludge method (Li et al., 2019). MBRs are easy to handle as trained operators are engaged and yield fewer sediment. MBRs should be set up at prime locations in populated metropolitan areas because of beneficial mini footprint. This technology has various benefits along with economical membrane materials and the high demand for effluent quality treatment; and the increasingly stringent requirements of treated effluent quality mean that MBR technology is more and more commonly used for effluent treatment (Abdelrasoul et al., 2018).

The membrane fouling impacts the operating flux and membrane life span. The exact mechanisms of membrane fouling have not been established in MBR till now. However, the following mechanisms have been suggested and approved:

- Constriction of the membrane orifices
- The solute's adsorption in the solution via the membrane

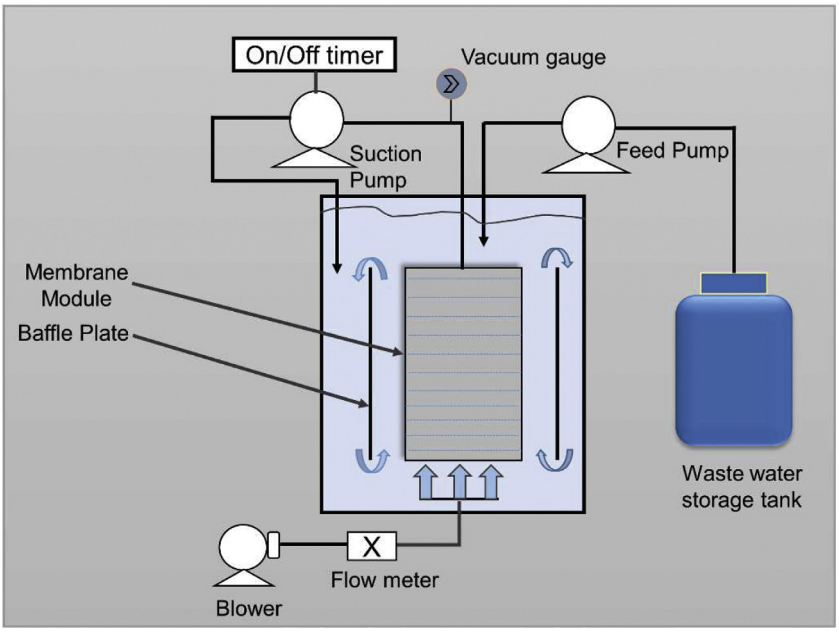

FIG. 18.4 Internal-loop-airlift reactor depicting the mechanism of empirical hydrodynamic model.

- The depositing mud floccule on the surface of the membrane
- The condensation of the clarifier cake coating on the surface of the membrane

These mechanisms alone or together play a leading role at different stages of the membrane filtration process. The various aspects affects the operating cost of a membrane system, for instance, power requirements, costs of power, membrane cleaning, scale prevention, labor, materials, and membrane lifespan, along with substitution. As soon as membrane fouling happens, it proliferates membrane maintenance, diminishes permeate flux, enhances system downtime, escalates feed pressure, decreases productivity, increases operation charges due to membrane cleaning, and reduces the membrane modules' life expectancy. Hence, the critical challenge is to find out an explanation of the membrane fouling in MBRs application (Du et al., 2020; Choudhury et al., 2019).

18.5 Classification of membrane fouling

Membrane fouling has been divided into three groups:

1. **Internal fouling (pore blocking):** It is the fouling produced by the deposition of colloidal particles along with the solute's adsorption inside the membrane orifices.

Table 18.2 Different types of MBR membrane fouling (modified from Du et al., 2020).

Classification of fouling	Fouling rate (Pa.min^{-1})	Duration
Reversible fouling	10–100	10 min
Irreversible fouling	1–10	1–2 weeks
Irreversible fouling	0.1–1	6–12 months
Non-restorable fouling	0.01–0.1	A few years

2. **External fouling:** External fouling is the deposition of elements, macromolecules, and colloids on the membrane surface, making a fouling sheet on the surface of the membrane. The fouling coating has been divided into a cake layer or gel layer. Because of the pressure difference among the feed and infiltrate margins of the membrane, the gel layer is constituted by the colloid's deposition, inorganic solutes, and macromolecules. On the other hand, the cake layer is formed by the solid's deposition on the membrane surface (Blandin et al., 2016).
3. **The aggregation of solutes and ions:** It is indicated by concentration polarization in the thin liquid film adjoining the membrane surface, which is a characteristic event in the filtration membrane method. The concentration polarization reduces the membrane flux and accelerates the flow impedance while its layer is firmed by the convective shear force (Li et al., 2016). The increase in the convective velocity could mitigate membrane impedance trigger via concentration polarization.

According to the degree of elimination of foulants, the membrane fouling is of two types: reversible and nonreversible. In reversible fouling the portion of foulants are eliminated through physical processes such as backflow or recurrent operation of membranes below crossflow filtration. Irreversible fouling can be eliminated from the membrane by chemical method and cannot be eliminated by physical process (Du et al., 2020). The reversible fouling is usually considered to be produced by a slack accumulation of pollutants on the membrane surface, while irreversible fouling is produced by the obstruction of membrane orifices and firmly adheres pollutants to the membrane surface. The establishment and condensation of the cake layer is the chief system of membrane fouling in comparison to membrane orifice hindering (Meng et al., 2009). Table (18.2) exhibits the beginning of several membranes fouling in MBR.

18.6 Membrane fouling in membrane bioreactor

Membrane fouling is the process resulting in loss of performance of a membrane because of the deposition of suspended or dissolved substances on its outside surface, at its pore openings, or within its pores. These foulants could be suspended

gritty (cell debris and microorganisms), solutes, and colloids in the mixed liquor suspended solids (MLSS) (Tu et al., 2010). The physicochemical connections in membrane fouling take place between the membrane material and the foulants. In some cases, failure to properly handle membrane fouling in MBRs could trigger a collapse needed to operate scheme flows appropriately.

In MBRs, fouling occurs in three major systems i.e., pore-clogging, cake formation, and pore narrowing. Pore clogging indicates the hindrance of membrane micropores by foulants. Pore clogging mainly relies on the particle size and the size of the membrane pore. Adhesive materials help the adherence of the ingredients in the pores in solution. On the other hand, cake formation refers to the continuous gathering of biopolymers, inorganic matter, and bacteria clusters, forming a layer (biocake) on the membrane (Meng et al., 2007). The cake layer escalates membrane filtration resistance.

In working positions, the MBR functions at constant transmembrane pressure (TMP), then membrane fouling declines the permeate flux, leading to TMP proliferation. There is an abrupt rise in TMP that has shown drastic change in membrane fouling, at constant flux functioning. This abrupt TMP escalation is known as "TMP jump". TMP jump is designated into a three-phase method:

Phase 1: It is an initial "conditioning" fouling triggered by initial orifice hindering and adsorption of solutes.
Phase 2: A linear or slight exponential steady increase in TMP because biofilm formation considerably prevents membrane orifice.
Phase 3: An abrupt fast rise in the rate of TMP increase (dTMP/dt) (Drews, 2010). Phase 3 is due to severe membrane fouling and is assumed to result from orifices cessation and alterations to the local flux, surpassing the essential local flux values that stimulate molecule accumulation and abrupt alterations of the cake layer assembly. Bacteria in the internal biofilms die because of oxygen deficiency, liberating higher extra-cellular polymeric substances (EPS) (Hwang et al., 2008). Indeed, the practical inference of this is a slowdown in phase 3 that permits a decrease in membrane washing leading to economical MBR functioning. The important work of fouling control is to impede TMP jump via alteration of sludge features (floc size, MLSS, apparent viscosity, and EPS content) or reducing flux working (Meng et al., 2009, Iorhemen et al., 2016).

18.6.1 Classification of foulants

In MBR, membrane foulants have been divided into three groups, such as biofoulants, organic foulants, and inorganic foulants based on chemical and biological features:

1. **Biofoulants:** Biofoulants refer to the bacteria or flocs whose growth, accumulation, and metabolism on the membrane lead to fouling (Meng et al., 2009). Membrane biofouling is a two-stage procedure, beginning

with initial bacterial attachment, followed by multiplication of bacteria on the membrane surface. Nevertheless, the organic substances produced by microorganisms are considered organic foulants. In membrane-based systems, membrane biofouling is a major significant operational complication (Guo et al., 2012).

2. **Organic foulants:** It indicates deposition of biopolymers such as polysaccharides and proteins on the membrane leading to deterioration of membrane permeability. These foulants are found in metabolic products of bacteria and is more difficult to eliminate (Mutamim et al., 2013). There is a direct association between membrane fouling rates and biopolymer concentration in sludge suspension.
3. **Inorganic foulants:** It is a set of inorganic materials (Ca^{2+}, Mg^{2+}, Fe^{3+}, Al^{3+}, $SO4^{2-}$, $PO4^{3-}$, $CO3^{2-}$, OH^{-}) that sediment on the surface of the membrane or into the membrane pores, causing membrane fouling (Wang et al., 2014). Indeed, inorganic fouling results from the chemical and/or biological precipitation of inorganic-organic complexes. Although moderate amounts of metal ions, such as, Ca^{2+} (up to 280 mg/L), can improve biofouling because of binding and bridging EPS (enhanced bio-flocculation). High concentrations (above 800 mg/L) of metal ions have been reported to significantly increase inorganic fouling of the MBR mixed liquor. The crystallization and particulate fouling are the two vital mechanisms that play crucial roles in MBR. Crystallization refers to the precipitation of ions that deposits at the membrane surface. In contrast, particulate fouling refers to the deposition of colloidal particulate matter to the membrane surface (Shirazi et al., 2010). Chemical cleaning is generally used to eliminate inorganic precipitation since it is efficient compared to physical cleaning (Meng et al., 2009; Iorhemen et al., 2016).

18.7 Factors affecting membrane fouling in membrane bioreactor

There are several characteristics in MBRs that impact membrane fouling. These features are of three types: operating conditions, feed and biomass characteristics, and membrane characteristics. Among them, membrane characteristics are significant that includes:

1. Membrane material
2. Water affinity
3. Surface roughness
4. Surface charge
5. Pore size

18.7.1 Membrane characteristics

18.7.1.1 *Membrane material*

In MBRs, membrane material affects its fouling tendency. Membranes have been categorized into three parts based on membrane material: ceramic membrane, polymeric membranes, and composite membranes.

1. **Ceramic membranes** have shown good filtration capability due to their high chemical resistance, inert nature, ease of cleaning, integrity, and low operational price. The ceramic membranes are lipophilic, which reduces fouling too (Mutamim et al., 2013). Nevertheless, their high cost of fabrication and fragile nature makes them economically impossible to use in MBR applications (Hofs et al., 2011).
2. **Polymeric membranes** are well-known membrane types, have good physical and chemical resistance, and are hydrophobic (Le-Clech et al., 2006). Their materials consist of polyethersulfone (PES), polyacrylonitrile (PAN), polysulfone (PS), polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF), polyethylene (PE), polyvinyl butyral (PVB), cellulose acetate (CA), polypropylene (PP), etc. Lately, they are extensively used due to the easiness of pore sizes fabrication and hydrophobic nature, which inclines foul easily.
3. **Composite membranes** refer to membranes made up of two or more substances vigorously mixed up with the integral substances in the final solution. Generally, the first substance incorporates the active surface while the second substance forms the supportive layer (Chu et al., 2006).

The characteristics of the membrane are altered to decrease the fouling degree. To study the features of antifouling, change in the surface of polypropylene membrane by treating with air plasma, using the altered membrane in a submerged MBR is suggested (Yu et al., 2008). The outcomes exhibited flux reclamation, 35% greater subsequent water and corrosive washing than the unmodified membrane. The discoveries have shown that the altered membranes fouled less compared to the control. These studies established that both under UV conditions and in darkness, the composite membranes (unmodified PVDF membranes) got flux stabilization very fast; as soon as filtration gets connected with UV irradiation at 365 nm, then the PVDF-TiO2 nano-composite membranes shown the best flux reclamation ratio (Moghadam et al., 2015).

18.7.1.2 *Water affinity*

The water affinity (hydrophobicity or hydrophilicity) characteristics of the membrane substance influence the MBRs fouling. By measuring the contact angle of a water drop on its surface, the behavior of the membrane substance is determined (Guglielmi and Andreottola, 2010). The greater angles indicate hydrophobicity, while smaller angles refer to hydrophilic behavior. The fouling plays a vital role in hydrophobic membranes because hydrophobic interaction occurs between the membrane material, solutes, and microbial cells (Le-Clech et al., 2006). The hydrophobic

materials adsorb hydrophobic substances in wastewater, causing fouling (Rana and Matsuura, 2010).

18.7.1.3 Membrane surface roughness

In MBRs, the membrane surface roughness could also impact fouling. Membranes with uniform surfaces have lesser chances to be contaminated compared with rough surfaces (Guglielmi and Andreottola, 2010). Investigations have shown that membranes with more significant surface unevenness foul quicker. The uneven surface of the membrane offers a gorge for the colloidal molecules to accumulate (Rana and Matsuura, 2010), triggering the hindrance in gorges, resulting the vigorousness of fouling. One study reported the association between uneven surface and membrane fouling and observed that membranes having more significant protrusions on their external surface have more antifouling characteristics, with the reclamation of porousness after subsequent backwashing (Hashino et al., 2011). Even though uneven surfaces enhance the susceptibility for fouling, coarser surfaces with bulging protrusions can entrap the foulants in their basins at the same time functioning normally.

18.7.1.4 Membrane surface charge

It is a second major characteristic association to membrane fouling, specifically, charged molecules in the feed. Under normal conditions, the majority of membrane substances are negatively charged (Guglielmi and Andreottola, 2010). It is partly referable to the colloidal molecules that sediment on the surface of the membrane (Rana and Matsuura, 2010). A particular cation (Ca^{2+} and Al^{3+}) in the MLSS react with the negatively charged membrane surfaces, causing inorganic fouling.

18.7.1.5 Membrane pore size

The membranes are broadly classified into two groups in wastewater treatment, such as porous membranes and non-porous membranes.

Porous membranes use sieving, filtration, or size segregation of dispersed molecules, including ultrafiltration (UF), loose end nanofiltration (NF), and microfiltration (MF) (Shirazi et al., 2010).

Nonporous membranes use the alterations in diffusivity or solubility amongst the solute and the solvent in the membranes for segregation (Crittenden et al., 2012), for example: reverse osmosis and tight end nanofiltration membranes. Since in MBRs, the segregation mechanism is sieving, UF and MF membranes are essential (Mutamim et al., 2013), for the complete physical maintenance of bacterial flocs and nearly all suspended solids inside the bioreactor (Le-Clech et al., 2006).

The orifice hindering mechanism tends to escalate with increasing membrane pore size (Guglielmi and Andreottola, 2010). It is due to fine particles entering the membrane pores quickly, causing pore obstruction (Van den Broeck et al., 2012). Large particles quickly form an upper coating, with smaller pores on the membrane and accumulate the lesser molecules. The subsequent layer formed on the surface

of the membrane could be detached *via* air cleaning or turbulence by crossflow purification.

Miyoshi et al. (2015) studied the impact of various polymeric membrane substances in an MBR amongst fouling and membrane orifice size with PVB, PVDF, and cellulose acetate butyrate (CAB) membranes. They reported reduced fouling for PVDF membranes with rising membrane pore size, but CAB membranes showed inclination with smaller pores resulting lesser fouling (Miyoshi et al., 2015). This study showed that the top membrane orifice size varies for different polymeric substances to reduce membrane fouling in MBR (Iorhemen et al., 2016).

18.8 Membrane fouling control

18.8.1 Modification of membrane material body

(1) Physical blending

It is a physical combination of the membrane material matrix with the definite proportion of altering additive (Mezohegyi et al., 2012). The alterations maintain uniformity, and the bulk membrane substance features benefit the procurement of superior cast film substances. Currently, lipophilic materials are mixed with PVDF membrane materials during physical blending (Xiong et al., 2019).

The benefit of blending hydrophilic polymer with PVDF polymer is that it could reimburse several flaws of the membrane with raw material alone and provide a significant advantage to the membrane material. In the polymer blend membrane, the compatibility between the polymers directly influences the formation and structure during membrane synthesis (Zhang et al., 2016).

In the last two decades, the use of lipophilic polymer combination compared with small-molecular inorganic particles using PVDF to advance the lipophilicity of the membrane has grown faster (Yan et al., 2018). The altered membrane using the mixture molding solution flawlessly incorporates the PVDF membrane features with the lipophilicity and heat resistance of the inorganic substance to operation a new organic-inorganic complex membrane (Zhan, 2002).

(2) Chemical copolymerization

The modification by chemical copolymerization in organic polymer film escalates its lipophilic nature. The execution takes place by adding an altered monomer to the innovative cast film material of the organic polymer film to generate an intricate reaction for copolymerization and produce a new copolymer. The membrane materials are modified by a standard procedure such as copolymerization, block, chain extension, grafting, etc. One study reported that induction of both sulfonamide amphiphilic (with acrylonitrile) and altered propylene amine groups copolymerization prevent adsorption characteristics of the protein. It also limits the copolymer of the polypropylene-sulfonamide membrane materials. Ten percent of sodium hydroxide can change the PVDF that develops the lipophilic nature in the membrane. The grafting of POEM accompanied with 5 weight percent to PVDF results in a significant enhancement of lipophilic nature in membrane complex (Li et al., 2019).

Recently, Hube et al. (2020) reported that membrane fouling is the core problem of direct filtration through a membrane. This technology has been used as encouraging techniques for wastewater retrieval and appliance restoration in several labs. The direct membrane filtration methods have a comparatively simple scheme arrangement, which needs minor investment. Wastewater treatment through direct membrane filtration may produce upgraded quality for permeability. In some cases, the reclamation of water and retrieval of resource from wastewater can be instantaneously attained, manifesting enormous prospective for energy utilization, boosting the neutrality of carbon, and diminishing footprint than traditional wastewater treatment methods (Xu et al., 2018; Ye et al., 2019).

18.8.2 Hydrophilic modification of the surface of membrane material

(1) Surface coating

This modification method covers lipophilic material just over the hydrophobic film layers to develop the film's anti-fouling performance. The polymer comb is covered on the membrane of PSF ultrafiltration. The membrane is distinguished by infrared and X-ray photoelectron-based spectroscopy, which confirm the coating layer (Meng et al., 2012). In addition, the FRR (flux restoration rate) of the altered membrane could have significant enhancement. Furthermore, the surface coating of PVDF ultrafiltration membrane with lipophilic substances could have >90% anti-fouling performance-based FRR. In one study, Zhao et al. (Meng et al., 2005) pretreated PVDF membrane with plasma and used it with 0.4 percent of TMC-hexane solution for developing PVDF-TMC membrane. This formed a coating-based modified layer over the film accompanied by 0.5 weight percent of SiO2-NH2 nanoparticle suspension and 0.1 weight percent of SA solution, efficiently developing anti-fouling.

18.8.3 Membrane modification by low-temperature plasma surface treatment

The modification for plasma-like-plasma polymerization graft coating treatment (PPG-CT), plasma triggered radical graft polymerization (PTRGP), and only plasma modify treatment (OPMT) on the surface of polymer materials can alter the membrane. In PTRGP technique, the inserting of the monomer on the membrane surface takes place (Zarebska et al., 2014). Copolymerization is a monomer penetration into the pores of the membrane to execute the grafting reaction. PPG-CT chiefly consists of the monomer radical's polymerization and provides a high grafting rate. The surface of membrane morphology changes immensely. OPMT is formed by ion rate of plasma, etching of plasma, and crosslinking of plasma surface. However, there is a risk of loss of membrane quality at high temperatures (Zhang et al., 2012).

The low-temperature-based plasma treatment alteration technology utilizes gaseous materials to hit the polymer and produces a reactions such as elimination of hydrogen on the surface of the membrane to insert a vast number of polar groups, for

example, OH^-, and $-NH_2$, etc. (Bagastyo et al., 2017). The low-temperature plasma treatment alteration technology might be recognizable in a medium to low-temperature environment without altering the outstanding features of the membrane. In contrast, plasma treatment needs the apparatus and expensive tools, and harsh operating conditions (Zhao et al., 2015).

18.8.4 Surface grafting

Surface grafting is the alteration of a thin coating on the membrane surface without affecting the main properties of the membrane substance. A long-lasting stable chemical bonding is made in the middle of the grafted polymer chain and the membrane surface (Du et al., 2020). Lately, researchers utilized UV radiation-based grafting to bring out acrylic acid into the polypropylene film, which significantly enhanced the lipophilicity of the polypropylene film (Zhang et al., 2014). Also, the thiol betaine methyl acrylate monomer is grafted on the polypropylene microporous membrane, leading to a decrease in the contact angle ultimately increasing the flux (Du et al., 2020). The mechanism of UV irradiation-based grafting depends on a free radical reaction that belongs to low polymerization temperature and mild polymerization conditions (Zhang et al., 2014). Furthermore, the repeated use of UV radiation hydrolysis causes graft of the pentaerythritol monoester to the polypropylene hollow fiber membrane's surface and significantly improved antifouling and lipophilicity of the membrane.

Jin et al. (2018) under UV irradiation and infrared spectrum, utilized polypropylene hollow fiber membrane for the lipophilic monomer as the matrix and sodium styrene sulfonate to make different grafting rate hollow fiber membrane. The 13.3% graft ratio, with 46° water contact angle is considered inferior to the original film (64°) (Wang et al., 2015). To some extent, the water flux gets enlarged with an increased grafting rate, but after some time, it reduces even with escalated grafting rate. The lipophilicity of the polypropylene hollow fiber membrane enhanced significantly, which gets altered by UV irradiation (Du et al., 2020).

18.9 Membrane bioreactor model description and assessment

18.9.1 Biomass kinetics models

(1) Activated sludge model (ASM) family

The International Water Association (IWA) formed a task force to plan and improve a feasible model for the biological wastewater treatment. This task force led to the development of Sludge model no. 1 in 1987 (Henze, 2021; Henze et al., 2015). Later, the upgraded version was introduced by this task force, known as activated sludge model no. 2 (Gujer et al., 1995), which have potential to eliminate phosphorus from wastewaters. In the activated sludge model no. 2d phosphorus-accumulating organisms use cell internal substrates for denitrification (Henze et al., 1999).

On the other hand, activated sludge model no. 3, does not have the ability to remove phosphorus but without any drawbacks present in the first model (Gujer et al., 1999). The ASM models can also be used to simulate biomass kinetics in an MBR system. The MBR method is the activated sludge process substituted by membrane filtration with the secondary clarification stage; so, it is sensible to use ASMs to depict the biomass dynamics in an MBR. A short description of four ASMs are described below. The task group publication from IWA should be referred to gain an insight in these ASMs (Ng and Kim, 2007).

(2) Activated sludge model no. 1 (ASM1)

This model was established to remove organic carbon, denitrification, and nitrification, to model biological management. It could be used in an activated sludge organization to forecast oxygen demand and sludge production. Two key ideas are included in this model- i) biodegradable COD comprising of slowly biodegradable COD (SBCOD) and voluntarily biodegradable COD (RDCOD) in wastewater. Organisms instantly uses RBCOD for synthesis, while SBCOD is fragmented before moving through the cell wall of organisms for metabolism. Total COD in this model is composed of biodegradable COD, non-biodegradable COD, and active biomass. ii) death regeneration delineates while the biomass deteriorates, a part of the decomposed cell material is inactive non-biodegradable substances. The rest of the decomposed parts is gradually biodegradable and active organisms processes for their growth (Henze, 2021; Henze et al., 2015).

In ASM1, the key processes comprised hydrolysis of gradually biodegradable material and the growth and deterioration of the organisms in the biomass. Autotrophs (XB, A) and heterotrophs (XB, H) are two groups of organisms included in this model. The oxidation of ammonia to nitrate (nitrification) fascinates the growth of autotrophs in aerobic conditions utilizing saturation (Monod) kinetics. The autotrophic decomposition rate is comparatively slower. On the other hand, heterotrophs carry out the removal of carbon and denitrifying jobs. Under both aerobic and anoxic conditions, they ingest soluble substrate, comprising of readily biodegradable decayed cell material, and ammonia for growth. The oxygen is used in the growth process under aerobic conditions while in the deficient oxygen; NO_3 serves as the electron acceptor and is reduced to N_2 under anoxic conditions. The heterotrophic growth process is also modeled utilizing the saturation-type kinetics. Nonetheless, heterotrophs can reutilize the biologically degradable decomposed material for growth. The basic framework of ASM1 is a mass balancing equation to depict the accumulation rate of a specific segment within the system:

$$\text{Accumulation} = \text{Input} - \text{Output} + \text{Reaction}$$

The reaction rate expressions for the several models constituent are applied to various process arrangements. A matrix format is utilized to permit simple identification of the rate processes that affect the fate of each component. Table 18.3 enlist the ASM1, ASM2, and ASM3 components and their corresponding growth processes.

Table 18.3 Components and rate processes comparison in ASM1, ASM2, and ASM3 (modified from Ng and Kim, 2007).

S.N.	Components of ASM1	Processes
1	Soluble inert organic matter (S_I)	Aerobic growth of $X_{B,H}$
2	Readily biodegradable substrate (S_S)	Anoxic growth of $X_{B,H}$
3	Particulate (suspended) inert organic matter (X_I)	Aerobic growth of $X_{B,A}$
4	Slowly biodegradable substrate (X_S)	Decay of $X_{B,H}$
5	Active heterotrophic biomass ($X_{B,H}$)	Decay of $X_{B,A}$
6	Active autotrophic biomass ($X_{B,A}$)	Ammonification of S_{ND}
7	Particulates arising from biomass decay (X_P)	Hydrolysis of entrapped organics
8	Oxygen (negative COD) (S_O)	Hydrolysis of entrapped organic nitrogen
9	Nitrate and nitrite nitrogen (S_{NO})	
10	Ammonia and ammonium nitrogen (S_{NH})	
11	Soluble biodegradable organic nitrogen (S_{ND})	
12	Particulate biodegradable organic nitrogen (X_{ND})	
13	Alkalinity (S_{ALK})	
	Components of ASM2	
1	Dissolved oxygen (S_{O2})	Aerobic hydrolysis
2	Fermentable (readily biodegradable substrate (S_F)	Anoxic hydrolysis
3	Fermentation products (S_A)	Anaerobic hydrolysis
4	Ammonium and ammonia nitrogen (S_{NH4})	Aerobic growth of X_H on S_F
5	Nitrate and nitrite nitrogen (S_{NO3})	Aerobic growth of X_H on S_A
6	Inorganic soluble phosphorus (S_{PO4})	Anoxic growth of X_H on S_F
7	Inert soluble organic material (S_I)	Anoxic growth of X_H on S_A
8	Alkalinity (S_{ALK})	Fermentation
9	Dinitrogen (S_{N2})	Lysis of XH
10	Inert particulate organics (X_I)	Storage of X_{PHA}
11	Slowly biodegradable substrates (X_S)	Storage of X_{PP}
12	Heterotrophic organisms (X_H)	Aerobic growth of X_{PAO} on X_{PHA}
13	Phosphate accumulating organisms (X_{PAO})	Lysis of X_{PAO}
14	Polyphosphates (X_{PP})	Lysis of XPP
15	Cell internal storage products of PAO (X_{PHA})	Lysis of X_{PHA}
16	Nitrifying organisms (X_{AUT})	Aerobic growth of X_{AUT}
17	Total suspended solids (X_{TSS})	Lysis of X_{AUT}
18	Metal hydroxides (X_{MeOH})	Precipitation of S_{PO4}
19	Metalphosphate (X_{MeP})	Redissolution of S_{PO4}

Table 18.3 Components and rate processes comparison in ASM1, ASM2, and ASM3 (modified from Ng and Kim, 2007). *Continued*

S.N.	Components of ASM1	Processes
	Components of ASM3	
1	Dissolved oxygen (negative COD) (S_O)	Hydrolysis
2	Inert soluble organic matter (S_I)	Aerobic storage of S_S
3	Readily biodegradable organic substrate (S_S)	Anoxic storage of S_S
4	Ammonium plus ammonia nitrogen (S_{NH4})	Aerobic growth of X_H
5	Dinitrogen (S_{N2})	Anoxic growth of X_H
6	Nitrate and nitrite nitrogen (S_{NOX})	Aerobic endogenous respiration of X_H
7	Alkalinity (S_{ALK})	Anoxic endogenous respiration of X_H
8	Inert particulate (suspended) organic matter (X_I)	Aerobic endogenous respiration of X_{STO}
9	Slowly biodegradable substrate (X_S)	Aerobic endogenous respiration of X_{STO}
10	Active heterotrophic organisms (X_H)	Aerobic growth of X_A
11	Cell internal storage product of heterotrophic organisms (X_{STO})	Aerobic endogenous respiration of X_A
12	Nitrifying organisms (X_A)	Anoxic endogenous respiration of X_A
13	Suspended solids (X_{SS})	

Though having a zero-reaction rate, the X_I and S_I, are merged into the model X_I, entrapped in the activated sludge, and are eliminated through sludge waste from the system. All biomass and organic ingredients are utilized to associate biomass, organic substratum and absorbs O_2 by electron equivalents. Similarly, O_2 is displayed as negative demand of O_2.

There is some limitation of this model. Firstly, the system works at a persistent pH (neutral) and temperature. The parameters of the model in the rate expression are kept constant. Secondly, the effects of low concentrations of nutrients on removing organic substratum and cell growth have not been specifically studied. The assumption is that adequate amounts of nutrients are available to permit the balanced growth of organisms. Third, the model composed of a constant value of parameters for nitrification, which in turns include inhibitory effects of waste ingredients coupled with a sudden enmeshed of particulate organics by the biomass (Henze et al., 2015).

(3) Activated sludge model no. 2 (ASM2)

In 1995, ASM2 was established, developed with modification of ASM1 by comprising biological P removal ability. This model includes new sets of organisms to the biomass, which initially consist of autotrophs and heterotrophs and called phosphorus-accumulating organisms (P_{AOs}). It could incorporate several microorganisms which assemble and save the phosphorous in the cell inner surface as polyphosphates

(X_{PP}) and polyhydroxyalkanoates (X_{PHA}). P_{AOs} are considered incompetent of denitrifying activity and only grow on organic material X_{PHA} stored in inner cell. In inner cell, storage material $X_{PHA,}$ P_{AOs} considered storing external fermentation products (S_A). It happens mainly in an anaerobic state, even though it also occur in anoxic and aerobic conditions. The hydrolysis of X_{PP} supply the energy, which in turn releases soluble phosphates (S_{PO4}).

Additionally, P_{AOs} accumulate P in the X_{PP} form, supply energy from the respiration of X_{PHA}. X_{PP} is redeveloped as P_{AOs} and needs S_A store in the X_{PHA} form for development. The storage of SA gets the energy from the hydrolysis of X_{PP}. Based on the model, growth of P_{AOs} takes place at the expense of XPHA, comprising the consumption of S_{PO4} and lysis of XPP only during aerobic state. For the lysis, P_{AOs} should supply different process rates in the model and each storage products capture all damaged biomass as a result of respiration and maintenance or demise.

In ASM2, the heterotrophic organism's growth (comprised of four different growth phases) takes place in both anoxic and aerobic state from fermentation products (S_A) and fermentable substrates (S_F). The yield coefficients (Y_H) and growth rates (μm) are considered same irrespective of the used up organic substratum (S_F or S_A). Heterotrophic growth methods consume nutrients (S_{NH4} and S_{PO4}) and oxygen (S_{O2}), under aerobic conditions, and probably produces alkalinity (S_{ALK}) and suspended solids (X_{TSS}). The anoxic growth use nitrate (S_{NO3}) rather than O_2, and reduced to dinitrogen (S_{N2}). Under aerobic conditions, denitrification (liberates alkalinity) is expected to be prevented by the presence of S_{O2}, and the maximum growth rate is reduced to a fraction. When both NO_3 and O_2 cannot be accessed, fermentation phenomena are expected to occur under anaerobic conditions. Here, SF is directly converted to SA by heterotrophs and alkalinity play a vital role because of the release of negatively charged SA. The scheme comprising autotrophic organisms is identical as in ASM1 and rate limitations executed by P concentrations.

The re-dissolution and precipitation of P and metal hydroxides and metal P are involved in ASM2 for capturing effects. Metals are naturally found in wastewater and precipitated with soluble ortho-phosphates, if present in high concentrations. Furthermore, iron or alum salts can be added to help phosphorous elimination via chemical precipitation in ordinary treatment methods. The 19 constituents and 19 rate processes in the ASM2 model are listed in Table 18.3. The hypothesis and limitations of ASM2 are: The inner infrastructure of a single specific cell is not notable. The hydrolysis of organic matter, organic N2, and organic P is considered to happen simultaneously, and XS includes a constant fraction of N2 and phosphorous. Hence, this model can be used only to induce processes or with low NO3 input into anaerobic tanks. This model assumes sufficient concentrations of P, NH3, K, and Mg. Lastly, NO3 and NO are reported to hinder the biological elimination of phosphorus, but such effects is not observed in this model (Judd and Judd, 2008; Wintgens et al., 2003).

(4) Activated sludge model no. 2d (ASM2d)

It includes the denitrification process, P_{AOs} may utilize inner cell organic storage products developed during an anoxic state. This observation caused the addition of

two rate procedures: the storage of polyphosphates and growth of P_{AOs}. The rest of the details of ASM2d are same as ASM2.

(5) Activated sludge model no. 3 (ASM3)

The task group of IWA updated ASM1 for generating a precise and revised model, ASM3 in 1999. The key alterations include internal cell storage compounds for heterotrophs that shifted the focus from hydrolysis to the storage of organic substratum. All voluntarily biodegradable substances are taken up by the heterotrophic biomass and stored as internal cell components before growth. The inclusion of internal cell storage structures differentiates the storage products and biomass decay under both anoxic and aerobic states. In ASM1, the decomposition of organisms occurs at a specific rate and a portion of the decomposed cell material returns to the heterotrophic growth scheme. In ASM3, endogenous respiration process is utilized to arrest all sorts of biomass loss and energy requirements.

Ingredients in ASM1 not included in ASM3, are particulates from biomass decomposition and biodegradable organic N2. Components added in ASM3 are di-N2, internal cell storage product of heterotrophic organisms, and suspended solids (Table 18.3). This model is developed to treat domestic wastewater and should not be persuaded to treat industrial wastewater. The optimum temperature and pH are 8–23°C and 6.5–7.5 respectively. This model is designed for the system having low loads and high SRT (>1 d) and is limited to low NO_3 concentrations (Wintgens et al., 2003).

(6) Assessment of activated sludge models

ASM1 was verified widely for activated sludge systems in contrast to experimental and operational data. The key problems detected with ASM1 were taken into account for improving ASM3. The ASM2, ASM2d, and ASM3 are also authenticated with experimental data for traditional activated sludge schemes. The ASMs seems to be feasible in an MBR system for describing biomass kinetics. Nevertheless, limited investigations have manifested the validity (or invalidity) of ASMs for modeling MBR systems.

In one study, Wintgens et al. (2003) suggested ASM3 as good modeling scheme for MBR. Further studies should be conducted to confirm its size preciseness for other elements and modeling transient states.

The ASMs application requires further studies to comprehend the effects of higher SRTs and MLSS concentrations on biomass for modeling MBR systems. Furthermore, investigations analyzing the traditional activated sludge method, including MBR procedure, may also help interpret the filtration results against clarification and measure the potential of ASMs to size effects (Ng and Hermanowicz, 2005). The benefit of utilizing ASMs is the excellent demonstration in a format of matrix. The matrix supports the realization of the biological treatment method and designing systematic experimental strategy. Another benefit is that some simulation schemes incorporate ASMs or models based on ASMs that supply easy access to the models for various applications. Additionally, biological phosphorous elimination is already integrated into ASM2 and ASM2d, a vital characteristic in biological treatment.

(7) Soluble microbial products (SMP) model

SMP is commonly known as the organic substances originated from substrate metabolisms and biomass decomposition. It is present in the effluent but absents in the influent of biological systems. The SMPs include a significant part of soluble organic substances in the discharge of biological treatment and the presence of SMPs is disadvantageous to the MBR and post-treatment processes (Barker and Stuckey, 1999). It is still uncertain whether the gathering of SMPs in the activated sludge hinders metabolic activity, the investigation showed that SMPs can cause a decrease in membrane permeability (Huang et al., 2000). Furthermore, SMPs drive the formation of trihalomethanes and other disinfection by-products in the permeate stream and produce bacterial growth in distribution systems (Furumai and Rittmann, 1992). Therefore, the modeling of biological water treatment methods must consist of SMPs.

Furumai and Rittmann (1992) revealed a model in biological treatment processes that depicts the interaction between heterotrophic and nitrifying bacteria. The model explains the generation and exchange of SMPs between nitrifiers and heterotrophs and are identified to compete with each other for dissolved O2. Nitrifiers may serve a vital energy sources for heterotrophs. They chemically reduce inorganic C atom to organic C atom in cell mass and SMPs and make organic substrates viable for heterotrophs growth. In this model, SMPs can be divided into two groups: utilization-associated products (UAPs), generated by biomass growth, and biomass-associated products (BAPs), originated by biomass decomposition.

This model was altered to comprise specific features for the MBR process (De Silva et al., 1998). The biomass was removed from the effluent mainly due to the membranes keeping the biomass in the system. The maintenance of a BAP fraction was investigated similarly, since parts of larger macromolecules are retained in the reactor by membranes.

In the SMP model, there is good correspondence between simulation results and measured data. Urbain et al. (1998) showed a relationship between MBR pilot plant data and model forecasts for sludge production, oxygen demand, nutrient removal, and biomass distribution at three different sludge ages under both steady and transient states. The model was not handled out precisely for the pilot plant. This model revealed precise presumptions under both steady-state and transient-state. Nonetheless, the SMP model could not handle technical issues in the wastewater features during operation and sudden deviations.

The advantage of SMP model over ASMs is its potential to precisely model biomass in MBRs without needing calibration by using experimental data. Besides, it also involves fewer materials and equations. In contrast, this model does not incorporate biological phosphorous removal and difficult to use among ASM family.

(8) ASM1-SMP hybrid model

It was established by Lu et al. (2001) with the main ideas of ASM1 in hybrid model. UAPs are liberated through metabolic process of heterotrophs and autotrophs. For growth purposes, heterotrophs can use UAPs. Furthermore, passive soluble and material substances, the decomposition processes by organisms producing BAPs

may also be recycled for heterotrophic growth. The X_P represents particulate substances ascending from biomass decomposition, is substituted with UAPs and BAPs. SMP consumption is added in the process rates for aerobic and anoxic growths of heterotrophs. In addition, the decay rates of the two organisms are divided in two methods i.e., causing particulate generation and BAP generation.

Under steady-state conditions, the simulation of model outcomes exhibited sound communication for soluble COD and N2 concentrations. Nevertheless, MLSS concentrations are unquestionably underestimated for both cycling orders. This hybrid model of ASM1-SMP is the first challenge to design MBRs by altering ASMs. Therefore, the insertion of SMP part for activated sludge with high SRTs has been highlighted. Integrating the SMP design into ASM1 has benefits over both models, even though more research is required to make a precise hybrid model (Lu et al., 2001).

18.10 Membrane fouling models

(1) Empirical hydrodynamic model

To study the impact of hydrodynamic conditions in MBR, the membrane fouling rate, and the mixed liquor crossflow velocity, 10 studies were conducted at varying conditions (Liu et al., 2003). The air was provided in the reactor's riser zone, which was detached from the downstream sections by baffle plates. A difference in the bulk density of the liquid was generated when the air hold-up in the riser section, which causes rotation in the middle of the two zones. During every single assessment, velocity for the upflow of the mixed liquor in the riser zone (Usr, m/s) and the transmembrane pressure (ΔP, Pa) was observed. The velocity for the upflow was examined as the real crossflow velocity of the mixed liquor through the membrane surface.

It should be noted here that the intensity of aeration, UGr, is distinctly recognizable from the mixed liquor crossflow velocity, Usr. The former is a controlled parameter in the experiment, while the later is a measured value. The transmembrane pressure was used to estimate the membrane fouling rate (K, m/h) and defined as the rate of increasing membrane filtration resistance (K = dR/dt).

The following equation was used to compute filtration resistance (R, m–1):

$$R = 3.6 \cdot 10^9 \frac{\Delta P}{\eta J} \; [4]$$

Here, η (mPa-s) is the permeate viscosity and is close to tap water viscosity. The factor, 3.6×10^9, stems from using the units given in parentheses for each of the variables.

The velocity of mixed liquor crossflow is distinguished since it indicates the influence of hydraulic state on membrane fouling regarding the impedance of sludge gathering on the membrane surface. Though the model is simple to use and capture the complex phenomena on the membrane surface. The model might be beneficial for demonstrating hydrodynamic results on membrane fouling, but it might not be appropriate for operational and design purposes (Wintgens et al., 2003).

(2) Fractal permeation model

Meng et al. (2005) evolved a permeation model (based on fractal theory and Darcy's law) to assess the formed cakes permeability from the microfiltration of activated sludge. The microstructure belonging cake layer usually is messy and complicated. Thus, cannot be narrated by conventional geometry. Fractal theory can be used here to identify the asymmetrical object regarding its average, self-similar characteristics. The authors first introduced a model to rule out the pore area fractal dimension, Ds, of a cake layer:

$$B(\geq a) = S_c - A = C_0 (a)^{2-Ds}$$

Where a is a threshold pore area, B is the total cake layer area (S_c) minus the sum (A) of all pore areas equal to or larger than an (i.e., A = Σa A = Σa), and C_0 is a constant.

Meng et al. (2005) provide a procedure for physically identifying the fractal dimension of a cake layer, involving an image analyzer to assess each pore area.

The permeability model was obtained by altering the Hagen–Poiseulle equation for flow rate through a tortuous capillary or pore (Yu and Liu, 2004). The equation was rewritten in terms of the threshold pore area, a, rather than the pore diameter, λ, as follows:

$$q(a) = \frac{G\Delta Pa2}{gL(a)\mu}$$

Where G is the geometry factor for fluid flow through a pore (i.e., π/128 for circular pores), g is the shape factor where a = gλ2, ΔP is the pressure gradient, L(a) is the tortuous length of a pore, and μ is the dynamic viscosity. Straight pores were assumed in the cake layer, allowing the replacement of L (a) by a constant, L0.

The following equation obtained Darcy's law for the permeability of porous c

$$\kappa = \frac{\mu L_0 Q}{\Delta P A_i} = \frac{G}{g^2} C_0 \frac{1}{A_i} \frac{2-D_s}{3-D_s} a_{\max}^{3-D_s}$$

Many membranes fouling assessments were conducted with varying activated sludge characteristics. The specific resistance of the cake layer, r_c, were identified indirectly in each evaluation. The inverse of the cake resistance is equal to cake permeability. Hence, the plot of the permeation factor against 1/ r_c should demonstrate high linearity if the model is valid. A correlation coefficient of 0.857 for the linear regression was identified. On this basis, the model was declared sensitive to certain level and is theoretically valid.

The fractal permeation model provides a method for identifying the permeability of cake grown up on a membrane surface. The model requires only a few parameters that are simple to identify and does not need intensive computation. The model is indirectly confirmed. Hence, confirmation is needed to identify its suitability. Additionally, the model does not exhibit how operational parameters and conditions influence the cake resistance but primarily depends on the fractal dimension to capture different outcomes. Hence, various parameters must be further correlated with the

pore area fractal dimension (or permeation factor) to identify their results on cake resistance (Henze et al., 2015).

(3) Sectional resistance model

In a submerged MBR, coarse bubbles from aeration provide a cleaning mechanism for the immersed membrane modules by scouring the membrane surface. The shear force from aeration is unevenly allocated, resulting in non-uniform fouling. Li and Wang (2006) applied a sectional approach to account for the uneven cake formation in determining total filtration resistance.

They divided the membrane surface into equal fractional areas, Δε, and calculated separate total resistances, R, for each section, consisting of inherent membrane resistance Rm, pore fouling resistance Rp, and resistances due to dynamic and stable sludge films, Rsf and Rsc, respectively. The total resistance in each section generated by the following equation:

$$\mathrm{R} = \mathrm{Rm} + \mathrm{Rp} + \mathrm{Rsf} + \mathrm{Rsc}$$

The pore fouling resistance, Rp, is proportional to the amount of permeate formed and is described as follows:

$$\mathrm{Rp} = \sum_{k=0}^{n} \mathrm{J}\theta\mathrm{f}$$

The following shear profile is supposed, for the shear intensity, G, at each section:

$$\frac{G}{G_0} = \begin{cases} \frac{1}{10} + \frac{9}{20}\left[1 + \sin\frac{(2\varepsilon_i - \varepsilon_a)\pi}{2\varepsilon_a}\right] & \varepsilon_i < \varepsilon_a \\ 1 & \varepsilon_i \geq \varepsilon_c \end{cases}$$

Where G_0 is the apparent shear intensity of the fluid turbulence, $\sum i$ is the accumulated membrane area fractions up to the i_{th} section, and $\sum a$ is the sectional area of the membrane surface with reduced shear intensity (where G/G_0 is less than 1).

The sectional resistance model was generated by a partially analytical method. The model is planned to specify membrane fouling in submerged MBRs where the membranes are put through shear flow from aeration (Henze et al., 2015).

(4) ASM3 and resistance-in-series model

The model was evolved by Wintgens et al. (2003) to characterize the filtration activities of submerged capillary hollow fiber components. Along with ASM3, the model was connected to the biological treatment approaches. It was well known that extra cellular polymeric substances (EPS) generated by microorganisms can obstruct membrane activities, but no moderation was done to ASM3 to figure out this substance.

This model is established on the resistance-in-series model and was improved in an MBR to narrate the filtration activities of submerged capillary hollow fiber components. This model interprets for cleaning cycles and includes time dependency to run a constant fouling profile in the same way as the sectional resistance model. This model was verified against operational data from a full-scale MBR with two external filtration modules. Data from the first unit were used to set model parameters

by curve-fitting using the least-square-error method. However, simulation outcomes from the calibrated model were associated with data from the second filtration module. The calculated permeability over time is related to measured data, apart from the initial period of operation. The model was also tested in submerged capillary hollow fiber membranes with experimental data from a pilot MBR (Geissler et al., 2005). Apart from the main deviation at the end of the considered period, the simulation outcomes for permeability development over time corresponded well with the data from the pilot plant. The variation was not investigated in the simulation which was elucidated by a drop in the organic load of the influent.

18.11 Advantages and drawbacks of membrane bioreactor technology

The benefit of the MBR system over traditional biological treatment methods spur the growing interest in MBR technology for water and wastewater treatment. MBR treatment of municipal wastewater generates high-quality water with 95%, 98%, and 99% removal percentages for COD, BOD, and SS, respectively (Mallevialle et al., 1996). This is necessary, as water standard regulations have become progressively strict. An MBR has autonomous control over the SS retention time (SRT) and hydraulic retention time (HRT) since membrane filtration rather than gravitational settling is utilized to differentiate the biomass from the effluent. This permits operation at a more extended SRT and higher loading rates, bringing about less sludge generation and shortening the necessary HRT. The utilization of membranes to seperate the biomass from the effluent also eliminates the requirement for enormous clarifying basins to settle out the biomass resulting compact system.

Membrane fouling is a major disadvantage of MBR since it decreases membrane activities and lifespan, leading to a rise in maintenance and operating costs. Membrane fouling in MBRs is attributable to suspended particulates (microorganisms and cell debris), colloids, solutes, and sludge flocs (Tay et al., 2007). These materials are staked onto the membrane surface and into the membrane pores, clogging the pores, leading to a declined membrane permeability. The heterogeneous character of SS and active microorganisms in MLSS makes membrane fouling an unavoidable challenge that is hard to control in long-term MBR applications (Chang et al., 2002).

18.12 Summary and conclusion

MBR is a sophisticated technology and has been utilized in wastewater recovery. However, membrane fouling seems to be the major hindrance to its widespread promotion. Therefore, research on the causes, mechanisms, and control of membrane fouling is vital to this technology. Albeit some advancement has been made, there is a definitive scope of improvements. We believe that future research should focus on the following aspects: An alternative solution for the advancement of direct membrane filtration with increased anti-fouling properties. Because of the absence of

large-scale direct membrane filtration processes in the market, future research should be focused on:

- Membrane fouling control technologies of direct membrane filtration, especially with low energy utilization, less chemical usage, and simpler operation and maintenance.
- Development of novel membranes, robust and cost effective, made up of environmentally friendly materials, and possess self-cleaning properties.
- Comprehensive monetary analysis, life cycle appraisal, and carbon footprint investigation of various direct membrane filtration processes to recognize the most suitable system configuration for further scale-up.

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Competing interests

The authors declare that they have no competing interests.

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Not applicable.

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Not applicable.

Abbreviations

MBR Membrane bioreactor

CAS Conventional activated sludge

WWTPs Wastewater treatment plants

MF	Microfiltration
UF	Ultrafiltration
NF	Nanofiltration
RO	Reverse osmosis
ED	Electrodialysis
EDI	Electro deionization
PES	Polyethylsulphone
PE	Polyethylene
PAN	Polyacrylonitrile
PVDF	Polyvinylidene difluoride
PP	Polypropylene
HF	Hollow fiber
IUPAC	International Union of Pure and Applied Chemistry
MLSS	Mixed liquor suspended solids
TMP	Transmembrane pressure
EPS	Extra-cellular polymeric substances
PS	Polysulfone
PVB	Polyvinyl butyral
CA	Cellulose acetate
PTFE	Polytetrafluoroethylene
PVP	Polyvinylpyrrolidone
CMPS	Chloromethylated polysulfone
PMMA	Polymethyl methacrylate
PVAc	Polyvinyl acetate
PVA	Polyvinyl alcohol
SPS	Sulfonated polystyrene

SPES-C	Sulfonated polyaryl ether sulfone
PPG-CT	Plasma polymerization graft coating treatment
PTRGP	Plasma trigger radical graft polymerization
OPMT	Only plasma modify treatment
ASM	Activated sludge model
IWA	International water association
COD	Chemical oxygen demand
BOD	Biochemical oxygen demand
SBCOD	Slowly biodegradable COD
RDCOD	Readily biodegradable COD
SS	Suspended solids
SRT	Solids retention time
HRT	Hydraulic retention time
ASM1	Activated sludge model no. 1
ASM2	Activated sludge model no. 2
PAOs	Phosphorus-accumulating organisms
ASM2d	Activated sludge model no. 2d
ASM3	Activated sludge model no. 3
SMP	Soluble microbial products
UAPs	Utilization-associated products
BAPs	Biomass-associated products
VSS	Volatile suspended solids
SI	Soluble inert organic matter
SS	Readily biodegradable substrate
XI	Particulate (suspended) inert organic matter
XS	Slowly biodegradable substrate

$X_{B,H}$	Active heterotrophic biomass
$X_{B,A}$	Active autotrophic biomass
XP	Particulates arising from biomass decay
SO	Oxygen (negative COD)
SNO	Nitrate and nitrite nitrogen
SNH	Ammonia and ammonium nitrogen
SND	Soluble biodegradable organic nitrogen
XND	Particulate biodegradable organic nitrogen
SALK	Alkalinity
XA	Nitrifying organisms
XAUT	Nitrifying organisms
SO2	Dissolved oxygen
SF	Fermentable (readily biodegradable substrate)
SA	Fermentation products
SNH4	Ammonium and ammonia nitrogen
SNO3	Nitrate and nitrite nitrogen
SPO4	Inorganic soluble phosphorus
SI	Inert soluble organic material
SN2	Dinitrogen
XI	Inert particulate organics
XS	Slowly biodegradable substrates
XH	Heterotrophic organisms
XPAO	Phosphate accumulating organisms
XPP	Polyphosphates
XPHA	Cell internal storage products of PAO
XTSS	Total suspended solids

XMeOH Metal hydroxides

XMeP Metalphosphate

SO Dissolved oxygen (negative COD)

SI Inert soluble organic matter

SS Readily biodegradable organic substrate

SNOX Nitrate and nitrite nitrogen

XI Inert particulate (suspended) organic matter

XH Active heterotrophic organisms

XSTO Cell internal storage product of heterotrophic organisms

XA Nitrifying organisms

XSS Suspended solids

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CHAPTER

Removal of pesticides from water and wastewater by solar-driven photocatalysis

19

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19.1 Introduction

The agricultural and pharmaceutical companies release chemical waste in the form of pesticides and other harmful chemicals in water which results in some chronic diseases that may be harmful to the human endocrine system, making water undrinkable or unusable (Pawar and Lee, 2015, Aliste et al., 2019). Pesticide pollution in water is one of the most severe environmental problems faced by communities in industrialized areas (Chong et al., 2010). Pesticides are fundamental in protection of crop from pests, yielding crop production, although the use of pesticides is good for crop production, but it has significant risks on human health and environmental ecosystem (Senthilnathan and Philip, 2012).

There is an urgent need to develop ecofriendly technologies that will help in pesticide degradation or complete elimination of the pesticide pollutants. One of the processes developed by researchers is advanced oxidation processes (AOPs) (Matilainen and Sillanpää, 2010).

AOPs are an environmentally friendly technique used for removal of pollutants such as air pollutants and water pollutants. Some of the chemical waste or pollutants that are found in water are aromatics, petroleum-based contents, petroleum hydrocarbons, chlorinated hydrocarbons, insecticides, volatile organic compounds (VOC), dyes, and pesticides (Rueda-Marquez et al., 2020, Poblete et al., 2020, Miklos et al., 2018, Souza et al., 2016). The mechanism of AOPs for pollutants removal and treatment works based on the generation of reactive oxygen species (ROS) like hydroxyl radicals with one unpaired electron which possess short lifetimes (Von Sonntag, 2008). Because of the reactivity of hydroxyl radicals, they actively react with a series of chemical species, which naturally are very difficult to degrade (Von Sonntag, 2008). Comparatively, AOPs are better than other conventional water treatment methods because they can generate thermodynamically stable oxidation products such as carbon dioxide, water, and biodegradable organics such as pesticides (Kenny et al., 2018). The AOPs include photocatalysis process, which plays a crucial role in harvesting sunlight by a photocatalyst (Ameta et al., 2018). These photocatalysts are used effectively to solve problems related to environmental pollution by removing the pollutants from the environment (Chong et al., 2010).

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19.2 Photocatalysts and photocatalysis

Solar-driven reactions require photocatalysts in order to occur, the photocatalysts are materials that alter the rate of a chemical reaction in the presence of light (Tsydenova et al., 2015). This phenomenon is referred to as photocatalysis. Photocatalysis includes reactions that involve utilizing light (i.e. sunlight) and a semiconductor; which serve as the photocatalyst (Zhang et al., 2019, Mills and Le Hunte, 1997). All the photocatalysts are semiconductors (Mills and Le Hunte, 1997). In solar-driven photocatalytic reaction, an electron-hole pair is generated on the exposure of a semiconducting material to light, which ultimately leads to generation of ·OH. There are two major types of photocatalytic reactions which are categorized based on their appearance of the physical state of reactants (Pawar and Lee, 2015). These are homogenous photocatalysis and heterogeneous photocatalysis (Ameta et al., 2018).

19.2.1 Types of photocatalysts

Photocatalysts are divided into two based on their oxidative state, these are oxide photocatalysts which include titanium (IV) oxide (TiO_2) and bismuth (III) oxide (Bi_2O_3) and nonoxide photocatalysts which include copper (II) sulfide (CuS), cadmium (II) sulfide CdS, zinc sulfide (ZnS), and carbon nitride (C_3N_4).

19.2.1.1 Oxide Photocatalyst

19.2.1.1.1 TiO_2-Based photocatalyst

In 1976, the nano-TiO_2 was demonstrated to dechlorinate polychlorinated biphenyls, a hard-degradable organic compound, under ultraviolet light, leading to exploitation of photocatalytic degradation using semiconductor nanomaterials (Zhang et al., 2019). In 1980, TiO_2 was proposed to be used as photocatalyst, which promoted the development of TiO_2 in the field of photocatalysis. The TiO_2 has three (3) crystal forms these include rutile, brookite, and anatase. Among these; the crystal structures, anatase and rutile type of TiO_2 are commonly used as photocatalysts (Kusior et al., 2018). TiO_2-based photocatalysts are widely used in air purification, antibacterial disinfection, deodorant, and water pollutants degradation among other applications, due to their high activity, stable properties, low-cost, and non-toxic environment. TiO_2 has a wide band gap of approximately 3.2 eV. Thus, TiO_2 can specifically absorb ultraviolet (UV) light when used as a photocatalyst. However, UV radiation occupies only 5% of solar radiation, this greatly limits the application of TiO_2 in the visible (Vis) range. A series of modifications to TiO_2 were conducted to improve its utilization of visible light and to reduce photogenerated electron-hole recombination rate on its surface which increased its photocatalytic efficiency. The common methods used to improve TiO_2 photocatalytic efficiency include the following: metal/nonmetal doping, semiconductor surface photosensitization, semiconductor surface noble metal deposition, and complex semiconductor modification (Papp et al., 1993).

19.2.1.1.2 Bi_2O_3-based photocatalyst

Bi-based oxides are widely used in many fields as electrolyte materials, electronic ceramic materials, high-temperature superconducting materials, and materials for

photoelectric conversion. The Bi_2O_3 possesses a unique property which include high electrical conductivity, low energy band gap of about 2.8 eV and low energy band structure meaning Bi_2O_3 can absorb visible light in the solar spectrum showing Bi_2O_3 has great potential for photocatalysis applications (Bessekhouad et al., 2004). The Bi_2O_3 semiconductor mainly has four (4) crystal forms consisting of α, β, γ, and δ. The band gaps of α-Bi_2O_3 and β-Bi_2O_3 are 2.85 eV and 2.58 eV, respectively, which can absorb visible light at 400 nm wavelengths. The α-Bi_2O_3 is the most widely used among the four types of Bi_2O_3 semiconductors in photocatalytic reactions, since it is the most thermodynamically stable among the four Bi_2O_3 crystal structures. The development of Bi-based semiconductor materials solves the problem of inefficient absorption of visible light by TiO_2. Although, the problem of low quantum efficiency and photogenerated carrier recombination still needs to be solved for the Bi-based photocatalysts. To improve the performance of photocatalysts the use of doping modification is an effective method. Some of the commonly used modification methods include metal & nonmetal doping, semiconductor surface photosensitization, semiconductor surface noble metal deposition, and complex semiconductor modification. To date, Bi-based photocatalysts have made significant contribution in important researches which results in the applications of atmospheric purification, heavy metal ion removal, and sterilization, and organic wastewater treatment (Cabot et al., 2004).

19.2.1.1.3 Other Oxide photocatalysts

Transition metals such as titanium (Ti), chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu), and zinc (Zn), and their corresponding oxides, have excellent physical and chemical properties. These physicochemical properties include multivalence, high redox potential, chemical resistance, and a high temperature resistance. The transition metals are relatively abundant and have low price, which means that transition metals and their oxides are good application prospects photocatalysis. The three (3) transition metal oxides generally used in photocatalysis include; Fe_2O_3, ZnO, and WO_3.

Iron (Fe) has since been investigated as an important metal used in redox reaction. Among iron oxides, Fe_2O_3 is widely studied for its high photocatalytic activity. The Fe_2O_3 is an n-type semiconductor, having a forbidden band width of 2.2 eV, it has a strong light absorption capability in the visible light region, and also has the ability to absorb a part of sunlight. Fe_2O_3 is also used as a reducing agent for photocatalytic reduction of silver (Ag^+) ions and can also be used to decompose reactive dyes (Sharma et al., 2010).

ZnO is one of the few oxide semiconductor materials capable of achieve a quantum size effect and has good UV absorption and piezoelectric properties. The forbidden band width of ZnO is 3.2 eV, which corresponds to UV of 387 nm wavelength. Studies on ZnO have revealed certain relationship between the surface composition and structure of ZnO nanoparticles and their corresponding photocatalytic properties. The oxygen vacancies on the surface of ZnO tend to capture photogenerated electrons, and therefore, generate a strong interaction between oxygen vacancies and adsorbed oxygen, which is beneficial for the oxidation reactions (Vela et al., 2018).

Tungsten trioxides (WO_3) are among the metal oxides that have photocatalytic activity. It shows several advantages that include excellent absorbing capability, large specific surface area, and great potential to be used as invisible material. WO_3 is stable which has the band gap of 2.8 eV. The WO_3 can be used as both catalyst and cocatalyst (Gusain et al., 2019).

19.2.1.2 *Nonoxide photocatalyst*

Many nonoxides also have good photocatalytic properties. Among them include semiconductor metal sulfides which have attracted the attention of researchers because of their special structure and excellent physical and chemical properties. Some of these nonoxides include tungsten sulfide (WS), molybdenum sulfide (MoS_2), copper sulfide (CuS), zinc sulfide (ZnS), and cadmium sulfide (CdS). In addition to sulfides, the nitrides such as C_3N_4 show excellent photocatalytic properties. Some of the nonoxide photocatalysts that were extensively studies include CdS, CuS, ZnS, and C_3N_4 (Erokhina et al., 2003).

19.2.1.2.1 CdS photocatalyst

CdS is a semiconductor with a band gap of 2.42 eV and a maximum absorption peak of 514 nm wavelength which shows CdS can absorb visible light and UV light within a wavelength of ≤ 514 nm. This makes CdS an efficient photocatalyst. In addition, the bandgap position of CdS semiconductors is well suited for many photocatalytic reactions, such as water decomposition and CO_2 reduction. The CdS has extensively been investigated as a photocatalyst. Of note, the position of the CdS conduction band edge is lower than the position of other common semiconductors such as TiO_2, ZnO, and $SrTiO_3$; this means in the photocatalytic reaction, the photoelectrons of CdS have a strong reducing power. However, the CdS material is prone to corrosion by light. This causes limitations on the number of recoverable CdS photocatalyst. To solve this fundamental problem, researchers have proposed measures to improve the CdS photocatalyst is to use its ratio. The most commonly used method is to prepare CdS composite material is by using different materials or ion doping methods. The CdS photocatalyst using composite enhances the absorption of long wavelength, thereby achieving photocatalysis and higher recoverability (Bessekhouad et al., 2004).

19.2.1.2.2 CuS photocatalyst

CuS is a crucial metal sulfide semiconductor material with excellent optoelectronic properties. It is a p-type semiconductor material with forbidden band width of 2.2 eV, which has a good visible light absorption capacity. When CuS material absorbs photons, this leads to generation of electron-hole pairs. These electrons and holes move to the surface of the CuS material and react with water molecules or oxygen molecules to produce several substances. The produced substances are characterized by high catalytic activity which subsequently degrade organic matter adsorbed on the surface of the CuS material. CuS is used in wide range of optical, electrical, mechanical, and sensor applications because of its excellent properties. Some of the applications which uses CuS include solar cells, lithium battery electrodes, photothermal conversion, and

photocatalysis. CuS nanomaterials have great potential for photocatalysis due to their appropriate energy band and absorption wavelength (Erokhina et al., 2003).

19.2.1.2.3 ZnS photocatalyst

ZnS is a group of II–VI wide band gap semiconductor materials with a band gap, which range between 3.6-3.8 eV. The ZnS has two types crystal structures namely zinc blende and wurtzite. Among the two, zinc blende also referred to as β-ZnS is stable at low temperature, whereas wurtzite, also referred to as α-ZnS is stable at temperature >1024°C. The ZnS is difficult to oxidize and hydrolyze. Of note, these properties are unaltered even when the size of ZnS is reduced to nanometer scale. Therefore, ZnS nanomaterials exhibit excellent photocatalytic activity. Moreover, ZnS is non-toxic, easily fabricated, and widely used. Many studies have successfully synthesized a low-dimensional nanomaterial such as ZnS nanoparticles, nanowires, nanotubes, and nanosheets. The following properties are the three most common approaches for enhancing the ZnS photocatalytic activity. (i) Surface area is increased by changing the ZnS morphology. A high specific surface area can increase the active site on the ZnS surface and can increase the contact area between ZnS and the reactant, hence increasing the ZnS photocatalytic activity. (ii) Altering the electronic properties and band structure of ZnS through doping with other metals and nonmetallic elements, the absorption rate of ZnS to visible light is improved, thereby improving the photocatalytic efficiency of ZnS. (iii) ZnS forms a heterojunction with other semiconductors or a composite structure with noble metals to reduce the electron-hole recombination rate, thereby improving the photocatalytic performance of ZnS (Zhang et al., 2007).

19.2.1.2.4 Nitride photocatalyst

The C_3N_4 is a graphite-like layered structure with an excellent electron/hole transporting ability, chemical stability, and high thermal stability. It has narrow band gap which ranges from 2.7 to 2.8 eV. The forbidden bandwidth of C_3N_4 allows it to absorb visible light with 400–450 nm wavelength. The structure and properties of C_3N_4 are easy to control, making it a suited as a photocatalysts. Studies have shown that C_3N_4 is an excellent photocatalyst which could be used for photo-hydrolysis process, hydrogen production, CO_2 reduction, sterilization, and synthesis of composite capacitor materials photodegradation of environmental pollutants such as pesticides. The forbidden band width of semiconductors is an important attribute which limit the wide application of photocatalysts. As such this attribute is estimated for all proposed photocatalysts to be used for solar-driven photocatalysis either homogeneous or heterogeneous photocatalysis (Fina et al., 2015).

19.2.2 Homogeneous photocatalysis

Homogenous photocatalysis is a process that was first recognized in the 1960s and it is the most applied AOPs because of its ability to degrade organic compounds in high salinity (Matilainen and Sillanpää, 2010). Several studies have investigated the application of homogenous catalysis in the degradation of water pollutants such as phenolics, chlorophenols and pesticides with organic loading of up to 25 g/L

(Zhang et al., 2020). The homogeneous photocatalytic processes that are of environmental significance and play an important role in the purification of wastewater by ultraviolet (UV) component of the sun are those that originated on hydro-complexes of transition metals such as iron (Fe), copper (Cu), chromium (Cr), and zinc (Zn) because of their higher oxidation state (Pawar and Lee, 2015, Ahmed et al., 2011). Thus, the generated hydroxyl radicals ($^{\bullet}OH$) react with the organic pollutants, leading to accumulation of various organic radicals (Prihod'ko R and Soboleva, 2013). One-channel flow photochemical process, in this case, is the oxidation of the substrate $^{\bullet}OH$ that are formed as a result of phototransfer charge in the hydraulic field inside the metal ions (Me) in a higher valence state (Prihod'ko R and Soboleva, 2013). The equation below illustrates the formation of organic pollutant radicals:

$$MeOH^{n+} + hv \rightarrow Me^{(n-1)+} + \cdot OH \tag{19.1}$$

$$Me\left(\text{organic pollutant}\right)^{n+} + hv \rightarrow Me^{(n-1)+} + \left(\text{organic pollutant}\right)\cdot \tag{19.2}$$

Numerous literatures over the years has provided a comprehensive understanding of the homogenous photo-Fenton reaction which is a process used in wastewater treatment. Hydrogen peroxide (H_2O_2) in the absence of light decomposes Fe^{2+} present in aqueous phase resulting in the formation of hydroxyl radical, however, in the presence of light the H_2O_2 is decomposed by ferrous (Fe^{2+}) or ferric (Fe^{3+}) ions resulting in the formation of free radicals (Le et al., 2004). The Fenton and photo-Fenton reaction occur simultaneously with a photocatalyst such as TiO_2 during UV-Vis irradiation period (Ameta et al., 2018). The mechanism of the Fenton reaction is shown in (Eq (19.3)). Fe^{3+} can revert to Fe^{2+} through a different mechanism shown in Eq. (19.4) and (19.5). Photo-Fenton reaction is positively enhanced in the presence of light. This is mainly due to Fe^{2+} regeneration by photochemical effect of light with simultaneous ·OH production in the system.

This reversible process $Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) \rightarrow Fe^{2+}(aq)$ leads to continuous generation of OH radical provided the concentration of H_2O_2 is substantial.

$$Fe^{2+}\left(aq\right) + H_2O_2 \rightarrow Fe^{3+}\left(aq\right) + OH^- + \cdot OH \tag{19.3}$$

$$Fe^{3+}\left(aq\right) + H_2O_2 \rightarrow Fe^{2+}\left(aq\right) + HO_2\cdot + H^+ \tag{19.4}$$

$$Fe^{3+}\left(aq\right) + HO_2\cdot \rightarrow Fe^{2+}\left(aq\right) + O_2 + H^+ \tag{19.5}$$

$$H_2O_2 + e^- \rightarrow \cdot OH + OH^- \tag{19.6}$$

$$O_2^- + H_2O_2 \rightarrow O_2 + \cdot OH + OH^- \tag{19.7}$$

$$\cdot OH + H_2O_2 \rightarrow HO_2^{\cdot} + H_2O \tag{19.8}$$

$$\text{Organic pollutant} + \cdot OH \rightarrow \text{degraded products} \tag{19.9}$$

The free radical generated from the photo-Fenton process attacks and degrade toxic organic compounds. Similarly, heterogeneous photocatalysis can be used to degrade hazardous materials.

19.2.3 Heterogeneous photocatalysis

Heterogeneous photocatalysis is when both the semiconductor and reactant are in different phases. Heterogeneous photocatalysis contribution to water treatment technologies is promising with advantages which include simplicity, efficiency, and the possibility of using solar light (Loeb et al., 2019). The exploitation of heterogenic photocatalysis on semiconductor materials have shown significant improvement in the processes of water purification of pollutants and contaminants of natural and man-made origin, artificial photosynthesis, developing methods of storing the energy of sunlight and photochemical water decomposition, and so forth (Zhang et al., 2020). Most studies consider heterogenic systems based on titanium dioxide (TiO_2) and TiO_2+ $S_2O_8^{2-}$ compared to other semiconductors (Fe_2O_3, ZnO, CdS, ZnS, SnO_2, and ZnO + $S_2O_8^{2-}$) because of their limitation of solubility in water or toxicity (Prihod'ko R and Soboleva, 2013). TiO_2 is a highly active, cheap, nontoxic, and chemically stable product of heavy-duty production.

The fundamentals of the heterogeneous photocatalysis have been reported in numerous studies showing that semiconductor surface under irradiation when in contact with organic compounds can induce series of reduction-oxidation (redox) reaction resulting in degradation of the organic compounds (Pawar and Lee, 2015, Wang et al., 2019). When a photon of energy (*hv*) is greater than the bandgap energy of a semiconductor is illustrated on its surface, the lone electron will be photoexcited to the empty conduction band in femtoseconds (Chong et al., 2010, Senthilnathan and Philip, 2012). The mechanistic formation of electron-pair when a semiconductor particle is irradiated with adequate *hv* under a wavelength of <400nm leads to photonic excitation which results in an unfilled valence band, thus creating electron-hole pair (e^-– h^+) as depicted in Fig. 19.1. The series of redox reactions that occur at the photon activated surface is shown as follows:

$$\text{semiconductor} + \text{hv} \rightarrow e^- + h^+ \tag{19.10}$$

$$h^+ + H_2O \rightarrow \cdot OH + H^+ \tag{19.11}$$

$$h^+ + \text{Organic pollutant} \rightarrow (\text{Organic pollutant})^+ \tag{19.12}$$

$$e^- + O_2 \rightarrow \cdot O_2^- \tag{19.13}$$

$$\cdot O_2^- + H^+ \rightarrow \cdot OOH \tag{19.14}$$

$$\cdot OOH \rightarrow O_2 + H_2O_2 \tag{19.15}$$

$$H_2O_2 + \cdot O_2^- \rightarrow \cdot OH + OH^- + O_2 \tag{19.16}$$

$$H_2O_2 + \cdot O_2^- \rightarrow \cdot OH + OH^- + O_2 \tag{19.17}$$

$$H_2O_2 + \text{hv} \rightarrow 2 \cdot OH \tag{19.18}$$

$$\text{Organic pollutant} + \left(\cdot OH, h^+, \cdot OOH \text{ or } \cdot O_2^-\right) \rightarrow \text{Organic pollutant degradation} \tag{19.19}$$

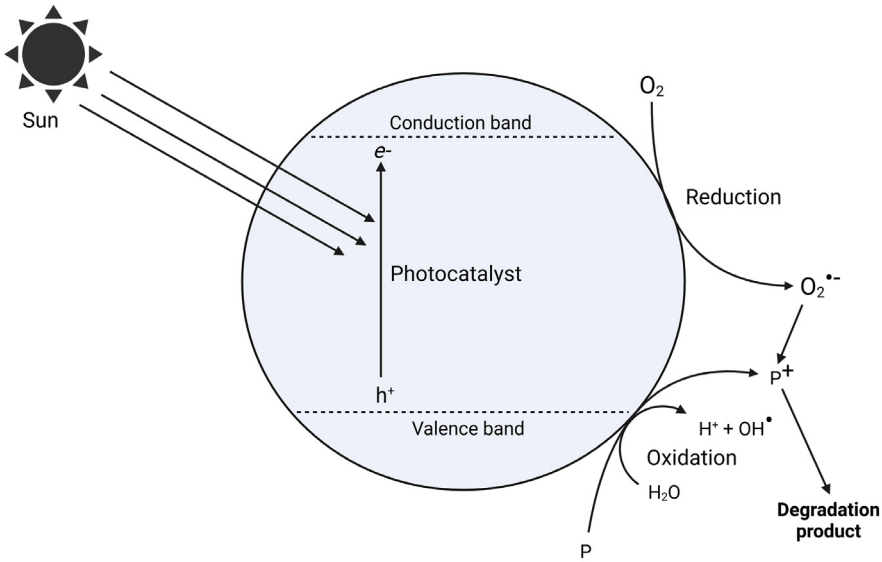

FIG. 19.1 Mechanism of photo-induced formation of electron-hole pair in semiconductors in the presence of water pollutants (P).

The Eqs. (19.10-19.19) is a clear heterogeneous catalytic process involving series of steps which include the generation of OH radicals. These radicals have strong oxidizing power and could degrade organic pollutants such as pesticides thereby converting them into harmless products. Both heterogeneous and homogenous photocatalysis were reported in literature as standard and cost-effective methods in soil and wastewater treatment.

19.3 Pesticides and toxicities

The increase in human population and industrialization has led to high demand of food and water supply. The treatment of crops with pesticides is central to increased crop yield and improve crop production. However, the large-scale use of pesticides in agriculture lead to environmental pollution especially soil and water pollution. The term pesticide refers to the chemicals that are constantly used to kill pests and preventing crop destruction. These pesticides are classified as herbicides, insecticides, and fungicides etc. Water pollution from pesticides is very common, especially in countries with intense agricultural and industrial activities (Choudri et al., 2018).

Pesticides and their residues are usually transported to contaminate crops, ground water and fresh water supplies in large geographical area. The accumulation of pesticide residues in fruits and vegetables affect human's health after consumption over time. Many of the pesticides are been classified as endocrine disruptors, substances

that disrupt the function of endocrine. Pesticides exist in four major groups; these are the chlorinated pesticides, nitrogen-containing pesticides, pesticides containing sulphur atoms, and organophosphorus pesticides. The most popularly used pesticides include organochlorine such as dichlorodiphenyltrichloroethane (DDT), chlorophenoxy, and pentachlorophenol; organophosphate such as glyphosate, parathion and malathion, nitrophenolic, arsenic-containing fungicides, fumigants; and rodenticides such as atrazine (Leemans et al., 2019).

The toxicity of pesticides in humans is lethal regardless if it is consumed as a residue in food or water. Pesticides are toxic by nature to some degree to different organisms, including humans. However, some of them are such potent toxins that they are extremely hazardous chemicals. Like other toxic substances, the active components in pesticides must come into contact with its target such as a receptors or enzymes (Leemans et al., 2019). A sufficient concentration of pesticides is required before it can exert a toxic effect. Therefore, the physical characteristics of the active component, stability, distribution, penetration ability, persistence, and degradation in the body are of considerably influential for a pesticide to be toxic (Bhattacharjee et al., 2012). These characteristics varies in different pesticide to another depending on the active component. The diversity of chemical structures among pesticides leads to the viable biological effects produced in both pests and humans. The structure of some selected pesticides is shown in Fig. 19.2. Of note the toxic effect of only some of these pesticides are well understood which are briefly summarized in Table 19.1.

19.3.1 Pesticides detection and quantitation in wastewater

Currently, there are several methods to detect pesticides in the surrounding environment, such as surface waters and soil. The most frequently encountered pesticides in water are herbicides and insecticide. The most common methods used for the detection and identification of pesticides in water samples are liquid chromatography (LC) and gas chromatography (GC) (Hossain et al., 2015). The chromatography-based methods are the most widely used techniques for the detection of organic pesticides such as organo-phosphorus. Researchers around the world have adopted different procedures for extraction and estimation of organic pesticides using chromatography. However, the low detection levels for these organic pesticides in environment indicate the challenge to use a new analytical instruments with a higher selectivity and detectability, such as liquid chromatography-tandem mass spectrometry (LC-MS/MS), gas chromatography-mass spectrometry (GC-MS), and ultra-high-performance liquid chromatography-tandem mass spectrometry (UHPLC-MS/MS) which are often necessary to identify and quantify these pesticides (Bhattacharjee et al., 2012).

Some pesticides cannot be detected in water sample using GC-MS due to their thermal instabilities and polarities. A practical technique preferred in this regard is liquid chromatography-mass spectrometry (LC-MS), which has been widely used to quantify thermally labile pesticides to confirm their identities in crops, and water sample. The LC is usually combined with full scan mass spectrometers, such as orbitrap and time-of-flight (TOF) mass spectrometers (Hossain et al., 2015).

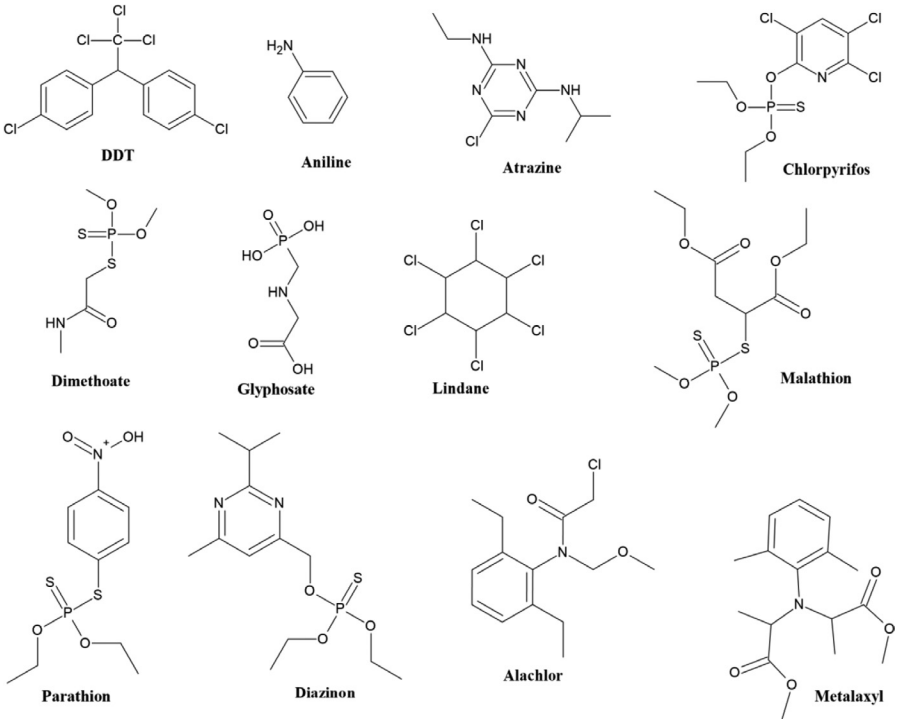

FIG. 19.2 Structures of some selected pesticides.

These types of mass analyzers are increasingly used as instruments for identification, quantification, characterization, and the structural elucidation of compounds such as pharmaceuticals, veterinary drugs, pesticides, and other unknown contaminants by obtaining excellent full MS scan sensitivity, and complete mass spectral information from chromatogram. In recent years, the development of advanced chromatographic methods and preparation procedures has attracted the interest of many chromatographers, which provide higher sensitivity than the conventional high-performance liquid chromatography (HPLC) (Zamora-Sequeira et al., 2019).

Capillary LC (CLC) and nano-LC offer the possibility to perform fast, highly effective and efficient analyses in different fields. The sensitivity these technics can be increased using limit of detection (LOD) and limit of quantitation (LOQ) within the range of 4.4–37.5 and 14.5–125.0 ng/mL respectively. Both CLC and nano-LC are alternative methods for detecting pesticides (Hossain et al., 2015).

The development of novel strategies such as sensor and biosensor devices have several advantages over traditional methods. Some of the advantages which include: their simplicity, sensitivity, selectivity and their capacity to be deployed in detecting and monitoring of pesticide contamination in water. Furthermore, the use of

Table 19.1 Example of some pesticides and their toxic effect.

Class of pesticide	Name of pesticide	Primary use	Mode of action in mammals	Oral acute toxicity in Rat (LD50; mg/kg)	WHO classification by hazard
Organophosphorus	Parathion	Insecticide	Inhibition of cholinesterases	13	Extremely hazardous
	Dichlorvos	Insecticide	Inhibition of cholinesterases	56	Highly hazardous
	Malathion	Insecticide	Inhibition of cholinesterases	2100	Slightly hazardous
Organochloride	Dieldrin	Insecticide	Disturbance of sodium (Na^+) and potassium (K^+) ion transport in nervous membranes	37	Highly hazardous
	DDT	Insecticide	Disturbance of sodium (Na^+) and potassium (K^+) ion transport in nervous membranes	113	Moderately hazardous
	Permethrin	Insecticide	Disturbance of sodium (Na^+) and potassium (K^+) ion transport in nervous membranes	500	Moderately hazardous
	Deltamethrin	Insecticide	Disturbance of sodium (Na^+) and potassium (K^+) ion transport in nervous membranes	135	Moderately hazardous
Organonitrate	Dinoseb	Herbicide	Electron transport inhibition	58	Highly hazardous
	DNOC	Insecticide	Electron transport inhibition	25	Highly hazardous
	Atrazine	Herbicide	Nonspecific irritant	2000	Slightly hazardous
	Paraquat	Herbicide	Excessive production of superoxide	150	Moderately hazardous
Organosulphate	Maneb	Fungicide	Nonspecific irritant	6750	Slightly hazardous

nanomaterials in the construction of sensors and biosensors could serve as highly efficient analytical tool for the detection of pesticides in contaminated wastewater. The use of sense and biosensor constructed with nanomaterial are sensitive and highly sensitive, in contrast to conventional detection techniques, which have various complications including sample decomposition, a limited number of samples in a specific time interval, matrix interference and a longer test duration. The use of biosensors in the detection of pesticides paves way for more efficient analysis, with higher precision, ability to detection low concentrations, continuous monitoring and cheap (Ejeian et al., 2018).

19.4 Wastewater treatment

Effluents from various sources such as farms, domestic, industrial, sludge, etc. consist of many nonbiodegradable organic compounds, xenobiotic chemicals, oil, petroleum waste, and dyes (Ranade and Bhandari, 2014).

An increase in industrialization has become a major source of environmental pollution (Ranade and Bhandari, 2014). Particularly, chemical, textile, paper, pesticides, and fertilizer industries. The discharge of industrial wastes in nearby water bodies without treatment is the major cause of water pollution (Souza et al., 2016). Water pollution is emerging as a serious threat to human health and environmental ecosystem (Ranade and Bhandari, 2014) Many of the conventional wastewater treatment methods such as chemical, physical, and biological methods involving adsorption, sedimentation, coagulation, filtration, chlorination, ozonation, reverse osmosis, UVC disinfection activated sludge process, trickling filter, oxidation ditch, aerated lagoon, and stabilization ponds are used for decades, however, these methods are not sufficient to treat large scale wastewater streams as these require high capital investment, operation, maintenance cost, and a large area (Bhuta, 2014). Also, these methods do not degrade the effluents up to the desired level for recycling and require analysis time in several days. Therefore, there is a vital requirement for developing new hygienically friendly purification technologies (Rani et al., 2017).

Researchers have supported the technique of homogenous and heterogeneous photocatalytic process to degrade, decompose, and eliminate the hazardous or nonhazardous hard-to-biodegrade organic, inorganic, pollutants or contaminants such as pesticides.

The variety of pesticides, their toxicities, and their persistence in the environment present a threat to humans through pollution of drinking water resources. The presence of pesticides in drinking water cause severe health conditions such as cancer, birth defect, reproductive effects, organ damage, and nervous system damage. The frequent occurrence in surface water and groundwater and its associated health effect have prompted the search for suitable and cost-effective methods to destroy them. Although conventional biological method of water treatment offers some advantages such as low cost and easy to operate, most studies with respect

to the method have concluded that the biological methods are ineffective due to their low biodegradability. Technologies such as adsorption without destruction merely concentrate pesticides by transferring them in other phases but remain without being properly eliminated. To solve this problem there is a need to search for a technology involving the destruction and elimination of the pesticides from the water. The chemical method of treating pollutants on surface water, wastewater and groundwater is a long-term strategy to improve water quality by removing toxic compounds. The Directive of 2013/39/EU promotes taking preventive action and polluter pays principle, to identify causes of pollution, deal with emissions of pollutant from the source, and finally initiate the development of innovative strategy for wastewater treatment and providing eco-friendly and cost-effective solutions. Therefore, a robust method of effective and low cost is required to decontaminate polluted water, if they are ecofriendly and do not further stress the environment or endanger human health. In recent years there has been growing interest in the use of AOPs (e.g. solar-driven photocatalysis) to remove pesticide residues as alternative to conventional methods because they can mineralize pesticides with higher efficiency and effectivity.

19.4.1 Photocatalytic degradation of pesticides for wastewater treatment

Pesticide accumulation in water is one of the major problems faced by developing and developed countries alike (Dutta et al., 2015). Although pesticides are important in crop production, however, it has significant risk on human health and environmental ecosystems (Aliste et al., 2019). Adsorption, degradation and movement are the processes that determine the fate of pesticide in the environment (Miklos et al., 2018). The movement of pesticides is based on volatilization, diffusion, erosion, run-off, and leaching (Li et al., 2009). Leaching and run-off are the two major processes via which pesticides are transferred to water bodies in farms and industries respectively (Aliste et al., 2019).

In photocatalysis of pesticides, the attack of hydroxyl radicals leads to mineralization of the parent organic compound into the desired product to eliminate their toxicity. Solar-driven photocatalysis is a promising method for mineralization of pesticides is application. Various photocatalytic processes such as homogeneous and heterogeneous photocatalysis use OH generated from either metallic salts, or semiconductors (e.g., TiO_2). The most-widely used photocatalytic process for pesticide degradation are photo-Fenton and Fenton-like systems (H_2O_2/UV/Fe^{3+}) and photocatalytic oxidation (TiO_2/UV).

Mineralization of chlorinated pesticides leads to release of chloride (Cl^-) ions in the water solution which are the first of the ions appearing during the photocatalytic degradation (Le et al., 2004). Similarly, the nitrogen-containing pesticides are usually mineralized into NO_3^- and ammonium (NH_4^+) ions (Calza et al., 2005). The NH_4^+ generated from the mineralization is relatively stable, and the proportion mainly depends on the oxidation stage of organic nitrogen and irradiation time

(Calza et al., 2005). The formation of N_2 in azo bounds can be accounted for by the same processes responsible for NH_4^+ formation. Di-nitrogen (N_2) evolution constitutes the ideal case for a decontamination reaction involving harmless nitrogen-containing final product (Calza et al., 2005). Mineralization in pesticides containing sulphur atoms involves the releasing sulphate (SO_4^{2-}) ions. The release of SO_4^{2-} is created by an initial attack by a photo-induced $^{\bullet}OH$ radical. All studies showed the stoichiometric formation of SO_4^{2-} was observed in the final steps of the photocatalytic process when organic intermediates were still present (Lapertot et al., 2008). Monitoring the initial rate, it was observed to be high indicating that SO_4^{2-} ions are initial products, directly resulting from the initial attack on the sulfonyl group. Nonstoichiometric formation of SO_4^{2-} is usually explained by strong adsorption on the photocatalyst surface (Burrows et al., 2002).

Organophosphorus pesticides mineralize into phosphate (PO_4^{3-}) ions. The PO_4^{3-} remain adsorbed on photocatalyst such as TiO_2, this strong adsorption somewhat inhibits the reaction rate, though it is still acceptable. In photo-Fenton, PO_4^{3-} sequestrates iron (Fe^{2+} /Fe^{3+}) forming the corresponding nonsoluble salt and retarding the reaction rate. Therefore, more Fe^{2+} is required when water containing organophosphorus pesticides is treated by photo-Fenton process (Matilainen and Sillanpää, 2010). The products of mineralization such as Cl^-, SO_4^{2-} and PO_4^{3-} at concentrations >1 mM can affect the reaction rate due to competitive adsorption at the photoactivated reaction sites of photocatalyzed (Amalraj and Pius, 2015). Studies have reported that photo-Fenton process efficiency is noticeably lowered in the presence of high concentration of Cl^- and SO_4^{2-}. Furthermore, decrease production or recycling of hydroxyl radicals was observed due to formation of Fe(III) chloro- and sulfato-complexes that affect the distribution and reactivity of Fe species and scavenging of hydroxyl radicals and formation of inorganic radicals ($Cl_2^{\bullet-}$ and $SO_4^{\bullet-}$), which are less reactive than $^{\bullet}OH$ (Malato et al., 2012).

The complete degradation of the initial compound does not determine its effectiveness. Reactants and products might be lost through adsorption on reactor components or evaporation which introduces uncertainty in results. The mineralization rate is determined by monitoring inorganic compounds, such as CO_2, Cl^-, NO_3^-, SO_4^{2-} and PO_4^{3-} (Malato et al., 2012).

The most widely used nanoparticles for the pesticide degradation are TiO_2 and ZnO nanoparticles (NPs), because they function at room temperature (25°C) and pressure with low energy photons and no chemical reagent is required except the atmospheric O_2. Several studies using TiO_2 NPs as semiconductor for photocatalytic degradation for both single pesticide and multiple pesticides have been reported. The photocatalytic reaction involves the adsorption of pesticide molecules onto the surface of TiO_2 NPs, free radicals generated causes chemical bonds breakage, which in turn, lead to formation and subsequent release of the degraded pesticide product molecules. The peculiarity of surface area and surface activity of semiconductors are crucial for catalytic reactions.

A study showed degradation of organic pesticide (atrazine) using TiO_2 nanowires because of their ability to simultaneously provide mechanical filtration and

photocatalytic degradation under UV irradiation. Similarly, photocatalytic degradation of atrazine was obtained using a combination of TiO_2 NPs with multiwalled carbon nanotubes (MWCNTs), however, this study used microwave irradiation for degradation and not UV light. Comparing using TiO_2 alone and TiO_2/MWCNT combination, the TiO_2/MWCNT showed higher efficiency (20–30% higher) for degradation of atrazine (Peshoria and Kumar Narula, 2018).

In another study, the authors reported using Au-coated TiO_2 nanotube (NT) arrays which can act as recyclable surface-enhanced Raman spectroscopy (SERS) substrates, although the primary objective of the study was to detect 2,4-D, methyl parathion, and 4-chlorophenol using SERS, they discovered that the system recycled itself by photocatalytic degradation under UV light. This phenomenon is made possible because of the catalytic functions of the substrate (Sarkar and Das, 2018).

Researchers over the years have fabricated TiO_2 NTs with diverse surface modifications to use it for various functions. One of its function include metallic inclusions capable of trapping photoinduced charge carriers to improve charge separation and enhance light absorption in semiconductor oxides. In this context, a semiconductor was designed using Au–Pd in combination with TiO_2 thereby forming Au–Pd–TiO_2 NT film photocatalyst for degradation of malathion and proposed a corresponding photocatalytic mechanism (Della Pelle et al., 2018). Direct contact between TiO_2 and Fe_2O_3 compromises photocatalytic activity, since Fe_2O_3 acts as recombination center for electrons and positive holes (Komiyama et al., 2018). To overcome this effect, a study reported the use of polyelectrolyte insulators. Their system is stable and does not suffer from photo dissolution, degrading chloroacetamide herbicides in good yields. Bi_2O_3 is another doping agent used with nanostructured TiO_2 for photocatalytic destruction of chlorophenols as reported elsewhere (Liu et al., 2018). Unlike other organic pesticides, chlorophenols cannot be degraded by either O^{2-} or H_2O_2, as in a typical system. Taken into consideration of the fact that the higher number of surface atoms in a material at the nanoscale (NS) enables reactions that cannot be accomplished in the corresponding bulk material, the authors in this study described the possibility of degrading chlorophenols using nanoporous (NPs) TiO_2 doped with β-Bi_2O_3. In addition, semiconductors such as AgNPs and ZnO/Au (NRs) were harnessed for photocatalytic destruction of organic pesticides (Yan et al., 2018).

Fenton-like processes have been reported for pesticide degradation, although few reports showed their use in photocatalytic reactions. The Fenton reaction is based on the production of hydroxyl radicals from Fe^{2+} (see Eqs. 19.1 and 19.7). Although this process is an attractive method for oxidizing organic compounds; it requires large amounts of Fe^{2+} and generates large amounts of Fe^{3+} that require subsequent treatment. Nanomaterials such as ferromagnetic NPs can solve the problems of the homogeneous Fenton reaction because they are highly stable, relatively cheap and easy to preparation, environmental soundness, and possess potential for reuse based on magnetic separation, as reported by several studies. Relative to the aforementioned condition, over 85% of phenol is believed to be

degraded at the optimal reaction conditions (Qiao et al., 2018). The efficiency of the Fenton reaction can be enhanced by using UV/vis irradiation, in what is known as photo-Fenton-like processes. In photo-Fenton-like process the UV/vis irradiation can regenerate Fe^{2+} species more quickly than in Fenton process, giving that more ·OH are ready for the organic pesticide degradation. Using the photo-Fenton process, metalaxyl was destroyed using bismuth-doped goethite–hematite nanostructures (NS) (Bu et al., 2018). Furthermore, the study confirmed the addition of bismuth affects the morphology of iron (Fe) NS. Also, it demonstrated that the catalytic activity is closely related to the morphology and phase composition, the highest activity recorded was by a homogeneous mixture of hematite and bismuth ferrite NPs, which had the largest surface area of all the materials that were tested. In addition to the studies described above, other reports on the use of Fe and nanomaterials used for degrading organic pesticides have been extensively discussed. Table 19.2 summerised some pesticides and nanomaterials used to remove them using different methods.

Taken all the discussed methods together, a stoichiometric increase in the concentration of inorganic anions is produced in treated water when organic pesticides decomposed. In water treatment, the photocatalysis process is done together with the adsorption process to separate pesticides from water. This ensures absolute purification of water devoid of pesticides making it suitable for use.

19.4.2 Adsorption of organic pesticides from wastewater

Nanomaterials and their composites are used for pesticide removal in wastewater. The morphological features, textural features, high surface area, variable surface chemistry, specific crystalline nature, and abundant availability make the nanostructured metal oxides and their composites highly selective materials for efficient removal of organic pesticides based on adsorption and photocatalysis (Gusain et al., 2019). A wide range of metal oxides such as Fe_2O_3, TiO_2, ZnO, CuO, MnO, and their composites are used for pesticides adsorption (Gusain et al., 2019). Similarly, these metal oxides are used as photocatalysts in solar-driven photocatalysis (Ahmed et al., 2011).

Over the years, researchers have assessed adsorbents based on surface feature, variable composition, structure and texture to select the most efficient in the removal of a wide range of organic pesticides from wastewater. The integration of adsorption characteristic of metal oxide and graphene in nanocomposites increased the adsorption capacity for organic pesticides, increasing the adsorption rate and ease the recovery of spent nanocomposites (Liu et al., 2014).

The metal oxide-graphene nanocomposites are extensively exploited for the removal of organic pesticides from contaminated water. The magnetic properties of metals in the metal-graphene nanocomposites facilitate the separation of organic pesticides captured with the adsorbent to separate from the water by applying the external magnetic force (Fig. 19.3) (Boruah et al., 2017). Table 19.3 summarized some organic pesticides and the adsorbent used to capture them in wastewater treatment.

Table 19.2 List of pesticides removed from water using different nanomaterials.

Pesticides	Nanomaterial	Strategy	Max. degradation or recovery (%)	Ref
Alachlor/ Fenitrothion	TiO2 NPs	photocatalysis	100	(Lapertot et al., 2008)
Atrazine	TiO2 NWs	photocatalysis		(Khavar et al., 2018)
Atrazine	TiO2 NPs coated MWCNTs	microwave-assisted photocatalysis	100	(Peshoria and Kumar Narula, 2018)
Malathion	Au–Pd–TiO2 NT film	photocatalysis	>96	(Della Pelle et al., 2018)
Methyl parathion/2,4-D	AuNP's-coated TiO2 NT array	photocatalysis	100	(Sarkar and Das, 2018)
Propachlor	TiO2 NPs/γ-Fe2O3	photocatalysis		(Komiyama et al., 2018)
Lindane	Pd NPs	catalytic de-chlorination	75	(Rahim et al., 2018)
PCP	nanoporous Ti-doped βBi2O3	photocatalysis		(Liu et al., 2018)
2-CP/DCP/TCP	Ag-AgBr NP/ MAP	photocatalysis	71–80	(Yan et al., 2018)
4-CP	ZnO/Au NRs	photocatalysis	91	(Cao et al., 2018)
Phenol	MNPs	Fenton-like catalysis	85	(Qiao et al., 2018)
Atrazine	NZVI/CTMA-Bent	chemical reduction	64	(Kusior et al., 2018)
Metalaxyl	bidoped goethite-hematite NS	photo-Fenton-like catalysis	99	(Bu et al., 2018)
Methyl parathion/ Lindane/ dichlorvos	Nano-TiO2 immobilized on Pyrex glass	photocatalysis	100	(Zheng et al., 2018)
Atrazine/ Dimethoate	nanoporous membrane	nanofiltration	95/90	(Kaur et al., 2018)

Abbreviation: CP, *chlorophenol;* DCP, *2,4-dichlorophenol;* MAP, *ordered mesoporous γ-Al2O3;* NR, *nanorods;* PCP, *pentachlorophenol;* NS, *nanostructures;* NT, *nanotube;* CTMA-Bent, *cetyltrimethylammonium bromide–bentonite;* ZVI, *zero-valent iron;* NW, *nanowires;* MNPs, *magnetic nanoparticle.*

19.4.3 Challenges in the development of large-scale photocatalytic water treatment plant

The importance of water treatment for global health and economic development cannot be overemphasized. Innovative strategies to providing affordable clean water safely and universally is a grand challenge of great severity as the demand for

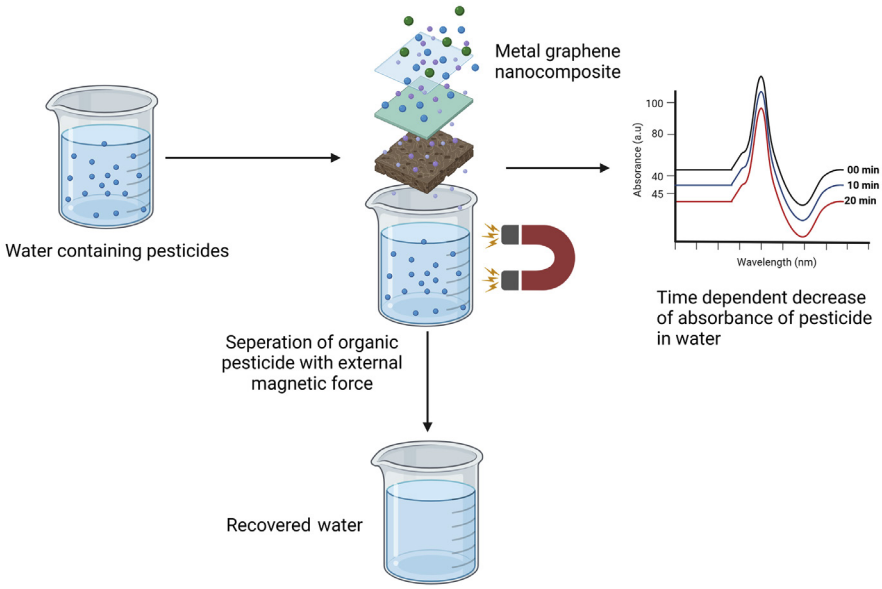

FIG. 19.3 An illustration of the mechanism of interaction between pesticide molecules and adsorbent.

A time-dependent decrease in absorbance showed the adsorption of pesticide by the adsorbent, which could be subsequently separated by external magnetism effect.

freshwater increases with a growing world population. One of the causes of freshwater scarcity is water pollution (Prüss-Ustün et al., 2014). Currently >650 million people worldwide lack access to safe water, and every 2 minutes, a child under 5 years of age dies due to poor water quality and inadequate sanitation (Prüss-Ustün et al., 2014, UNICEF, 2015). Purification technologies such as photocatalysis target pollutants that are not easily detectable, but can cause chronic toxicity, ranging from infertility to cancer (Alvarez et al., 2018).

Pollutants and emerging contaminants are frequently detected in drinking water sources, sewage treatment plant effluents and natural waters at levels that may jeopardize public or ecosystem health (Loeb et al., 2019). This condition provides the need for technological innovation and capacity vitalization of marginally effective water treatment infrastructure (Loeb et al., 2019). Improved wastewater treatment and pollution control will significantly alleviate health care costs and loss of productivity, it will also increase economic development. Eco-friendly technologies such as solar-driven photocatalysis are important to alleviate the financial burden of maintaining and operating ageing drinking water and wastewater treatment plants (Kumar and Devi, 2011).

Large-scale water treatment via solar-driven photocatalysis could help transform method of water and wastewater treatment to meet global water-quality standards (Kumar and Devi, 2011).

Table 19.3 Types of adsorbent used for pesticides removal in wastewater.

Organic pesticides	Type of pesticide	Adsorbent	Structure	Adsorption capacity (mg/g)	Ref
Malathion	Organophosphate	Fe3O4@SiO2@GO-PEA	Nanocomposite	10.6	(Wanjeri et al., 2018)
Malathion	Organophosphate	Zn2+-doped TiO2	Nanoparticles	NM	(Nasseri et al., 2018)
DDT	Chlorinated pesticide	Fe3O4@nSiO2@mSiO2	Core-shell microspheres	97	(Liu et al., 2014, Salem et al., 2009)
p-nitrophenol	Nitrogen-containing pesticide	MWCNTs/iron oxide/β-CD	Magnetic microspheres	69.6	(Liu et al., 2014)
Trichlorophenol	Chlorinated pesticide	ZrO2-C	Flower-like morphology	306	(Liu et al., 2014, Tan et al., 2015)
Nitrobenzene	Nitrogen-containing pesticide	Fe-loaded SiO2	Nanoparticles	11.55	(Mangal et al., 2013)
Parathion	Organophosphate	Fe3O4@SiO2@GO-PEA	Nanocomposite	10.9	(Wanjeri et al., 2018)
Chlorpyrifos	Organophosphate	Fe3O4@SiO2@GO-PEA	Nanocomposite	11.1	(Wanjeri et al., 2018)
Glyphosate	Organophosphate	UiO-67/GO	Nanocomposite	482.69	(Yang et al., 2017)
Aniline	Nitrogen-containing pesticide	Fe3O4/graphene	Nanocomposite	202.8–375.9	(Chang et al., 2012)
p-chloroaniline	Chlorinated pesticide	Fe3O4/graphene	Nanocomposite	35.5–43.9	
Diazinon	Organophosphate	TiO2/Fe2O3	Nanocomposite	NM	(Gar Alalm et al., 2015)
Atrazine	Chlorinated pesticide	In and S co-doped TiO2@rGO	Nanocomposite	NM	(Lapertot et al., 2008, Khavar et al., 2018)
Dimethoate	Organophosphate	SBA-15 loaded with 8–42% TiO2	Nanocomposite	NM	(Li et al., 2018)

DDT: *Dichlorodiphenyltrichloroethane*, NM: *Not mentioned*

19.5 Concluding remarks

Evidence from the literature search on photocatalysis and adsorption, have shown their potential benefits in removing organic pesticides from wastewater. Solar-driven photocatalytic in wastewater treatment could also apply to organic hazardous contaminants, which are capable of water pollution by deep penetration into the soil and reach groundwater, lakes, streams and seas. Solar AOPs have an advantage over other types of AOPs by using sunlight to mechanistically degrade organic contaminants because it is an eco-friendly technology. However, there is still nveeded to determine the practical utility of this technique on a commercial scale.

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CHAPTER

20

Recent applications, reaction mechanism, and future perspective of hybrid ozonation process for water and wastewater treatment

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20.1 Introduction

Advanced oxidation processes (AOPs) are effective and environmental-friendly methods developed to oxidize organic pollutants in wastewaters. Usually, AOPs work with an in-situ generated oxidizing agent like hydroxyl radicals (•OH), Fenton's reagent, chlorine, hypochlorite, peroxy disulfate, and ozone, which can be obtained at a sufficient concentration to decontaminate the effluents effectively. The ozonation process is an emerging oxidation process among the existing AOPs; very promising and alternative wastewater treatment method without sludge generation and also decomposed into water and oxygen of residual ozone (Asghar et al., 2015). Ozone is popularly known as a strong oxidant; as its oxidation potential is in order of 2.07 V as well as a disinfectant in water treatment used for a long time. Ozonation is well known for its high oxidation capability and effectively applied to remove TOC,COD and colour (Soares et al., 2006), CN^-, SCN, and phenolic compounds (Chang et al., 2008) from industries effluents such as, coke wastewater, textile, leather tanning, paper and pulp industry, and petrochemicals. But operating cost due to power consumption is a limitation for its application and requirement of costly chemicals make it cost-prohibited. Thereby, the ozonation process required hybrid system to increase the efficiency at low cost. Hybrid ozonation could be a promising technique for the wastewater treatment because of low operating cost and reaction time. As an oxidant, ozone attacks primarily functional groups that are electron-rich like amines and activated aromatic rings (Wu et al., 2000).

Various studies have been established to improve the efficiency of ozonation process as a hybrid method such as alkaline solution ($O_3 + OH^-$), UV (O_3 + UV), peroxone ($O_3 + H_2O_2$), catalytic ozonation, and ozone electrocoagulation (O_3/EC)

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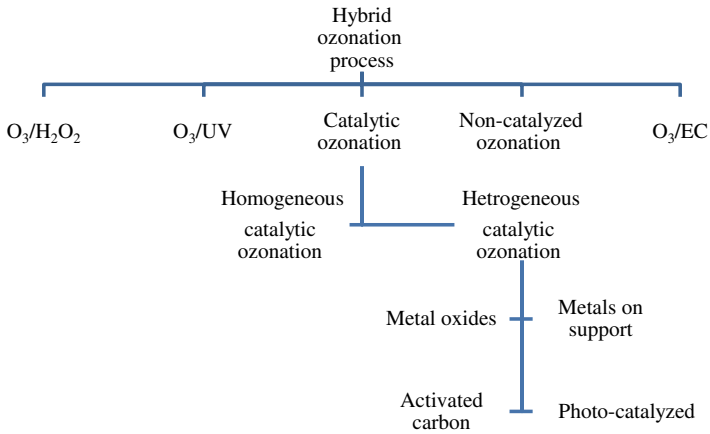

FIG. 20.1 Brief layout of hybrid ozonation process.

for mineralization of different type of refractory organic pollutants. Therefore this chapter reviewed the literature of ozonation and modified ozonation with the detailed reaction mechanism (Fig. 20.1) and brief description of the experimental results the process.

20.1.1 Direct ozonation

The reaction of ozone with organic pollutants present in the water depends on the electron density, oxidation-reduction reaction, cycloaddition reaction, electrophilic substitution reaction (Wang & Chen, 2020), and selective reaction rate constants (i.e. $1.0\text{-}10^6\ M^{-1}s^{-1}$) (Malik et al., 2020). In the direct reaction mechanism, the hydroxyl radicals are produced as per reaction (1) through participation of ozone molecules:

$$3O_3 + OH^- + H^+ \rightarrow 2OH\bullet + 4O_2 \tag{20.1}$$

The ozonation process has been effectively applied in the recent years to degrade the toxic organic pollutants in water/wastewater. The application of ozonation process is highly depend upon the selected pollutants and types of water for detoxification. Recent studies have justified the significance of the ozone process as a pretreatment option in the field of wastewater treatment (Fernandes et al., 2018; Malik et al., 2020).

20.1.2 Ozone micro nanobubbles

Micro nanobubbles (MNBs) are emerging approach applied in the field of wastewater treatment to intensify the process of decomposition of pollutants, especially to enhance the effective performance of the ozone in the aqueous medium. Nano-Ozone bubbles have longer life spans and high specific areas in comparison to the macro bubbles and therefore, increase the efficiency to ozonation due to its nanoscopic

size. In the form of micro and nanobubbles, the oxygen can produce high oxidizing potential, hydroxyl radical in abundance that would cause the destruction of different chemical pollutants (Paul et al., 2013) and more radicals generation in the Ozone usage (Von Gunten, 2003). Large size ozone bubbles leave the solution in less time that cause less contact time to dissolve in water. This issue can be solved through nanomicrobubbles, due to its buoyancy reduction property, since smaller bubbles inside pressure is higher as well as longer contact time due to which diffusion rates increases that allow super saturation of gas in water (Batagoda et al., 2018). Literature demonstrated that the ozone MNBs is a novel approach in ozonation technology that improves the removal efficiency of organics-contaminated groundwater. Mass transfer efficiency can be greatly affected by the quantity and quality of the MNBs. MNBs in larger amounts leads to large total surface area which enhances the mass transfer flux from bubbles to solution whereas higher specific area and excessive internal pressure associated with smaller bubble size (Zhiran & Liming, 2018). Khuntia et al. (2013) claimed that microbubble-based ozonation was an effective process in the wide ranges of pH of aqueous solution as much the biological degradation of ammonia. MNBs ozonation was also used for oxidation of most toxic element arsenic in groundwater (Khuntia et al., 2014). In another studies, micronano bubbles ozonation have been applied for removal of BOD and COD; 90.2% and 92.5% respectively from hospital wastewater (Menendez& Flores, 2018); coliform reduction from 1400 CFU/100 mL, to 56 CFU/100 mL presents in marine water (Abate & Valverde, 2017) reported removal and 95% removal of methyl in surface water treatment. Thus, ozone MNBs has shown its effectiveness in the oxidation of water and groundwater.

20.2 Combined ozonation for enhanced treatment of water

20.2.1 OH^-/O_3 process

The pH play an important role in the reaction solution and has effective control on direct as well as indirect ozonation (generation of •OH) efficiency. At alkaline pH, (pH > 8), the more yield of OH^- can improve the generation of •OH [Eqs. (2)–(6)], resulted accelerated the reaction with pollutants. However, more alkaline (pH> 11.9) solution might be responsible either for the decreased efficiency and calcium carbonate precipitation or create other problems. Thus, it could be suggested that the pH, 9-10 might be the optimal conditions for removal of organic pollutants while the neutral condition was also the optimal choice for wastewater preozonation (Chang et al., 2008).

$$O_3 + OH^- \rightarrow HO_4^- \tag{20.2}$$

$$HO_4^- \leftrightarrow HO_2\bullet + O_2^-\bullet \tag{20.3}$$

$$O_3 + O_2^-\bullet \rightarrow O_2 + O_3^-\bullet \tag{20.4}$$

$$O_3^-\bullet \rightarrow O_2 + O^-\bullet \tag{20.5}$$

$$O^-\bullet + H_2O \rightarrow \bullet OH + OH^- \tag{20.6}$$

20.2.2 O_3/H_2O_2 process

The O_3/H_2O_2 system is the effective method for enhanced removal of organic pollutants since H_2O_2 accelerates the decomposition of ozone as a strong oxidant to form the hydroxyl radicals as represented by the Eqs. (7)–(9).

$$H_2O_2 \rightarrow H^+ + HO_2^- \tag{20.7}$$

$$HO_2^- + O_3 \leftrightarrow HO_5^- \tag{20.8}$$

$$HO_5^- \rightarrow HO_2 \bullet + O_3^- \bullet \tag{20.9}$$

The O_3/H_2O_2 process is also term as the peroxone process that involves the both direct and indirect oxidation of pollutant. The addition of H_2O_2 leads to more generation of •OH through fast consumption of O_3. The yield of •OH can be obtained about 50% of the consumed O_3 (Fischbacher et al., 2013). The hydroxide radicals (•OH) can also be generated by the reaction between ozone and peroxide anion (HO_2^-) to form a precursor of •OH which consequently reacts with •OH (Merényi et al., 2010). Moreover, residual H_2O_2 should be destroyed before discarding/ releasing the treated effluent to the natural water bodies. The efficiency of ozonation influences directly with pH of treated water because of the different rate constant, k_{O3} values of dissociated target organic compounds (Calderara et al., 2002). Since the presence of hydroxide (OH^-) ions facilitates the formation of the •OH that leads to indirect ozonation. In addition, (Pisarenko, A. et al., 2012)has reported the optimum molar ratio, H_2O_2/O_3 = 0.5 mol/mol for the peroxone process as per the dose range of 1–20 mg/L. O_3/H_2O_2 is more approved and accepted method in drinking water treatment whereas some researchers have explored that the benefits for its application are limited due to high competitive reactions (Hübner et al., 2014). Along with this, radicals have also formed as a side product when ozone reacts with organic matter (i.e., phenol and amine functional groups) (Buffle, M. and von Gunten, 2006). Some methods are developed to initiate the formation of radicals actively causes ozonation at increasing pH and its combinations O_3/H_2O_2 (peroxone-process), O_3/catalysts, and O_3/UV.

20.2.3 UV/O_3 process

Photolysis of ozone is an advanced oxidation process with in which photo decomposition of ozone at UV radiation less than 300 nm leads to formation of hydrogen peroxide, hydroxyl radical and oxygen atoms (oxygen atom in excited state, ground state and oxygen molecule). The ozone reacts with hydrogen peroxide at slow rate constant in the range of $6.5 \times 10^{-2}\ M^{-1}s^{-1}$ as per equation 11 (Malik et al., 2020).

$$O_3 + H_2O + h\nu \rightarrow H_2O_2 + O_2 \tag{20.10}$$

$$O_3 + H_2O_2 \rightarrow HO_2 \bullet + OH \bullet + O_2 \tag{20.11}$$

(Reisz et al. 2003) has observed low quantum yield of free •OH relatively which generated with decomposition of a small proportion of H_2O_2 because of the cage

re-combination. Besides this, UV/O_3 system application is the limited in actual practice due to consumption of high energy relatively (Miklos, D. et al., 2018). In addition, photolysis of hydrogen peroxide produces two hydroxyl radicals. This UV/O_3 system contains subsequent reactions order of 'UV-radiation, Ozone, and hydrogen peroxide' to produce hydroxyl radicals or to oxidize the pollutants.

$$H_2O_2 + h\nu \rightarrow 2OH\bullet \tag{20.12}$$

Shang et al. (2007) has studied the O_3/UV oxidation of methyl methacrylate (MMA) and reported 96 and 22% removal of MMA and COD respectively, after contact time of 30 min, ozone dosage of10 mg/L, and UV power of 35.96 W/m^2. Additionally, they also observed more degradation of COD up to 51% within 120 min in the presence of the UV radiation that decompose the dissolved ozone concentration and facilitated the more OH radical's generation simultaneously which have high reactivity toward the mineralization of organic compounds. Shu & Chang (2005) has reported that decolorization rate is not affected by the both O_3 as well as for O_3/UV processes for azo dye. Such a behavior of decolorization was attributed to pH effect and chemical structures of azo dye. Pillai et al. (2009) has found that the pH of the solution is also decrease from its initial value 8.5–6.9 for the O_3/UV system similar to single O_3system i.e. more acidic pH of 4.5 at the end of the treatment. The recent application of O_3/UV process is depicted in Table 20.1 for wastewater treatment.

20.2.4 O_3/biological treatment

The ozonation has also been reported as an effective hybrid process in combination with biological method in which operating cost reduced significantly. The ozonation/biological treatment technology could be applied used either as pre-treatment to aeration (Ding et al., 2018), aerobic biological system (Bijan and Mohseni, 2005), activated carbon process (Lee et al., 2009) or as post-treatment, such as sequencing batch biofilm reactor/ozonation (Di Iaconi et al., 2002), membrane bioreactor/ozonation (Dogruel et al., 2006) and activated-sludge biological treatment/ozonation, (Treguer et al., 2010). Ozone-based processes are generally known for by- products formations which are more biodegradable than their parent compounds that further can be removed easily by biological treatment processes (Itzel et al., 2020). A biological treatment followed pretreatment ozonation would be suitable for the application for water that contains toxic inhibiting compounds. Thereby, biological treated method followed by ozonation may be a more suitable technology for considerable amount of biodegradable compounds (Oller et al., 2011).

20.2.5 O_3/electrocoagulation (O_3/EC)

Electrocoagulation is a promising process; and involves chemical and physical mechanisms simultaneously to remove pollutants from wastewaters. Electrocoagulation is not a new technology; as literature indicates that it has been reported since last

Table 20.1 Recent application of hybrid ozonation process for the degradation of toxic organic pollutants (SO: single ozonation; CO: catalytic ozonation).

Pollutants	Catalysts	Experimental conditions	Removal efficiency	References
Phenol	FeMgO/CNT	pH: 7; C_0: 400 mg/L; dose of O_3: 0.304 g/L h; catalyst: 1 g/L; reaction time: 60 min	TOC removal: 11% SO; 20% CO	Nguyen et al. (2018)
4-nitrophenol	MnO_2/rGO-B	C_0: 50 mg/L; catalyst: 0.1 g/L; dose of O_3: 50 mg/L; flow rate: 0.1 L/min; 25 °C; reaction time: 60 min	TOC removal: 16% SO; 84% CO	Wang et al. (2016c)
Phenol	$NiFe_2O_4$	pH: 6.5; C_0: 300 mg/L; catalyst: 1.0 g/L, dose of O_3: 0.75 mg/min; 20 °C; reaction time: 60 min	Phenol removal: 38.9% SO; 55.2% CO	Zhao et al. (2013)
Phenol	MgO	pH: 6.8; C_0: 100 mg/L; catalyst: 0.04 g/L, dose of O_3: 3.6 mg/min; reaction time: 10 min	Phenol removal: 35.9% SO; 70.1% CO	Wang et al. (2017)
4-nitrophenol	α-MnO_2-50	C_0: 25 mg/L, dose of O_3: 2 mg/min; catalyst: 0.1 g/L; pH: 7; reaction time: 90 min	TOC removal: 36.2% SO; 91.1% CO	Nawaz et al. (2017)
Phenol	CeO_2-OCNTs	pH: 6.2; C_0: 20 mg L; catalyst: 0.10 g/L; dose of O_3: 12 mg/L; reaction time: 60 min	TOC removal: 30% SO; 96% CO	Wang et al. (2019)
Atrazine	Zero-valent iron (ZVI)	pH: 6.7; C_0: 5 mg/L; dose of O_3: 10.8 mg; flow rate: 0.2 L/min catalyst: 3.0 g/L; reaction time: 30 min	atrazine removal: 35.3% SO; 98.5% CO	Li and Zhou (2019)
Atrazine	oxygen functionalized graphitic carbon nitride (O@g-C_3N_4)	pH: 6.0; C_0: 2 mg/L; catalyst: 0.5 g/L; dose of O_3: 5 mg/min; 20 °C; reaction time: 15 min	atrazine removal: 63.15% SO; 92.91% CO	Yuan et al. (2019)
2,4-dichlorophenoxyacetic acid	Fe–Ni/AC	pH: 4.18; C_0: 10 mg/L, catalyst: 0.5 g/L, dose of O_3: 50 mg/h; flow rate: 1.2 L/min; reaction time: 60 min	TOC removal: 34% SO; 72% CO	Lü et al. (2015)
Acetochlor	$Pr_6O_{11}/SiO_2@Fe_3O_4$	C_0: 20 mg L; catalyst: 0.50 g/L; dose of O_3: 60 mL/min; 30 °C reaction time: 120 min	TOC removal: 12.7% SO; 37.3% CO	Wang et al. (2018)

Table 20.1 Recent application of hybrid ozonation process for the degradation of toxic organic pollutants (SO: single ozonation; CO: catalytic ozonation). *Continued*

Pollutants	Catalysts	Experimental conditions	Removal efficiency	References
C. I. Acid Orange 7 (AO7)	$CuAl_2O_4$	pH: 6.54; C_0: 100 mg/L; dose of O_3: 10.06 mg/min, flow rate: 40 L/h; catalyst: 0.5 g/L; reaction time: 120 min	COD removal: 40% SO; 87.2% CO; AO7 removal (25 min): 76.4% SO; 96.0 CO	Xu et al. (2019)
Remazol black 5 (RB5)	nano-ZnO/perlite	pH: 11; C_0 = 100 mg/L; catalyst: 20 g/L; dose of O_3: 1.533 g/h; reaction time: 10 min	TOC removal: 26.9% SO; 50.5% CO	Shokrollahzadeh et al. (2018)
reactive orange 4 (RO4)	Cu/SBA-15	pH: 5.7; C_0: 100 mg/L; catalyst: 0.2 g/L; dose of O_3: 5 mg/L; 60 min	TOC removal: 40% SO; 70% CO	Ghuge and Saroha (2018)
methyl orange (MO)	Fe-Mn GAC	C_0: 50 mg/L, dose of O_3: 2 L/min; catalyst: 5 g/L; pH: 7; 20°C: reaction time: 25 min	TOC removal: 18.0 % SO; 42.5% CO	Tang et al. (2016)
Sulfathiazole (ST); Ofloxacin (OFL); Tetracycline (TC)	nano-$Mg(OH)_2$	C_0: 50 mg/L; catalyst: 0.15 g/L, dose of O_3: 0.5 g/h, flow rate 0.1 L/min; reaction time: 60 min	TOC removal: 14.9% (ST) SO; 37.6% (ST) CO; 18.7% (OFL) SO; 47.3% (OFL) CO; 17.8% (TC) SO; 37.7% (TC) CO	Sun et al. (2019)
Ibuprofen	FeOOH	pH: 7; C_0: 20 mg/L; dose of O_3: 4.0 mg/L; flow rate 0.5 L/min; reaction time: 30 min	TOC removal: 17% SO; 35%-45% CO	Wang et al. (2018c)
Diclofenac (DCF)	Fe-MCM-48	C_0: 15 mg/L; catalyst: 0.15 g/L; dose of O_3: 100 mg/h; reaction time: 60 min	TOC removal: 23.1% SO; 49.9% CO	Li et al. (2018)
Sulfamethazine (SMT)	$Ce_{0.1}Fe_{0.9}OOH$	pH: 7; C_0: 20 mg/L, catalyst: 0.2 g/L, dose of O_3: 15 mg/min; reaction time: 120 min	TOC removal: 24% SO 44% CO	Bai et al. (2016)
Sulfamethoxazole (SMX)	Fe_3O_4/Co_3O_4	C_0: 20 mg/L, dose of O_3: 15 mg/min; catalyst: 0.1 g/L; pH: 5.2; reaction time: 60 min	TOC removal: 16% SO; 60% CO	Chen and Wang (2019)

hundred years as a batch and continuous applications. It is generally accepted that the EC process involves three successive stages (Mollah, M. et al., 2004):

i. Formation of coagulants by the dissolution of metal ions anode.

The prominent reaction is dissolution that occurred at the anode metal.

$$M(s) \rightarrow M\,(aq)^{n+} + ne^- \tag{20.13}$$

Besides, electrolysis of water molecules also occurred at the anode and cathode.

$$2H_2O\,(l) + 2e^- \rightarrow H_2\,(g) + 2OH \text{ (cathodic reaction)} \tag{20.14}$$

$$2H_2O\,(l) \rightarrow 4H^+\,(aq) + O_2\,(g) + 4e^- \text{ (anodic reaction)} \tag{20.15}$$

ii. After the dissolution next step is destabilization of the pollutants, particulate suspension, and breaking of emulsions.

At the cathode surface, a direct electrochemical reduction of metal cations (M^{n+}) may take place:

$$M^{n+} + ne^- \rightarrow nM^0 \tag{20.16}$$

Moreover, the OH^-ions are also generated at the cathode that changes the pH pf the wastewater to alkaline and induces the precipitation of metal ions as corresponding hydroxides.

$$M^{n+} + nOH^- \rightarrow M(OH)_n(s) \tag{20.17}$$

iii. Aggregation of the destabilized colloidal suspension phases to form flocs.

There are various operating parameters which affect efficiency of the EC process such as, electrode material, electrode arrangements, reactor design, electrode distance, current density, pH, reaction time, conductivity and temperature of the solution. However, in some study the EC process is not found an appropriate method for degradation of toxic organic pollutants in the complex wastewater because of oxidation capacity electrode material. But it is found an effective technology in combination with ozonation for the degradation of more toxic organic compounds in the wastewater (Daghrir et al., 2016). In combined process, electrocoagulation-ozone process mechanism can be understood by the following equations:

$$O_3 + H_2O \rightarrow 2HO_2\bullet \tag{20.18}$$

$$2HO_2\bullet + O_3 \rightarrow 2O_2 + HO\bullet \tag{20.19}$$

$$O_3 + M^{2+} \rightarrow MO^{2+} + O_2 \tag{20.20}$$

$$MO^{2+} + H_2O \rightarrow M^{3+} + HO\bullet + HO^- \tag{20.21}$$

$$MO^{2+} + M^{2+} + 2H^+ \rightarrow 2M^{3+} + H_2O \tag{20.22}$$

In EC-ozonation process, the metal ions generated during electro dissociation acts as a catalyst for the decomposition of ozone to produce more yield of hydroxyl radicals. In addition, the $HO_2\bullet$ radical formed during ozone decomposition recombined to form hydrogen peroxide (H_2O_2), resulting initiation of Fenton reaction that

improves the process efficiency if the iron electrodes were used. There are number of studies are available in literature in which efficiency was assessed of a specific pollutant removal by adjusting the operating parameters during O_3/EC process. As an example, it is reported that the color removal efficiency has increased with increasing the pH in the range of 2.0–10.0 and drop down by 10% at pH 12. This can be attributing due to Fe^{2+}/ Fe^{3+} conversion and oxidation of hydroxide ions at the anode, at high pH Song et al., 2007). In addition, the presence of $Fe(OH)_6^{3-}$or $Fe(OH)_4^-$ ions might be responsible for less decolorization efficiency at high pH (Mollah, M.Y. et al., 2010). Daghrir et al. (2016) has investigated the combined effect of electrochemical and ozonation treatment in the grey wastewater and found about 90 % removal of both organic as well as inorganic pollutants because of production of coagulating agent and reactive oxygen species in abundance. Current density and concentration of pollutants in effluent are important parameters in the hybrid electrochemical processes for controlling the reaction rate. It has been proved in the literature that the increased current density leads to a larger amount of anodic metal dissolution that enhanced the coagulation and flotation due to formation of more bubbles at the cathode (Şengil, İ. et al., 2009). Some recent application of O_3/EC process is depicted in Table 20.1 for water/wastewater treatment.

20.3 Catalytic ozonation

Various types of catalyst are used in catalytic ozonation process to improve the efficiency of ozonation which can be categorized as homogenous and heterogeneous based on the types of catalyst used in order to achieve controlled ozone decomposition and hydroxide radical's formation by utilizing the transition metal ions and solid catalyst respectively

20.3.1 Homogeneous catalytic ozonation

To decompose ozone by transition metal ions, there are two mechanisms for homogenous catalytic ozonation process.

i. Metal ions present in the aqueous solution enhance the decomposition of O_3 that leads to the generation of free radicals which oxidizes organic pollutants.
ii. Formation of complexes between organic molecules and subsequent oxidation of complex by O_3 and other oxidizing species.

The transition metal ions it its different oxidizing state, such as Mn(II),Fe(II), Fe(III), Cu(II), Co(II), Cr(III), and Zn(II), have been used as an effective catalysts in homogenous catalytic ozonation process to degrade organic compounds (Malik et al., 2020). Metals acts as a catalyst that increased the performance of the ozonation process by yielding morehydroxyl radicals in respective of single ozonation. The mechanism of ozone decomposition by metal-catalyst can be understood by Eqs. (23)–(26) in which metal ions enhances the decomposition of ozone for more generation of •OH, resulting into the effectiveness of hybrid ozonation for the removal of different

compounds. Since the effective contaminant removal was mainly associated through more generation of •OH and the improvement in ozone decomposition. The optimization of catalyst dosage is essential step for catalytic ozonation process because excessive metal ions could scavenge the generated •OH as per to equation (26).

$$M^{n+} + O_3 + H^+ \rightarrow M^{n+1} + \bullet OH + O_2 \tag{20.23}$$

$$O_3 + \bullet OH \rightarrow O_2 + HO_2^- \bullet \tag{20.24}$$

$$M^{n+1} + HO_2^- \bullet + OH^- \rightarrow M^{n+} + H_2O + O_2 \tag{20.25}$$

$$M^{n+} + \bullet OH \rightarrow M^{n+1} + HO^- \tag{20.26}$$

Ferrous is reported as the most effective homogenous metal catalyst that leads to low treatment cost. Ma and Graham (2000) investigated the degradation of atrazine by Mn^{2+}/O_3 system followed the radical-type mechanism at neutral condition. However, in another study, no catalytic activity of $Mn^{2+}$was observed for dinitrobenzene ozonation (Trapido et al., 2005). Addition of •OH scavenger (ethanol) in the Mn^{2+}/O_3 system has no significant effect in the removal of C.I. (Wu, C. et al., 2008). Since, Mn^{2+} does not follow the OH-radical based mechanism pathway in the degradation of Reactive Red 2 dye, even Mn^{2+} can promote formation of •OH and O_3 decomposition to some extent. So, it can be revealed that the free radical mechanism is not uniformly felicitous to different types of homogeneous catalyst assisted ozonation process. In another study, Pines and Reckhow (2002) found enhanced degradation of oxalic acid within the pH range of 5.3-6.7. The formation of hydroxyl radicals in Co^{2+}/O_3system is confirmed in the removal of p-chlorobenzoic acid (pCBA) while no effect of tertbutanol was observed at pH 6; as the •OH was not competent to facilitate the oxalic acid removal. The possible mechanism of Co^{2+}/ozone-oxalate system is shown in Fig. 20.2. In the first step, Co^{2+}-oxalate complex was generated which further oxidized by ozone to form Co^{3+}-oxalate. Eventually, products and oxalate radicals are oxidized by the oxidizing species. In addition to this, Beltrán et al. (2002) have also proposed the similar mechanism at acidic pH for oxalate removal by this Co^{2+}/O_3 process.

Some more studies in the literature have also been reported for such type toxic organic pollutants like chlorobenzenes, 2-dichlorophenol, CI Reactive Red 2 dye, and m-dinitrobenzene by homogenous catalytic ozonation system. It has been

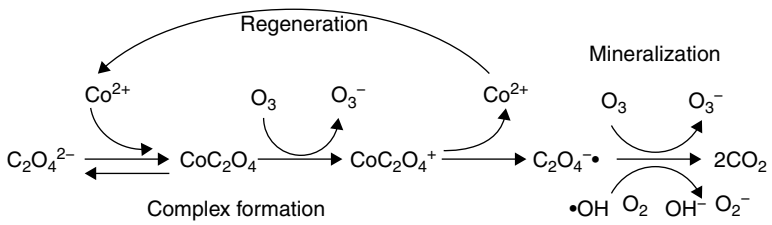

FIG. 20.2 Possible mechanism of oxalic acid oxidation in Co^{2+}/O_3 process (Wang et al., 2020).

investigated that the metal ions (Fe^{2+}, Mn^{2+}, Ni^{2+}, Zn^{2+}, and Cr^{3+}) in solution significantly enhanced the removal of carboxylic acids in the catalytic ozonation process (El-Raady and Nakajima, 2005). However, reported the mineralization of phenol has been reported in the presence of Ce^{3+} (Matheswaran et. al., 2007) and compared results with single ozonation process. Thus, homogeneous catalytic ozonation has been proved an effective hybrid ozonation process for removal of organic contaminants at laboratory scale as well as field application in water and wastewater. Following conclusions can be drawn from the homogeneous catalytic ozonation system: (i) the major reaction pathway for such type of catalytic ozonation is the complex formation between the metal ions and the pollutants; (ii) the homogeneous catalytic mechanism pathways can be affected by the pH value of the solution, the different types of metal ions and the organic pollutants; and (iii) identification of intermediates or the active species and the regeneration capacity of the metal ions during the reaction, are the necessary factors to explain the detailed mechanism of homogeneous catalytic ozonation process.

In homogenous system, the use of transition metal ions requires more attention because most of them are hazardous to the environment for which separation steps should be implemented to segregate from treated effluent that is a tough task as their presence in the water is very low.

20.3.2 Heterogeneous catalytic ozonation

To overcome the limitations of homogeneous catalysts, solid catalysts are introduced in the catalytic ozonation, known as heterogeneous catalytic ozonation. Solid catalysts are easy to segregate and keep up catalytic activity for a longer time. It is widely used due to its lower adverse effect in ecosystem and high mineralization of refractory organic pollutants. There are some catalysts which reported effectively in the literature such as metal oxides (MnO_2, TiO_2, Al_2O_3, FeOOH, and CeO_2), Metals (Cu, Ru, Pt, and Co) on supports (SiO_2, Al_2O_3, TiO_2, CeO_2, activated carbon, and zeolites modified with metals). The heterogeneous catalytic ozonation process has included two possible mechanisms; (i) decomposition of ozone on reduced/oxidized metal form that are deposited on the surface of a solid support; and (ii) decomposition of ozone on Lewis centers of the metal oxides. Besides of the reaction mechanism, the performance of this process is also significantly depending on the pH of the solution and the textural properties of the catalysts in addition to reactants' chemical structure (Orge et al., 2012). Thereby, the mechanism and effectiveness of the process using different catalyst are briefly explained in the following section to understand heterogeneous catalytic ozonation.

20.3.2.1 Used of metal oxides

The catalytic efficiency of metal oxides is significantly depending on physical (surface area, pore size, and surface charge) and chemical properties (chemical stability and active surface sites).Various catalytically active metal oxides have been studied as an effective catalyst in the heterogeneous catalytic ozonation process such

as manganese oxides, iron oxides/oxyhy- droxide, aluminum oxides and bimetallic/ polymetallic oxides. The catalytic efficiency depends mainly on the selective catalyst and solution pH that can affects the properties of the surface-active sites such as Lewis acid sites and Bronsted acid sites.

Generally, used of manganese oxides (MnO_2) are considered a most effective catalyst for the decomposition of gaseous ozone (Oyama, S., 2000). Manganese oxide-based catalysts are reported as an efficient and cost-effective catalyst for the decomposition of ozone. Manganese oxide-based catalysts are recognized due to its peculiar properties like high redox potential, different oxidation states, low water solubility, and diverse crystallographic structures environmentally friendly. In addition of this (Nawaz, et al., 2015) found that "both MnO_2 synthesized with cetyltrimethylammonium bromide and commercial MnO_2 (0.1 g/L)" improved the degradation of 4-nitrophenol (4-NP) (100 mg/L) with a flow rate of 100 mL/min O_3 at initial pH of 5.8–5.9. Additionally, Nawaz et al. (2017) reported the oxidation of 4-NP over six types of MnO_2 (α-, β-, γ-, δ- ε- and λ-) and they explored that among all the α-MnO_2 is most active catalyst. However (Tong, S. et al., 2003) reported that the catalytic activity of MnO_2 is highly depends upon the solution pH and type of compounds while it was independent upon types of MnO_2 used.

Trapido et al. (2005) have used different metal oxides for the ozonation of m- dinitrobenzene by reported catalytic capability in the order of: Fe_2O_3>CoO> MoO_3>CuÕ=Ni_2O_3>Al_2O_3> TiO_2>Cr_2O_3=MnO_2=without catalyst (pH = 3). In addition of this, a study investigated the catalytic activity in order of ozone alone <FeOOH< CeO_2< MnO_2 of three metal oxides at pH 5.5 for petroleum refinery wastewater in order to enhance TOC removal. However, Li et al. (2018) have assessed the performance of Fe-based material (Fe-MCM-48) as a catalyst for the oxidation of diclofenac (DCF) and found that the addition of 0.15 g/ L Fe-MCM-48 enhances the removal of TOC up to two times higher than single ozonation process with ozone output of 100 mg/h, effectively. Thus, it can be revealed that the reaction condition has significant effect of the catalysts activity to degrade the pollutants.

Recently, in order to effectiveness of catalytic ozonation, aluminum-based materials (γ-AlOOH, γ-Al_2O_3, and α-Al_2O_3) have been reported as catalysts or supporters as an alternative hybrid ozonation method for water treatment for the degradation of organic matters (Ncanana and Pullabhotla, 2019; Salla, J. et al., 2020; Wu et al., 2017). (Qi et al., 2009) used γ- AlOOH as a catalyst in ozonation process for removal of 2,4,6-trichloroanisole at pH 6.0 and achieved 80% efficiency within 10 min, rather than 37.3% efficiency in single ozonation. However, Salla et al. (2020) studied the comparable performance α-Al_2O_3 and MnO_2 at pH 5.5 and found that α-Al_2O_3 demonstrated superior catalytic activity for humic acids removal. Further more, a low dosage of α-Al_2O_3 is found significant in respect to other catalyst (i.e.γ-alumina catalysts, iron coated zeolite, granular activated carbon etc.) to remove humic acids by catalytic ozonation.

Bai et al. (2018) has investigated the removal efficiency of carbamazepine and found 50.3 and 64.1 % after 4 min reaction using catalyst Fe_3O_4-CeO_2/MWCNTs in single and catalytic ozonation process, respectively. In another study, an increase in

the catalyst dose of Mn-Cu/Al_2O_3 has increased the COD removal in tannery wastewater (Huang et al., 2016). The application of nano-MgO (Zhu et al., 2017), mesoporous CeO_2 (Zhang et al., 2019), CeO_2 nanometer catalyst particles (Dai et al., 2014), TiO_2 (Yang et al., 2014), and ZnO (Bashiri and Rafiee, 2016) were also reported in catalytic ozonation process. By using mesoporous catalyst, the removal efficiency has been improved from 51.6% (ozonation alone) to 91.7%, and 21.0% (single ozonation) to 69.2%, for phenol and COD respectively (Zhang et al., 2019). The activation energy is also decreased (from 54.7 kJ mol^{-1} to 20.7 kJ mol^{-1}) in CeO_2 assisted catalytic ozonation for phenol degradation in respect to single ozonation.

Recently, application of bimetallic/polymetallic oxides ($ZnAl_2O_4$, $CuFe_2O_4$, $CoFe_2O_4$, and Mn-Ce-O composites) are reported most popular catalyst for the heterogeneous catalytic ozonation systems due to their high catalytic activities and stability compared with monometallic oxides. Zhao et al., 2015 reported catalytic performance and mechanism of $ZnAl_2O_4$ as a novel high-surface-area catalyst for ozonation that effectively enhanced the phenol removal. Zhang et al. (2018) reported the performance of copper ferrite ($CuFe_2O_4$) magnetic nanoparticles (MNPs) for degradation N, N-dimethylacetamide (DMAC) and found that $CuFe_2O_4$ ozonation process improved the removal of efficiency of DMAC along with biodegradability ratio of BOD_5/COD from 0.03 to 0.33.

20.3.2.2 Metals on supports

The metal or metal oxides catalysts are generally loaded on supporters to increase the catalytic activity with special surface property and the active sites of the catalysts (Kermani et al., 2018; Wei et al., 2019). The metals on supports have distinguished the heterogeneous catalytic ozonation; since there is no hydroxyl free radicals' generation whereas the reaction takes place on the catalyst surface. The primary function of the catalyst supporters is to provide an effective surface area and appropriate pore structure that provide excellent mechanical strength, thermal stability to the catalysts along with the active center. Moreover, the ordered mesoporous materials having large surface area are found appropriate for the catalyst supports. Wang et al. (2016a) reported the catalytic ability of γ-Al_2O_3 supported manganese oxide (Mn/γ-Al_2O_3) for the phenol removal and found that 4% Mn/γ-Al_2O_3demonstrated highest catalytic efficiency other than ratio of Mn:γ-Al_2O_3 catalysts at initial pH of the solution to3.45. The X-ray photoelectron spectroscopy (XPS) results revealed that the enhancement of electron transfer on the surface MnO_2 play the major role for the catalysis and promoting the formation of active oxygen species.

Roshani et al. (2014) studied catalytic ozonation of benzotriazole (BTZ) over alumina supported transition metal oxide catalysts in water the catalytic ozonation of benzotriazole and reported the catalytic performance in order of Cu/Al_2O_3> Mn-Cu/Al_2O_3> Mn/Al_2O_3> Ozone over wide range of pH. However, it was in order of Mn/Al_2O_3>Mn-Cu/Al_2O_3> Cu/Al_2O_3> Ozoneat pH 2 and Mn-Cu/Al_2O_3> Mn/Al_2O_3> Ozone > Cu/Al_2O_3 at pH 10. Moreover, (Wu et al., 2018) claimed complete removal of 1-amino-4-bromoanthraquinone-2-sulfonic acid (BBA) by using mesoporous alumina-supported mixed oxides (Mn-CeOx/γ-Al_2O_3) in comparision of 32.7% BBA

removal in the sole ozonation process. In a study (Wang et al., 2019) have reported 2–3 times higher TOC removal using CeO_2-carbon nanotubes (CeO_2-CNT) catalyst ozonation than that of alone CeO_2 and OCNTdue to well- dispersed CeO_2on thecarbon material.

20.3.2.3 Carbon-based materials

Recently, carbon-based materials have been widely reported like activated carbon, carbon nanotube, graphene etc., which had proved better catalytic performance in the ozonation technology (Feng et al., 2019; Jothinathan and Hu, 2018; Wang et al., 2016b; Tizaoui et al. 2015). The activated carbon has property to work as an adsorbent and a catalyst during the process of ozonation. The formation of hydroxyl radical by ozone decomposition is mostly dependent on the surface properties of the carbon for higher activity of activated carbon. The activated carbon is reported as most active catalyst in the process of ozonation for oxalic acid due to large specific surface area and high basicity of the carbons Cao et al. (2014) which can be enhanced by treating carbon with nitrogenized agents e.g. ammonium carbonate or urea.

Vatankhah et al. (2019) has studied the performance of the ozone with granular activated carbon (O_3/GAC) at pilot-scale to enhance the removal of micropollutants (MPs) from wastewater and found effective removal of tris (2-carboxylethyl) phosphine (TCEP), sucralose, and meprobamate in compared to the single ozonation. Beltrán et al. (2002) has conducted a series of ozonation with activated carbon by heterogeneous catalytic ozone decomposition for ozonation of oxalic acid. A significant inhibition of oxalic acid oxidation was observed in the presence of a hydroxyl radical scavenger (t-butanol). There is an increase in basic groups and decline of acidic groups on carbon nanotube CNT which favors the removal of oxalic acid (Liu et al., 2010). The catalyst dose and the reaction temperature has shown positive effects while pH shows contrast decreasing for removal of the oxalic acid with increasing pH from 3.0 to 6.1 in catalytic ozonation by using multi-walled carbon nanotube (Liu et al. 2011). Fan et al. (2014) investigated the performance of multi-walled carbon nanotubes (MWCNTs) as catalyst in ozonation of atrazine and found effective improvement in the presence of MWCNTs. However, Qu et al. (2015) revealed good performance of carboxylated carbon nanotubes (CNTs-COOH) catalyst in degradation of indigo because it consists of large amounts of acidic functional groups. The graphene-based materials have effectively enhanced the removal of iopromide because oxygenated functional groups including epoxy and hydroxyls showed the strongest intensity on the surface. Furthermore, the carbon-based materials are porous and possess high surface area due to which they are explored more as a catalyst supporter in recent years (Bao, 2019; Song et al., 2019; Wang et al., 2016c).

20.3.2.4 Photocatalyzed ozonation

Photo-catalytic ozonation is a new advanced oxidation process which has a different mechanism of oxidation in respect of ozonation process due to the presence of photo-catalyst. In this process, photoactivated electron-hole pair is produced from exciting the surface of the photo-catalyst by the use of photo light in an aqueous medium. As per Equation (28) ozone molecule adsorbs on the surface of photo-catalyst leads

to the generation of active oxygen radicals which further react with water molecule (Eq. 29) resulting the formation of hydroxyl radicals (Chen et al., 2015).

$$\text{Photocatalyst} + h\nu \rightarrow \text{Photocatalyst} + e^- + h^+ \tag{20.27}$$

$$O_3 + \text{Photocatalyst} \rightarrow O\bullet + O_2 \tag{20.28}$$

$$O\bullet + H_2O \rightarrow 2OH\bullet \tag{20.29}$$

The overall possible reactions of photogenerated holes on the photocatalyst surface:

$$\text{Pollutant}_{(ads)} + OH\bullet \rightarrow \text{Pollutant}\bullet_{(ads)} + H_2O \rightarrow CO_x, NO_x, SO_x, \text{etc.} \tag{20.30}$$

Tanaka et al. (1996) suggested more effective process for degradation of hydrophilic compounds like monochloro acetic acid and dimethyl-2,2,2-trichloro-l-hydroxy ethyl phosphonate (DEP) present in water. The degradation of phenolic compounds was also observed in some extent as compared to aromatic compounds in photo-catalyzed ozonation process. Photo-catalyzed ozonation process by using TiO_2 catalyst has been reported for higher removal natural organic matter (NOM) in ground water. Moreover, the application of TiO_2 as a catalyst during the ozonation process has achieved 60 % TOC removal along with complete decolorization of textile effluent (De Moraes et al., 2000).

20.3.3 Heterogeneous catalytic ozonation Mechanism

The heterogeneous catalytic ozonation process is a complex process, that involves several reactions steps which can get affected by various factors. This system involved three phases i.e. solid (catalyst), liquid (water) and gaseous (ozone gas) due to which reaction detail mechanism is difficult to investigate. For example, catalyst may have different role in this process like providing reaction sites for adsorption and catalysis. Thus, three possible conditions could take place in a heterogeneous catalytic ozonation system based on the catalyst interaction with O_3 and organic compounds as shown in Fig. 20.3.

Polarity of the compounds and the surface property of catalyst are more responsible for adsorption of organics i.e. charge of material is strongly dependent upon solution pH. As per literature, polar compounds easily adsorbed onto the catalyst surface in comparison to nonpolar organics, unless some hydrophobic sites are present (Kasprzyk-Hordern, 2004). To some extent, adsorption capacity of catalyst for organic ions depends on the dissociation constant of the compounds and the surface charge of catalyst. (Legube and Leitner, N. K., 1999) proposed two possible mechanisms of heterogeneous catalytic ozonation; mechanism I, for adsorption on catalyst and oxidation by ozone or HO radical and mechanism II, for adsorption on catalyst and oxidation by ozone or HO radical of adsorbed organic. First is the interfacial reaction mechanism in which catalyst acted as adsorptive material. The large surface provide active adsorptive site and combine with targeted pollutants to form active complexes with lower activation energy by adsorbing and then remove it. In another mechanism, the catalyst reacts with O_3 and adsorbed compounds. In second

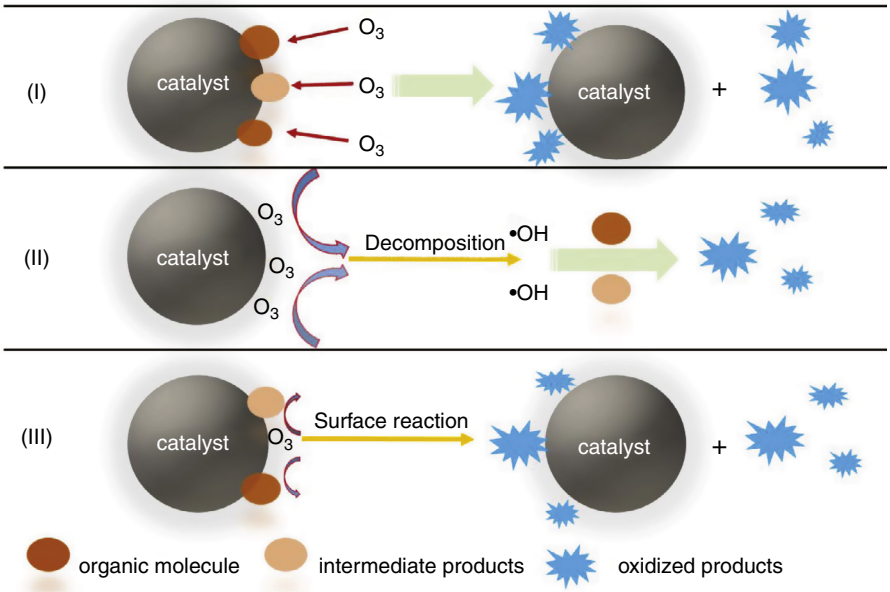

FIG. 20.3 Possible cases of heterogeneous catalysis system (Wang et al., 2020).

mechanism, surface hydroxyl groups of metal oxides lead to a vital role in the formation of HO• and soluble ozone is adsorbed to the catalyst surface through which a series of radical chain transfer can be observed for more HO• generation, which hold a high oxidation potential.

In a three-phase system mechanism of catalytic ozonation process, carbon materials adsorbed O_3 molecules and then act as initiator to promote O_3 decomposition to form the yield of •OH. The hydrogen peroxide is also formed by adsorbed O_3 molecules which then react with O_3 to generate •OH in bulk solution (Liu et al., 2009). The activated carbon does not act as an initiator for O_3decomposition and •OH formation rather than a catalyst. Since the catalytic properties of activated carbon is reduced because of the oxidation of basic groups on the activated carbon by O_3 (Sánchez-Polo et al., 2005).

20.4 Application of ozonation process for the degradation of toxic organic pollutants

Hybrid ozonation process have been widely applied for the degradation of toxic organic pollutants such as phenols, pesticides, dyes, pharmaceuticals, nitrobenzenes, phthalic acid esters, and so on as listed in Table 20.1. These pollutants are known for harmful impact on human health and our environment. Therefore, need an effective hybrid ozonation process to increase biodegradability and reduced the toxicity in

the natural environment. There are different hybrid ozonation like O_3, O_3/UV, O_3/H_2O_2, catalytic ozonation, and combined with biologically treatment in the field of water and wastewater. The catalytic ozonation process has been reported an effective process among all ozonation processes.

Liu et al. (2018a) have applied catalytic ozonation process with zinc-carbon nanotubes (Zn-CNTs) catalyst for removal of 4-chloro-3-methyl phenol (CMP) and found improved efficiency because of •OH generation and formation of H_2O_2 on the surface of catalyst in Zn-CNTs/O_3 process which also facilitates the mineralization of CMP. As on demand development and production of agriculture are on peak that leading application of pesticides for increasing production that cause discharges of pesticide effluent that imparts contamination in natural water. The catalytic ozonation technology has also been used for the degradation of pesticides as alternative treatment technology. The releases of dyes containing wastewater into water bodies includes chemicals that have stable aromatic molecular structures, which are also most possible cause of deteriorate of the environmental elements. In recent years, other emerging pollutants are generated from the pharmaceutical industries and personnel care products (PPCPs) and enter into the environment by the incomplete sewage treatment (Wang and Wang, 2016). The PPCPs are recognized as a new class of emerging environmental contaminants which required more attention. Number of scientific researchers have included to antibiotics in their study as the most concerned pollutants among the all pharmaceuticals (Liu et al., 2018b; Tang and Wang, 2019). Some aromatic pharmaceutical substances are more persistence and toxic; some are non-biodegradable that has potential risk to fauna along with human health. Catalytic ozonation processes are reported very effective process for the degradation of these pharmaceuticals in water and wastewater. Recent application of hybrid ozonation process for the degradation of all these toxic organic pollutants are listed in Table 20.1.

20.5 Shortcomings of hybrid ozonation processes

Ozonation has been proved an effective process as a single use or in combination with other oxidation processes for oxidation of various types of toxic organic contaminants. In spite of strong a strong oxidant, ozone is also hazardous in handling. The excess ozone gas treatment is required effective operation and maintenance of ozone supply, and contact tanks and piping due to leakage resulting corrosion. The high operation cost because of high consumption of electricity is a major limitation of ozonation processes due to which treatment costs of hybrid ozonation process become more expensive. Besides of treatment cost, the second problem is the formation of intermediate by-products during treatment of water/wastewater using hybrid process that is a big problem in the significant application hybrid ozonation processes. These by-products may be more toxic and hazardous to a next treatment stages as compared to the target pollutant, which require special attention to monitor and identify the intermediate compounds.

20.6 Benefits of hybrid ozonation processes

Ozone can be applied in treatment of drinking water and industrial wastewater in a large scale. The hybrid ozonation processes have been found promising technique for wastewater treatment because of its ability to destroy most hazardous organic contaminants. The hybrid ozonation process has overcome the issue of treatment cost of ozonation process to some extent with higher removal rate of contaminants present in the wastewater. The use of catalyst in the ozonation process using metals and metal oxides overcome the issue of huge generation of sludge which is the significant advantage in the field of hybrid process. The introduction of micro-nano bubbles technology in the recent development of ozonation has found most effective to reduce the doses of ozone as well as reaction time because of longer life span as well as high specific area that significantly can reduce the operational and capital cost of hybrid ozonation process. Thus, hybrid ozonation with micronano bubbles technique can be sustainable technology in the field of oxidation of toxic pollutants.

20.7 Conclusions and future perspective

This book chapter has involved the reaction mechanism, advantage, limitation as well as the performances of some successful applications of hybrid ozonation process in removal of organic and inorganic pollutants and decolorization in water and wastewater. Various studies on catalytic ozonation have been conducted, but some conclusions about the catalytic mechanisms are still inconclusive that required further attention. A systematic approach for evaluating the reusability performance of catalyst should be established for the cheap, stable and reusable catalysts. The possible mitigation strategies should be taken in the application of ozonation in order to intermediate by-products which are considered to be a serious threat to human health and ecosystem,

Hence in the future, the major attention should be devoted on the identification of reaction intermediates, identification of design parameters and criteria for cost effectiveness. A systematic approach consisting design model, evaluating toxicity and biodegradability is usually reported during and after the degradation process. Most accurate method to identify the intermediate product is the chromatography that must be include in the all hybrid ozonation process. Additionally, it should be more viable if process is carried out with real industrial wastewater. In addition to the experimental, modeling work must also be conducted with best modeling tool for complete economic studies which could help for innovative technology as a cost-competitive aspect. Moreover, the solar energy inbuilt ozonation can be proven modified and more economic solution for the wastewater treatment and recycle of these innovative technologies.

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CHAPTER

21

Removal of emerging contaminants from pharmaceutical waste through application of bio nanotechnology

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21.1 Introduction

The detection of emerging contaminants (ECs) such as pharmaceuticals, personal care products and endocrine disrupting compounds has emerged as an environmental issue due to their harmful effects on both aquatic and terrestrial life. They may be of industrial origin or may have originated from agricultural, domestic, or hospital wastewater. The presence of ECs has been well reported in ground water, surface water, drinking water, and wastewater treatment plant (WWTPs) effluents (Yang et al., 2014, Cabeza et al., 2012) Industrial wastewater is one of the major sources of discharge of ECs in the environment. The composition of industrial wastewater is complex consisting of high concentration of organic matter, microbial toxicity and salts which are difficult to biodegrade (Guo et al., 2017). It contains high concentrations of chemical oxygen demand (COD), ammonia nitrogen, salts, and metals (Rana et al., 2017). The current design and treatment technologies employed at WWTPs fail to completely eliminate ECs and their metabolites and are released into the water bodies.

Pharmaceuticals that are identified in wastewater majorly belong to different classes of human or veterinary antibiotics, steroid hormones and other drugs. Personal care products include chemicals used in different consumer products such as triclosan, parabenes and phthalates. Endocrine disrupting compounds such as polychlorinated and polybrominated biphenyls have androgenic or estrogenic activities even at low concentrations and can therefore have negative impacts on the endocrine systems of both aquatic and terrestrial life. The potential side effects include physiological and reproductive impairment, development of antibiotic resistance and other toxic effects. Furthermore, amongst all ECs, antibiotics are of the biggest concern due to their role in the development and spread of resistant bacteria even at very low concentrations (Nazaret and Aminov, 2014).

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At present release of ECs in the environment is not regulated around the world. However, there are some regulations in Europe and North America to monitor their release in the environment. In countries such as Canada and Switzerland, strategies for the controlled release of ECs from WWTPs have been developed (Morales-Caselles et al., 2016).

Recent progress in the fields of biotechnology and nanotechnology has offered ample opportunities to develop next-generation water treatment processes. Bionanotechnology is an emerging technology that combines the features of biomolecules and nanomaterials. As compared to traditional materials which are in the bulk form, nanomaterials have shown better potential in removing emerging contaminants. Adsorption and photocatalysis by nanomaterials has been widely studied, however their practical applications are limited due to operational and cost issues. Biogenic nanoaparticles and enzyme immobilized nanomaterials are both potential candidates in this regard due to their nontoxicity, cost effectiveness, and reliability. These have been discussed in detail in this chapter in the upcoming sections. The last section of the chapter gives a brief overview of other treatment technologies namely, nanobiochar, bio-MOFs, and nanozymes.

21.2 Challenges in current wastewater treatment technologies

In the recent years, there have been increasing concerns over the presence of ECs in the aquatic environment and the risks and hazards associated with them for both ecosystem and human health. Studies have demonstrated that the continuous exposure of low concentrations of certain pharmaceutical and personal care products can result in in endocrine developmental and epigenetic disruption to aquatic organisms and can have negative impact on human health (Ebele et al., 2017). ECs are primarily synthetic in origin and have been present in the environment for some time. These have recently been detected due to improved analytical techniques and increased risk awareness (Tran et al., 2018). Most ECs enter the aquatic environment mainly through discharge of treated or raw municipal wastewater or from industrial waste discharge (Tran et al., 2018). Municipal wastewater treatment plants have the maximum contribution in discharge of ECs in the aquatic environment ranging from 25 to 200 compounds already reported by various studies (Tran and Gin, 2017, Villar-Navarro et al., 2018). However, the number and concentration of different ECs depends on the socioeconomic conditions of the community that is contributing to the discharges. Majority of the studies have reported ECs concentrations typically ranging from nanograms to micrograms in wastewater but some contaminants like ciprofloxacin antibiotic have been reported as high as miligrams to grams per litre (Nakayama et al., 2019).

Conventional wastewater treatment plants (WWTPs) are not designed to remove ECs efficiently from the influent. While some ECs are removed partially through adsorption on activated sludge (Guerra et al., 2014), relatively high concentrations

of ECs still remain in the effluent (Tran and Gin, 2017). The disposal of this EC laden sludge on land results in the surface run off and percolation in ground water resulting in further contamination. Many technologies including electrocoagulation, constructed treatment wetlands, chemical precipitation, and anaerobic bed reactors have been used for removal of ECs but they are often ineffective due to difficulty in their implementation, high operational costs, and low concentrations of ECs in the influent (Ali et al., 2018). Due to the persistence of ECs in the environment and their potential adverse effects which includes bioaccumulation in the food web, there is an increasing need for cost effective treatment technologies that can be implemented for a large range of ECs at an industrial scale. The identification of degradation products in the environmental samples is a challenge because firstly, are they present at very low concentrations and secondly they are present in complex matrices that may interfere making their detection difficult.

The traditional wastewater treatment systems comprise of a primary treatment, secondary treatment and occasionally a tertiary step, with various biological and physicochemical procedures at each phase of the treatment. In primary treatment solid waste is removed mechanically by sedimentation or filtration. In the secondary step biological treatment is done where degradation of organic substances takes places. Conventional activated sludge (CAS) is the most well-known treatment technique. Other treatment techniques include fixed bed bioreactors, membrane bioreactors, and moving bed biofilm reactor. In the last tertiary step precipitation and filtration is done involving techniques such as disinfection by UV irradiation or chlorination, before discharging them in the environment. These treatments do not ensure complete removal of ECs. Moreover, biological and chemical degradation may transform ECs into a form that is more toxic as compared to the parent compound (Batt et al., 2007).

Hence there is acute need to develop and implement efficient, economical, convenient treatment, and removal technologies. Various advanced treatment technologies being implemented presently include advanced oxidation process, adsorptive removal and advanced biological processes. The high installation and operational costs is a drawback which can be overcome by using enzyme immobilized nanoparticles and biogenic nanoparticles as a treatment option for removal of ECs which are discussed in Sections 21.3 and 21.4.

21.3 Enzyme immobilized nanomaterials for removal of emerging contaminants

Biocatalytic treatment using enzymes is a promising technology to remove ECs from wastewater. Enzymatic reactions require mild conditions (ambient temperature, pH, and pressure) and require low activation energy, making the process quick as compared to non-enzymatic processes. Moreover, it is a green technology producing less or no waste (Sheldon and Pelt, 2013). To increase the stability and usability of enzymes abundant progress has been made in developing new support materials

which improve immobilization, making them more favorable and economical as compared to free enzymes. Immobilization of enzymes on a solid support can not only help in retaining the enzyme activity and stability but also make the recovery of enzymes from reaction medium easier. This is advantageous in terms of industrial applications (Li et al., 2012). There are typically three types of immobilization approaches—(1) entrapment, (2) cross-linking, and (3) binding to carrier (Fig. 21.1). Entrapment is usually carried out using polymer matrices, whereas in cross-linking, enzymes form aggregates, which are further fixed to a suitable carrier. The binding of enzyme to the support can be covalent, ionic, or adsorptive (van der walls interactions or hydrophobic) (Sheldon and Pelt, 2013). The immobilization method and support materials play a key role in determining the properties of the immobilized enzymes (Bilal, 2018). Covalent immobilization makes a stronger bonding and gives higher removal efficiency as compared to adsorption, but it requires pretreatment steps making the process complicated (Wen et al., 2019). In adsorption, however the bindings are weaker than in covalent but it is economical, fast and simple process and in some case adsorbed enzymes show a better efficiency than covalently immobilized enzymes (Brugnari et al., 2018). For environmental applications the support material should be biocompatible, economical, nontoxic, and environmental friendly (Bilal, 2018).

With the advances in nanotechnology over the past few years, various nanomaterials have been developed for varied applications. Nanoparticles possess a very

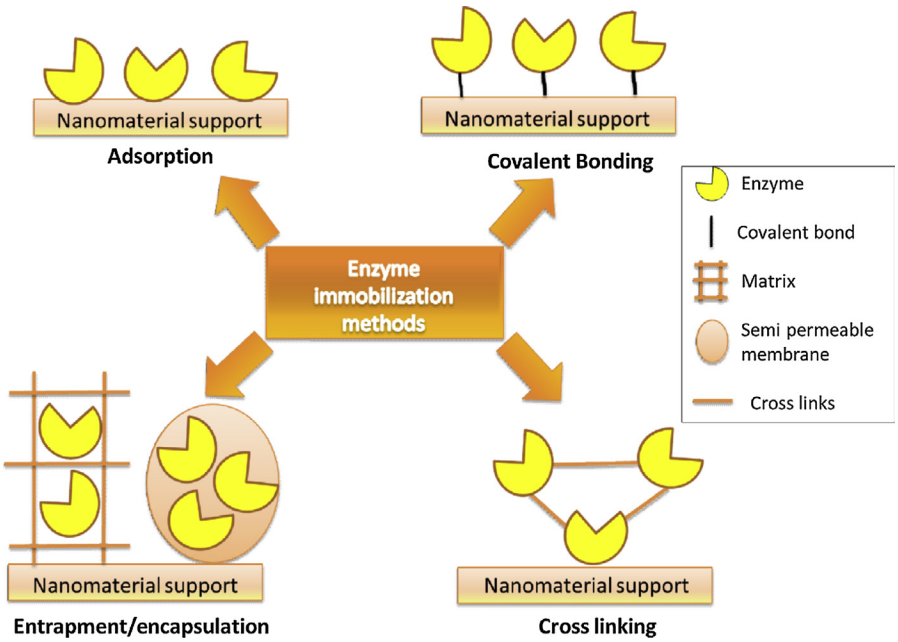

FIG. 21.1 Enzyme immobilization methods.

high specific surface area and unique optical, chemical and mechanical properties. These have proved to be very efficient platforms for enzyme immobilization. The advantages include high enzyme loading, improved enzyme stability, easy separation, and reduced costs when employed in various chemical reactions (Ansari and Husain, 2012).

The most widely used enzymes for the removal of ECs are oxidoreductase enzymes (such as laccase, lignin peroxidase, manganese peroxidase, horseradish peroxidase, and tyrosinase) as these have low substrate specificity and can catalyze the oxidation of a wide range of compounds including phenols, dyes, herbicides, fungicides, and pharmaceuticals and personal care products (Zdarta et al., 2018). oxidoreductase enzymes are found in many microorganisms, mainly found in white rot basidiomycetes (Naghdi et al., 2018). Amongst all the oxidoreductase enzymes only laccase and tyrosinase require O_2 as the cosubstrate whereas the others require presence of H_2O_2.

Shao et al. immobilized laccase on hollow mesoporous carbon nanospheres to study the degradation of ciprofloxacin and tetracycline antibiotics (Shao et al., 2019). The activity of free and immobilized enzymes was calculated at different times at 60°C. It was reported that the relative enzyme activity for immobilized laccase was higher than the free enzyme and 74% was retained at the given temperature. The enzyme activity was evaluated in a pH range of 2.5–8.5. Immobilized laccase showed high activity in both acidic and basic pH. The storage stability was also analyzed for a 30-day period. Improved stability was reported for immobilized laccase.

Nagdi et al. carried out immobilization of laccase on nanobiochar using different acid solutions, namely, HCl, H_2SO_4, HNO_3, and their mixtures and used them for the removal of carbamazepine (Naghdi et al., 2017). It was observed that the storage, pH and thermal stability of immobilized laccase on functionalized nanobiochar improved as compared to the free laccase. Reusability studies were conducted using of 2, 2′-azino-bis (3-ethylbenzothiazoline-6-sulphonic acid) (ABTS), which showed that the immobilized laccase retained 70% of its activity after 3 cycles. The degradation efficiency of carbamazepine reported was 83% in spiked water and 86% in secondary effluent.

Yang et al. investigated the degradation of tetracycline using magnetic cross linked laccase aggregates (Yang et al., 2017). Glutaraldehyde was used for cross linking of laccase to magnetic nanoparticles. It was reported that 40 U/mL laccase eliminated 100 μg/mL tetracycline at pH 6 and 25°C in 48 h in the absence of any redox mediator. More than 80% degradation was observed in the first 12 h of the reaction. Laccase treatment also significantly reduced antimicrobial activity of tetracycline.

In another study by Pylypchuk et al. removal of acetaminophen, diclofenac was studied by laccase immobilized on Fe_3O_4/SiO_2-DTPA hybrid nanocomposites (Pylypchuk et al., 2018).The study reported that immobilized laccase retained up to 100% activity in 50 ABTS (2,2′-azino-bis(3-ethylbenzothiazoline-6-sulphonic acid) oxidation cycles. The adsorbent was able to remove 95% acetaminophen and 85% diclofenac. The synthesized laccase composites showed high activity towards

acetaminophen removal which is polymerized by the immobilized laccase and the hydrophobic degradation products are adsorbed on the magnetic adsorbent surface.

Ji et al. demonstrated the biocatalytic degradation of carbamazepine using TiO_2 nanoparticles coated PVDF membranes (Ji et al., 2016). To increase the redox potential of laccase, natural phenolic compounds including p-coumaric acid, syringaldehyde, and acetosyringone were studied for both free and immobilized laccase. Among all the mediators p-coumaric acid resulted in the optimal carbamazepine removal with 60% degradation rate in 96 hours in conventional suspension system. The degradation of carbamazepine was also carried out in a membrane hybrid reactor using suspended biocatalytic TiO_2 nanoparticles. The effect of all the operational parameters was also analyzed. Toxicity tests were done by algal viability using the fluorometric indicator alamar Blue, which indicated that carbamazepine treatment using the hybrid reactor was effective in removing the toxicity of the parent compound.

Xu et al. investigated the removal of paracetamol using horseradish peroxidase immobilized on Poly(vinyl alcohol)/poly(acrylic acid)/SiO_2 electrospinning nanofibrous membrane with a diameter of 200–300 nm (Xu et al., 2015). These membranes were synthesized to be water insoluble using thermo-cross-linking. Immobilization on this membrane helped in retaining catalytic activity, stability and reusability. The paracetamol removal rate was reported to be 83.5 %. This was found to be similar to that of free enzyme (84.4 %), but immobilized horseradish peroxidase showed excellent reusability.

Hence it can be concluded that oxidoreductases are green biocatalysts that possess remarkable potential in catalyzing the oxidation and removal of a wide range of emerging contaminants without any requirement of additional cofactors except hydrogen peroxide or molecular oxygen which are widely available. More importantly the enzyme-assisted biodegradation is highly efficient and cost-effective and takes place under mild environmental conditions without requiring high energy, toxic solvents or use of advanced equipment.

Table 21.1 summarizes some recent reports for the removal of emerging contaminants using oxidoreductase enzymes immobilized on nanotized support matrices.

21.4 Biogenic nanoparticles for removal of emerging contaminants

Recently biogenic nanoparticles synthesized using microorganisms are getting immense research interest due to their unique properties like high surface area and high catalytic reactivity, for the biodegradation and biosorption of PPCPs (Martins et al., 2017, Xiao et al., 2017). The fabrication of nanoparticles through microbial route is less hazardous and inexpensive as compared to the conventional synthesis methods which require toxic reducing and stabilizing agents (Rezić, 2011). During the synthesis of biogenic nanoparticles, microbes are used as reductant (Kitching et al., 2015). Most of the studies state that the variety of reducing substances

Table 21.1 Removal of PPCPs using oxidoreductase enzymes immobilized on nanoparticles.

Contaminant	Enzyme	Nanomaterial	Immobilization method	Removal %	Remarks	References
Bisphenol A, Diclofenac	Lac	Fused silica nanoparticles	Sorption assisted immobilization	100	Improved enzyme stability	(Arca-Ramos et al., 2016)
Carbamazepine	Lac	TiO_2 nanoparticles coated PVDF membranes	Covalent	71	No residual toxicity	(Ji et al., 2016)
Sulfamethoxazole	Lac	Supermagnetically Tuned Halloysite Nanotubes Functionalized with Aminosilane	Covalent	78	Reusable for 10 cycles	(Kadam et al., 2017)
Bisphenol A, 17a-Ethinylestradiol	Lac	Polyamide 6/chitosan nanofibers	Mechanical agitation	100	Increased removal efficiency after immobilization	(Maryšková et al., 2016)
Carbamazepine	Lac	Oxygen functionalized nanobiochars	Mineral acid treatment	86	Improved storage, pH and thermal stability	(Naghdi et al., 2017)
Diclofenac, Carbamazepine	HRP, LiP	Magnetite nanoparticles	Adsorption	68, 64	Reusable for 20 cycles,	(Pylypchuk et al., 2020)
Acetaminophen and Diclofenac	Lac	Fe_3O_4/SiO_2-DTPA Hybrid Nanocomposites	Multipoint enzyme immobilization	95, 85	Reusable for 50 cycles	(Pylypchuk et al., 2018)
Ciprofloxacin hydrochloride, Tetracycline hydrochloride;	Lac	Modified hollow mesoporous carbon nanospheres	Adsorption & covalent	77, 55	Reusable for 5 cycles, increased enzyme stability	(Shao et al., 2019)
Sulphonamide	Lac	Fe_3O_4 nanoparticles	Adsorption	82.8	Reusable for 10 cycles	(Shi et al., 2014)
Diclofenac	Lac	PVA/CS/MWNTs composite nanofibrous membrane	Covalent	72.7	Reusable for 7 cycles	(Xu et al., 2015)
Paracetamol	HRP	Nanofibrous membranes	Adsorption	98	Reusable for 7 cycles,	(Xu et al., 2015)
Tetracycline	Lac	Magnetic nanoparticles	cross linking with glutaraldehyde	80	Green alternative in residual antibiotic removal in water	(Yang et al., 2017)

CS: Chitosan, DTPA: diethylenetriamine penta acetic acid, HRP: Horseradish peroxidase, Lac: Laccase, LiP: Lignin peroxidase, MWNTs: Multi-walled nanotubes, PVA: Polyvinyl alcohol, PVDF: Polyvinylidene fluoride.

generated by the microbial cells and the presence of specific functional groups which are oppositely charged to target pollutants is the main reason responsible for the removal of contaminants through ion exchange and electrostatic interactions (Qu et al., 2017, Yue et al., 2016). Different types of biogenic nanoparticles including organic, inorganic, semiconductor, and chalcogenide quantum dots can be manufactured using different microbial strains with varying applications. The morphology and properties of the synthesized nanoparticles vary with the microorganism, synthesis conditions and the precursor used.

A broad range of nanoparticles can be fabricated using various biological entities like fungi, bacteria, yeast, algae and plants. The biochemical process varies for each entity like oxidation or reduction of metal ions through enzymes, sugars, phenols, proteins, and carboxylic groups (Lu et al., 2017). Different kinds of biogenic nanoaparticles can be synthesized using different metal ions (such as gold, silver, palladium, silica, titanium, etc.). Microbes generally produce nanoparticles through bio mineralization which are either biologically induced or biologically controlled (Fig. 21.2) (Martins et al., 2017). In biologically controlled mineralization, nanoparticles are formed inside the cells in defined conditions. The nucleation and growth of the particles is controlled by the organism. In contrast, in biologically induced

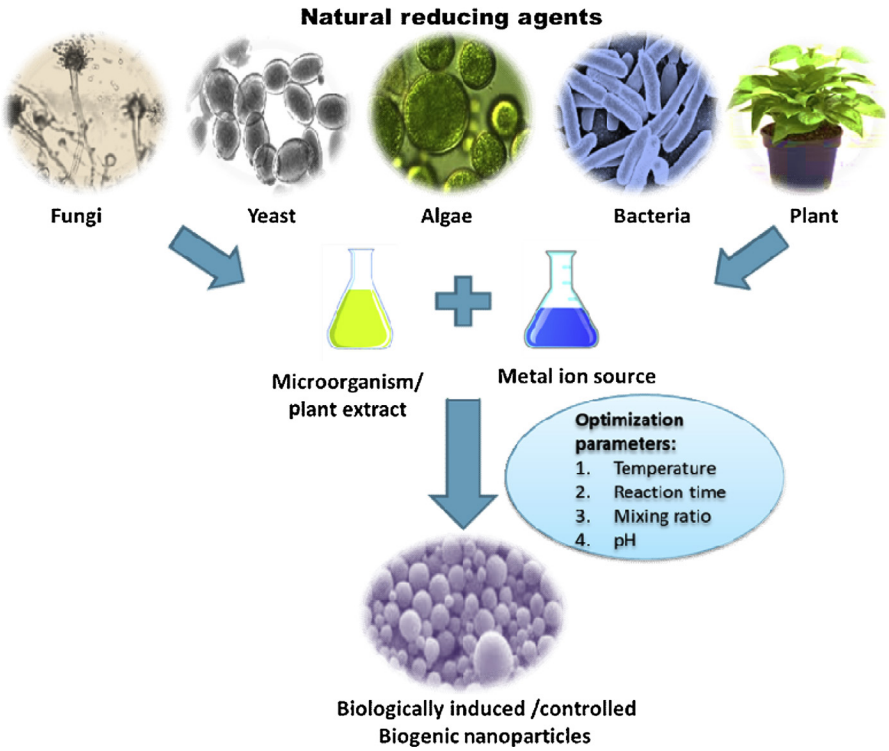

FIG. 21.2 Synthesis of biogenic nanoparticles using natural reducing agents.

mineralization, bacterial cell wall of the organism is treated with the solution of metal ions solution and biogenic nanoparticles are formed as a result of reduction, precipitation or both (Yue et al., 2016). The interaction of electron donor with metal ions solutions plays important role in fabrication of biogenic nanoparticles under aerobic or anaerobic conditions (Xiao et al., 2015). Reduction of metal ions takes place on the cell wall due to presence of different metabolites like thiol, carboxyl, amino, etc. (Furgal et al., 2015). After this growth and nucleation of biogenic nanoparticles takes place which can be controlled by controlling the synthesis protocol (Deplanche et al., 2014).

Metal nanoparticles as catalysts are a promising approach for wastewater treatment as nanosized catalysts are more efficient as compared to their bulk counterparts as they offer large surface to volume ratio. Hence, use of biogenic nanoparticles as catalysts for wastewater treatment is a promising and environmental friendly approach. Various studies have been carried out for the removal of ECs from wastewater using biogenic nanoparticles. Studies on removal of PPCPs through the use of biogenic nanoparticles have been summarized in Table 21.2.

Furgal (2015) used biogenic nanoparticles to remove estrone, 17-α ethinylestradiol, diclofenac, and carbamazepine in a WWTP (Furgal et al., 2015). The studies were carried out using biogenic manganese oxide nanoparticles and it was reported that residual organic matters influence the removal of ECs. The total organic carbon in wastewater affects how rapidly the oxidation and re-oxidation of Mn^{2+} takes place, and thus the amount of biogenic manganese oxide nanoparticles that are actually available for oxidizing the ECs. The authors reported 100% removal for estrone and 17-α ethinylestradiol and 26 % for diclofenac. However, this approach proved ineffective for the removal of other ECs namely, terbutryn, carbamazepine, Ibuprofen, and tebuconazole because the presence of organic carbon which was reported to affected the redox mechanism by biogenic manganese oxide nanoparticles.

Martins compared the efficiency of biologically synthesized platinum (Pt) and palladium (Pd) nanoparticles synthesized using the bacterial strain *Desulfovibrio vulgaris* for the removal of Ciprofloxacin, Sulfamethoxazole, Ibuprofen and 17β-estradiol (Martins et al., 2017). Bio-Pt showed a better performance than bio-Pd in reducing the ECs in the presence of hydrogen (H_2). The authors hypothesized that hydrogen hydride which is a strong reducing agent is formed by the interaction of bio-Pt with H_2 and promotes reduction of ECs. In case of ciprofloxacin it was speculated that a dehalogenation reaction following the replacement of fluoride and reduction of quinolone or carboxylic acid group might occur. In case of sulfamethoxazole, reduction of sulphonamide group or oxazole ring can occur and in case of 17b-estradiol, degradation may take place due to presence of alcohol and phenol groups. More than 80% removal efficiency was reported for bio-Pt.

Tran studied the removal of 17α-ethinylestradiol from effluent of secondary wastewater treatment by a biofilm process incorporating biogenic manganese oxide and *Pseudomonas putida* strain MnB1 (Tran et al., 2020). Modified granular activated carbon was used as a packing carrier for the biofilm and its removal efficiency was compared with that of conventional biofilm using feasibility tests. It was reported

Table 21.2 Removal of PPCPs using biogenic nanoparticles.

PPCP	Biogenic Nanoparticle	Microbe system	Metal precursor	Conditions	% Removal	Remarks	References
Diclofenac, Carbamazepine	Bio-Pd/Au	*Shewanella oneidensis* MR-1	Pd, Au	Aerobic, Temp: 28°C, time: 4h	100	Removal by combination of oxidation, co precipitation and co metabolic process	(De Corte et al., 2012)
Diclofenac	Bio-MnOx +Bio-Ag^0	*Pseudomonas putida* MnB6	Manganese chloride	Aerobic, Temp: 28ºC, pH: 7, time: 144h	94	Removal by combination of microbial metabolic/redox and biomass sorption	(Meerburg et al., 2012)
17α-Ethinylestradiol (EE2)	BMO	*Pseudomonas putida* strain MnB1	MgSO4 .7H2O	Anaerobic, Temp: 30ºC, pH: 5.56, time: 2h	87	Removal by combination of electrostatic interactions, ion exchange and redox	(Kim et al., 2012)
Steroid hormones estrone, 17-α ethinylestradiol, diclofenac	BioMnOx	*Pseudomonas putida* MnB6	MnCl2	Anaerobic, Temp: 30°C, pH: 6.8, time: 50h	100, 100, 26	Removal by comination of microbial metabolic and biomass sorption	(Furgal et al., 2015)
Ciprofloxacin, Sulfamethoxazole, Ibuprofen, 17β-estradiol.	Bio-Pt + H2	Desulfovibrio vulgaris	Pt (IV)	Anaerobic, Temp: 37°C, pH: 7.2, time: 24-35h	70, 85, -, 35	Combination of adsorption, cometabolism of microorganisms, and oxidation reduction	(Martins et al., 2017)
17-ethinylestradiol	BMO	*Pseudomonas putida* strain MnB1	Mn(II)	Aerobic, Temp: 26°C, pH: 5.6, time: 168h	95	Removal by adsorption and biodegradation	(Tran et al., 2020)
Tetracycline	Zirconia Nanoparticles	*Pseudomonas aeruginosa*	zirconium oxychloride octahydrate	Aerobic, Temp: 26°C, pH: 6, time: 15 min	99	Removal by adsorption	(Debnath et al., 2020)

Bio-Pd/Au/Pt: Biogenic nano-palladium/gold/platinum, BioMnOx: Biogenic manganese oxide nanoparticles, BMO: Biogenic manganese oxide.

that in the conventional biofilm, 17α-ethinylestradiol is removed mainly by adsorption and biodegradation. biogenic manganese oxide and *Pseudomonas putida* M1B1 outperformed conventional biofilm treatment as the removal efficiency reached to about 95%. Less than 4% of the total removed 17α-ethinylestradiol was extracted from the biofilm which confirmed that the removal was mainly either due to biodegradation by*putida* MnB1 or by chemical oxidization of biogenic manganese oxide.

Debnath et al studied the adsorption driven bioremediation of tetracycline antibiotic in wastewater using zirconia nanoparticles synthesized using pseudomonas aeruginosa bacteria (Debnath et al., 2020). The synthesized zirconia nanoparticles were tetragonal in structure with a particle size of around 15 nm and mediated adsorption of tetracycline in a time period of 15 min at solution pH 6.0. The mechanism which governed adsorption was strong electrostatic interaction between zwitterionic form of tetracycline and protonated surface of zirconia nanoparticles. The maximum tetracycline adsorption capacity was reported to be 526.32 mg g^{-1}.

The above studies indicate that use of biogenic nanoparticles is an effective technique for removing toxic organic pollutants from wastewater due to their excellent adsorptive and catalytic properties. They are a sustainable, safe, and ecofriendly alternative to chemically synthesized nanoparticles.

21.5 Other technologies for removal of emerging contaminants

21.5.1 Nanobiochar

Biochar is a carbonaceous material that has excellent adsorption properties, low cost, and is environment friendly (Lyu, 2018). It is produced from pyrolysis of biomass, like wood chips in the absence of oxygen. Nanobiochar offers a very high surface area which results in high adsorption efficiency. Like other adsorbents, regeneration of nanobiochars is also essential as they eventually get saturated during the adsorption process (Nguyen, 2016). Biochars are modified using both chemical and physical methods. The chemical modification includes acid or base treatment, oxidation, and activation using CO_2. Physical modification methods generally include use of ball milling for the production of nanobiochars.

Li et al. studied the adsorptive removal of tetracycline using ball-milled magnetic nanobiochars derived from wheat straw (Li, 2020). Ball milling conversion of pristine magnetic biochar to nanochar improved the removal efficiency of tetracycline. More than 99% tetracycline was adsorbed on the synthesized nanobiochar at 700°C within 12 h. The maximum adsorptive removal capacities of was reported to be 268.3 mg/g.

The adsorption studies using nanobiochar for removal of emerging contaminants from water showed that nanobiochar has higher adsorption capacity as compared to raw biochar and the removal efficiencies are equivalent to commercial activated carbon. However, the studies for removal of emerging contaminants using nanobiochars are limited.

21.5.2 Bio-metal-organic frameworks

Metal-organic frameworks (MOFs) have attracted tremendous attention over the last decade due to their high porosity. MOFs have a distinct crystalline structure consisting of metal ions and organic moieties. MOFs can be used for adsorptive removal of emerging contaminants by simply selecting suitable metals or linker. Depending on the properties of the building units of MOFs and the synthesis conditions like temperature, time, presence/absence of oxygen, and the properties and structure of the resulting materials varies (Howarth, 2017). MOFs that are synthesized with the incorporation of simple biomolecules are known as Bio-MOFs. The sustainability and recyclability of biomolecules makes them an interesting candidate for the removal of emerging contaminants.

Bhadra et al. synthesized Bio-MOF-1, Zn8(adenine)4(biphenyldicarboxylate)6O, and used it as a precursor to fabricate porous carbons by carbonization of the MOF and studied their application in removal of Bisphenol A from water by adsorption (Bhadra et al., 2018). Carbonization of Bio-MOF-1 was conducted at 1000°C for 12 h and the obtained BioMOF-1-derived carbons were characterized by various methods. In a comparative study of Bisphenol A removal using Bio-MOF-1 and activated carbon, Bio-MOF-1 showed remarkable adsorptive performance. Hydrogen bonding was suggested to be the main mechanism for adsorption. The authors also reported perfect reusability via simple solvent washing.

Hence, Bio-MOFs have wide prospects in the adsorptive removal of emerging contaminants from wastewater.

21.6 Nanozymes

Over the past few decades, researchers have developed artificial enzymes with various materials to mimic the properties of natural enzymes. In the recent years, nanozymes, which are nanomaterials with enzyme like characteristics have attracted enormous attention. They possess unique properties as compared to natural and classical artificial enzymes (Wang et al., 2016). Until now, many nanomaterials have been studied to mimic natural enzymes for various applications.

Fu et al. synthesized laccase-loaded magnetic nanoflowers by attaching amino-functionalized magnetic nanoparticles onto the laccase-inorganic hybrid nanoflowers for the adsorptive removal of bisphenol A (Fu et al., 2019). The characterizations indicated that laccase-loaded magnetic nanoflowers were spherical and porous with an average diameter of 15 μm to which magnetic nanoparticles was attached through electrostatic force. The studies indicate that these had excellent catalytic activity on Bisphenol A degradation at room temperature and in the presence of ABTS as mediator. Under optimized conditions, 100% degradation was obtained in 5 min. Additionally 92% of initial activity was still retained after 60 days of storage at 4°C which indicated an improvement in its thermal and storage stabilities. The synthesized nanozyme was recyclable and reusable for 5 cycles.

Nanozymes are superior to natural enzymes because of their enhanced stability, recyclability, low-cost, and can be efficiently used for the removal of emerging contaminants.

21.7 Conclusions and future prospects

Development of new methods and materials for removal of ECs from wastewater has gained increasing interest. Nanomaterials for enzyme immobilization and biogenenic nanoparticles have both shown promising results in this regard. For a wider application of enzyme mediated degradation, new nanomaterials should be developed such that they are economical, have high enzyme loading capacity and easy synthesis. Furthermore, the immobilization methods that are currently in use should be improved in terms of enzyme efficiency, stability, and reusability. Also more research should be done in addressing ways to improve production of enzymes in a cost effective manner to be able to scale up for industrial applications. Efficient enzyme immobilization and separation techniques should be developed such that they can achieve efficient treatment at a favorable pH and ambient temperature of wastewater. More studies should be taken up on the identification of the transformation products produced after enzyme catalysis in municipal and industrial wastewater and analyzing their toxicity.

Biogenic nanoparticles have also shown efficient performance in removal of toxic pollutants from wastewater due to their high specific surface area, high biocatalytic activity and unique morphology. However, more research efforts are needed to optimize the synthesis protocols in terms of costing and handling of the microbial cultures. Rugged protocols are needed to be developed to obtain purified biogenic nanoparticles with the desired size. To maintain an anaerobic environment during the synthesis, optimization of the hydrogen generation of *in situ* using fermentative strains to make the process more economical is needed. At present, such studies are limited to laboratory scale. Thus, in nutshell, studies are required to develop an optimized protocol for the synthesis of biogenic nanoparticles with higher removal efficiencies for their implementation at industrial scale. Nanobiochar, bio-MOFs, and nanozymes have also shown efficient results however more studies are required in this regard as the present reports on their application in the removal of emerging contaminants are limited.

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CHAPTER

22 Antimicrobial activities of different nanoparticles concerning to wastewater treatment

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22.1 Silver nanoparticles

Silver has been used as an antimicrobial and antiseptic against microbes for the ages due to its low cytotoxicity. AgNP antimicrobial action is seen in its application in wound dressing and biomedical devices which release low levels of silver ions to fight against bacterial infection. To harness the antimicrobial potential, AgNP is used for the treatment of potable water and in water purifiers. Silver nanoparticles containing sheets were used to filter water (Dankovich and Gray, 2011). Silver inactivates the bacteria and the leaching of silver along with the escape of bacteria from the membrane is minimal. AgNP has characteristics for wastewater treatment related applications. It is studied that silver nanoparticles can remove pollutants such as pesticides, heavy metals, and microorganisms (Que et al., 2018). Recent studies have shown the involvement of silver nanoparticles in the oxidation or partial oxidation of organic matter present in wastewater (Que et al., 2018). AgNP kills particularly the microorganisms without causing any hazard to human health moreover it is cheap, easily available, and shows its effect in a short time without being able to generate toxic byproducts after use. AgNP can adhere to the cell directly and further infiltration leading to membrane damage, leakage and further death of the microorganisms.

AgNP interacts with ribosomes, inhibits the translation and intracellular biological functions. It produces free radicals, releases Ag^+ ions causing protein deactivation and Ag^+ intercalates between purine and pyrimidine (Qing et al., 2018). AgNP

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is used in wastewater treatment as it not only targets individual microorganisms but also the biofilms and drug-resistant strains. AgNP has been successfully implied in the area of water and wastewater treatment. Since direct application is problematic as nanoparticles tend to aggregate in aqueous solution and thus reduces their efficiency in long term use. AgNP attached to filter membranes for water treatment is more promising. AgNP are deposited on cellulose fibers of absorbent blotting paper sheets. These sheets show antibacterial properties against suspension of *Escherichia coli* and *Enterococcus spp*. by inactivating them during filtration with minimal loss of silver from the sheet (Lu et al., 2016). Silver nanoparticles for wastewater treatment not only remove microbes but also degrade or partially degrade selective organic matters. The action of AgNP on bacteria depends on its shape, size and concentration. In a study spherical, rod, and triangular-shaped AgNP are made. Surprisingly, it showed that 1μg/100μl (10^7 CFU/ml of *E. coli*) concentration of triangular AgNP completely inhibits bacterial growth. Whereas in case of spherical AgNP, 50 μg /100μl to 100μg/100μl concentration of AgNP is required for 100% inhibition. There was very poor effect of rod-shaped AgNP on bacteria (Pal et al., 2007).

Sometimes AgNP is modified to enhance its activity. AgNP is functionalized with glucosamine. It is a naturally occurring amino sugar results from amidation of Fructose-6-phosphate. It provides a larger surface area for contact and interaction and also makes the nanoparticle hydrophilic, biodegradable, and stable. A comparative study was made on minimum inhibitory concentration (MIC) between AgNP and GlcN-AgNP. Gram-positive bacteria; such as *Staphylococcus aureus*, *Bacillus subtilis*, *Bacillus cereus;* and gram-negative bacteria; such as *E.coli*, *Pseudomonas aeruginosa*, *Klebsiella pneumoniae;* showed lower MIC of GlcN-AgNP than AgNP (Veerapandian et al., 2010). AgNP is also functionalized with chitosan. It is composed of polymeric 1→ 4 linked 2 amino-2 deoxy-β-D-glucose. It binds to the negatively charged bacterial cell wall and destroys it. It generally binds to the thiols containing protein of the cell wall. To determine the minimum bactericidal concentration (MBC) and MIC, GFP expressing *E.coli* were taken, scanning electron microscope micrograph showed that within 90 minutes the fragmentation and deformation of bacteria started. The amount of GFP fluorescence released into the medium indicated the degree of membrane destabilization (Sanpui et al., 2008). Graphene oxide (GO) is a monolayer of carbon atoms that forms a structure that contains an epoxide and hydroxyl functional group on the two sides and carboxylic group at its edge. It also exhibits antibacterial activity against bacterial species. AgNP functionalized with GO applied on *E. coli* and *Staphylococcus aureus* shows more antibacterial effect (Song et al., 2016).

22.2 Gold nanoparticles

Gold nanoparticles (AuNP) are valuable antibacterial agents due to their high ability to functionalize, nontoxicity, ease of detection, polyvalent effect, and polythermal activity (Dizaj et al., 2014). AuNP has excellent properties of catalytic activity,

excellent chemical, and mechanochemical stability, easy surface functionalization, excellent optical, and electronic properties (Shedbalkar et al., 2014). Further AuNP is crystallizable, resistant to oxidation and has good size dispersion properties and controllable morphology (Shedbalkar et al., 2014). The gold nanoparticles are effective in water and wastewater treatment along with exhibiting antimicrobial activity. It has also been employed as potential delivery vectors as well as computed tomography contrast agents (Miladi et al., 2014). The gold particles prepared with the help of *Ananas comosus* possess excellent anti-microbial properties against many gram-positive and gram-negative bacteria present in water as well as wastewater (Bindhu and Umadevi, 2014). Functional groups are attached to the gold nanoparticles to enhance stability. However, some disadvantages still prevail due to the conjugation of functional groups which limits the exploitation of gold nanoparticles to the fullest (Nicol et al., 2015). Antimicrobial peptides conjugated with nanoparticles bring down the survivability of certain pathogens (Rajchakit and Sarojini, 2017). Gold nanoparticles along with gallic acid can be used in treating the pathogens of wastewater from food processing industries (Rattanata et al., 2016).

The mechanism of antibacterial effect is the sequestration of calcium and magnesium ions leading to disruption of the cell membrane which results in membrane leakage (Shah et al., 2014). AuNP activity also involves collapse of membrane potential, inhibits the ATPase activity; leading to decrease in ATP level and inhibiting ribosomal subunit from binding to tRNA. It has been reported that AuNP shows more activity on gram-negative bacteria than gram-positive bacteria due to easy internalization. In a study, glucosamine functionalized AuNP is used. Glucosamine is used to prevent the aggregation of AuNP. GlcN-AuNP showed more bacterial inhibition than AuNP. In yet another study GlcN-AuNP was conjugated with graphene oxide (GO). The possible mechanism for increase in its microbicidal activity is that GO contains many functional group such as epoxy group, hydroxyl group and carboxyl group. AuNP has been produced from aqueous extract of different algae such as *Sargassum wightii, Laminaria japonica, and Chorella pyrenoidosa*. AuNP is synthesized from *Citrus maxima* peel extract exhibits strong antibacterial effect against *S.aureus* and *E.coli* (Yuan et al., 2017). Another innovative approach was made where a non-pathogenic bacteria *Bacillus fusiformis* was used to prepare AuNP nanoparticles. AuNP was synthesized *in-vitro* by using cell lysate supernatant. It showed clear zone against *E.coli* and *P. aeruginosa* (Singh et al., 2014).

22.3 Zinc oxide nanoparticle

Over the years, zinc nanoparticles have been extensively used in industrial as well as biological applications. Several types of zinc nanoparticles are synthesized. ZnS, ZnO, ZnSe and quantum dots. Bioimaging is another field where zinc nanoparticles have gained importance due to its extraordinary property of luminescence (Jiang et al., 2018). The zinc nanoparticles have also been used in antimicrobial activities and treatment of water and wastewater. Microorganisms such as *Bacillus subtilis*,

E. coli, *Bacillus megaterium*, *Proteus vulgaris*, *S. aureus*, *P. aeruginosa*, *Sarcina lutea*, *Candida albicans*, *Aspergillus niger*, and *K. pneumoniae* are mostly affected by the zinc nanoparticles. The zinc oxide nanoparticles break the cell membrane and then aggregates within the cytoplasm. Upon interaction with the biomolecules inside the cells, apoptosis mediated bacterial cell death is induced (Siddiqi et al., 2018). The municipal wastewater is highly contaminated with pathogenic microbes and can be effectively treated with the zinc nanoparticles (Mujeriego and Asano, 1999, Baruah et al., 2013). In one of the investigations, zinc nanoparticles are found effective against *Pseudomonas putida* and *Pseudomonas aureofaciens* (Sur and Mukhopadhyay, 2019). In an experiment, ZnONP is synthesized using cobalt doping. It is tested against *Shigella dysenteriae, Salmonella Typhi*, *Vibrio cholerae*, and *E. coli* and observed significant increased activity of 20 to 26% (Oves et al., 2015). Heterostructure of $Ag/Fe_2O_3/ZnO$ synthesized through ultrasonic assisted hydrothermal method inactivated 90% *E.coli*. The greater inactivation in visible illumination is observed due to the generation of the ROS on the surface of the $Ag/Fe_2O_3/ZnO$ heterostructure (Kaur et al., 2019). In recent years, plant-mediated ZnO synthesis has become a popular method as it is safe, effective, simple and environmentally benign. Secondary metabolites are natural and plentiful in plants that have therapeutic properties for improving human health. Biosynthesis of ZnO are done from different plant parts such as *Ziziphus nummularia* leaf, *Ephorbia prolifera* leaf, *Momordica charantia, Silybium marianum* and *Amaranthus caudatus*. The rich leaf extract content performs a capping agent in controlling the shape, size and aggregation of ZnO nanoparticles. It also stabilizes the nanoparticle (Bayrami et al., 2019).

22.4 CuO nanoparticles

Copper is known for its high thermal and electrical conductivity. Engineered Cupric oxide nanoparticle (CuONP) was used widely in industry and commercial production. CuONP stimulates ROS generation, causes high oxidative stress within the cell, binds to DNA and causes DNA damage and donates and accepts electrons of Cu^{++} facilitating binding to the cell membrane. Positively charged Cu^{++} ions get attracted to the negatively charged cell membrane. When attached to the cell, the ions cross the membrane and crosslink DNA. It also damages the biochemical processes of the cells. The amine and carboxyl group on the surface shows great affinity towards the Cu^{++} ions. The CuONP incorporated in the membrane to act as antibacterial agent in the wastewater plant or wastewater effluent (Shimabuku et al., 2017). It was seen that cells with multiple mutations or deletion of genes are more susceptible to the toxic effect of CuONP (Bao et al., 2015). Organic pollutants discharged immoderately into freshwaters are hazardous to human health and the environment. These toxic contaminants of wastewater can be removed effectively with the help of CuONP (Das et al., 2018).

Advanced oxidation processes (AOPs) are one of the most powerful technologies for the removal of organic pollutants by *in situ* generation of highly reactive

radicals, such as hydroxyl (•OH) and sulphate radicals (SO4•-) (Kasprzyk-Hordern et al., 2003, Lee et al., 2016). Cu^{++} doped aluminium pillared montmorillonite (Cu-Alpill-MMT) enhances the decolorization efficiency in dye stained wastewater because Cu^{++} acts as catalyst in AOPs (Wang et al., 2009, Wang et al., 2013, Yang et al., 2007). The nanomaterial Cu-Alpill-MMT possesses antibacterial property as it is attributed to the catalytic activity of Cu^{2+} ions, leaching out from the CuO of the Cu-Alpill-MMT leading to the generation of highly reactive free radicals (Timofeeva et al., 2009). These free radicals destroy bacteria such as *E.coli* by damaging their cell integrity (Borkow and Gabbay, 2005). Thus, when the nanomaterial Alpill-MMT is doped with Copper (II), the effectiveness in wastewater treatment and anti-bacterial activity is increased (Tepmatee and Siriphannon, 2016).

22.5 Iron oxide nanoparticles

Iron is regarded as one of the troublesome chemicals in water. Oxidation of dissolved iron converts to solid. Iron oxide nanoparticles (IONP) efficiently remove heavy metal contaminants by magnetic separation with ionic exchange (Santhosh et al., 2018). Iron oxides are found in many forms such as magnetite (Fe_2O_3), hematite (α-Fe_2O_3), and maghemite (γ-Fe_2O_3). It is widely studied due to high surface area to volume ratio, nano-range, super-paramagnetism, high magnetism, chemical inertness, controlled size, and low toxicity (Xu et al., 2012, Saqib et al., 2019). It is also used in wastewater treatment due to its low cost, antibacterial activity, enhanced stability (Xu et al., 2012). IONP damages bacterial cell wall by developing direct contact with it. Also, ribosome, lysosome, protein deactivation, and changes in cell permeability takes place. IONP interacts with amino (NH), mercapto (SH) and carboxyl group damaging enzyme activity and physiological process (Saqib et al., 2019).

The use of iron oxide nanoparticles in wastewater treatment can be divided into two basic groups; absorptive technologies and photocatalytic technologies. In absorptive technology, where the iron oxide NPs are used as absorbent or immobilization carrier to remove the contaminants. The nano-size of the nanoparticles is advantageous for the diffusion of metal ions from the solution onto the active site of the absorbent surface. Thus, iron oxide NP is an economical absorbent for rapid removal of heavy metals present in a media. However, aggregation caused by the aquatic environment due to high surface area to volume influences many operations in the environment like uptake of the ions and numerous interactions in water also affect the absorption of metals. Using photocatalytic technology, the nanomaterial in combination with light speeds up a certain reaction. The photodegradation of congo red is a good example of the effective and safe use of nanoparticles in wastewater treatment (Xu et al., 2012).

Chitosan coating on the nanoparticles increases the efficiency of the antimicrobial effect. Chitosan, a linear polysaccharide, is an antibacterial agent. Chitosan coated IONP is tested against *E.coli* and *B. subtilis* and found effective. The interaction between amino group of chitosan with cell membrane component result in chelating

transitional metal ion and inhibiting enzyme (Nehra et al., 2018). Graphene oxide has rewarded remarkable performance in antibacterial activity and absorbing dyes. Chitosan-graphene oxide IONP is tested on *E.coli* and observed antibacterial activity (Song et al., 2016). Streptomycin is also functionalized with chitosan magnetic particle and showed antibacterial activities against *Mycobacterium tuberculosis*, *E.coli*, *P.aeruginosa,* and *S.aureus* (El-Zowalaty et al., 2015). ROS along with hydroxide radical (OH-) and superoxide radical are inhibitory to bacterial growth (Gabrielyan et al., 2019). IONP is also effective against antibiotic-resistant bacteria. To study this, ampicillin resistant *E.coli* DH5α-pUC18 and kanamycin resistant *E.coli* pARG-25 are taken and Oleic acid-coated IONP was used. Kanamycin-resistant strain is more susceptible to IONP than ampicillin resistant strain. Decreased H^+ efflux, inhibition of ATPase indicates changes in membrane permeability (Gabrielyan et al., 2019). Increase antibacterial activity of Gold-functionalized IONP was observed. It targets the protein F, which is known to maintain the shape of the bacterial cell and controls ions and molecules transport and also contributes in antibacterial resistance of *P.aeruginosa* (Niemirowicz et al., 2014). Silver functionalized IONP shows inhibitory effect on *S. aureus* whereas only Fe_3O_4 NP shows no inhibitory effect on it. It dissolves the bacterial cell wall causing leakage of cellular constituents, resulting in cell death (Tung et al., 2016). Poly γ-glutamic acid (PGA) is a polymer of glutamic acid can be functionalized with IONP connected via γ-amide linkages between α amide and γ-carboxyl group. Na-PGA and CaPGA coated IONP have shown antibacterial activities against *S. enteriditis* and *E. coli* (Inbaraj et al., 2011).

22.6 Magnesium oxide nanomaterials

Magnesium constitutes about 2% of the earth's crust and abundant in sea and ocean water in soluble form responsible for its hardness. Magnesium being inexpensive is in use for water and wastewater treatment since 1960s with a large commercial potential (Luo et al., 2018). It was seen that within alkaline PH, magnesium compounds remove organic substances, suspended solids and turbidity of the wastewater. Fecal bacteria or coliforms present in the wastewater are inactivated by magnesium compounds. It helps in phosphorus and nitrogen cycling by utilizing the soluble form phosphate and ammonium in the wastewater. In early times Mg^{++} ions were also used as coagulants for the treatment of municipal water. MgO is regarded as safe for humans. They are stable under harsh chemical processes. Mg^{++} binds to negatively charged membrane of bacteria and initiates pore formation to cause leakage in case of gram-positive strains. ROS was produced in a higher rate such that the bacterial cells fail to produce superoxide dismutase and cause damage to bacterial cells. In gram-negative bacteria, the MgONP is seen to cross thin peptidoglycan and bind to cell membrane distorting its shape. MgONP disrupts not only planktonic cells but also the matrix of the biofilm by the mechanism of chelating proteins and enzyme and ROS production to disrupt the internal structure of biofilm (Nguyen et al., 2018). It is also known to remove heavy materials (Yang et al., 2019). MgONP absorbs azo and anthraquinone dyes from industrial wastewater (Moussavi and Mahmoudi, 2009).

The azo dyes from textile industries have toxic, carcinogenic and mutagenic effects on living beings. To remove these recalcitrant contaminants, a combination of processes such as coagulation, using $AlCl_3$ as coagulant, and photocatalytic degradation using MgO nanoparticles, may be efficient (Jorfi et al., 2016). Blue-203 dye is a component of textile wastewater, which can be removed by using ferrate (VI) oxidation process, enhanced by MgO nanoparticles (Eskandari et al., 2019). In an aqueous environment, MgO nanomaterials can also act as a bactericide due to the formation of superoxide (O_2^-) anions on its surface (Huang et al., 2005). Thus, MgO nanoparticles can be applied in a variety of areas, such as in sterilization, catalysis, adsorption, oxidation, and wastewater treatment.

22.7 Titanium dioxide nanoparticles

Titanium dioxide (TiO_2) nanoparticles (TNPs) display good thermal and chemical stability, have good photo-catalytic properties, and have nearly endless lifetime, as they do not get changed during the degradation of organic compounds and microorganisms. Thus, TNP may be successfully applied in the treatment of wastewater, water purification, removal of microorganisms, chemical compounds, and heavy metals (Ursino et al., 2018). Nanocrystalline TiO_2 has specific features of semiconductors with self-cleaning and self-disinfecting potential, has broad-range of antimicrobial activity due to high photoreactivity and chemical stability (Rincón and Pulgarin, 2004). TNPs can be used as an oxidizing agent against bacteria and other organic substances (Shiraishi and Hirai, 2008). This oxidizing power is generated by the release of hydroxyl radicals and superoxide ions when exposed to non-lethal UV light (Shiraishi and Hirai, 2008). The antibacterial activity of TNP is due to decomposition of bacterial outer membrane by ROS and phospholipid peroxidation leading to cell death by hydroxyl radicals (Shiraishi and Hirai, 2008, Priyanka et al., 2016). In the case of drinking water treatment plant, TNP can remove organic contaminants including natural organic matter and disinfection by product precursors (Gora and Andrews, 2017). Therefore, versatile beneficial features of TNP and further study with TNP may lead to its greater application in the field.

22.8 Al_2O_3 nanomaterials

Aluminium oxide (Al_2O_3) NP has antimicrobial effect against some common strains like *P. aeruginosa*, *B. subtilis,* and *E.coli*. The production of ROS and free radicals is a key feature of the Al_2O_3 NPs toxicity which leads to oxidative stress, inflammation and consequent damage to protein membranes and DNA of its targeted microorganism. Further, Al_2O_3 NP treated *P.aeruginosa* shows structural alteration in the cell envelope (Ansari et al., 2015). The membrane becomes highly modified creating multiple pits and gaps. Also, Al^{3+} ions show cytotoxicity in freshwater algae along with other bacterial strains (Pakrashi et al., 2013). Due to wide industrial applications, Al_2O_3 NPs find their way to wastewater treatment plants. The process of sludge

activation is commonly used for the nitrogen and phosphorous removal from the wastewater. Al_2O_3 NPs can show an enhancing impact on methane production in anaerobic digestion of wastewater treatment plants (Kökdemir Ünşar and Perendeci, 2018). Al_2O_3 nanoparticles have high hydrophilicity, which reduces the possible adsorption of foulants, and help in the prevention of membrane fouling in wastewater treatment (María Arsuaga et al., 2013, Saleh and Gupta, 2012, Mojtahedi et al., 2013, Dong et al., 2013). Thus, due to their antifouling and antibacterial properties, nanomaterials can be successfully applied in the treatment of wastewater.

22.9 Nanomaterials enabled with antimicrobial peptides

Antimicrobial peptides are oligomers of amino acids, which show activity against microorganisms. Antimicrobial peptides may contain 5-50 amino acid chains, and the numbers of amino acids vary. They may exhibit activity against bacteria, fungi, viruses, and protozoa. A nanomaterial enabled with antimicrobial peptides, for example, damages the bacterial cell envelope (Li et al., 2008). Recently, nanoparticles are produced with Dioctadecyldimethylammonium bromide bilayer fragments (DODAB-BF), combined with antimicrobial peptide, gramicidin D, as the active molecules (Brandelli, 2012, Carmona-Ribeiro and Carrasco LD de, 2014, Carvalho et al., 2012, Ragioto et al., 2014, Liu et al., 2009, He et al., 2018). This yields broad-spectrum microbicidal formulations in which, at the borders of the bilayer fragments, peptide dimer is formed, and the peptides may also be embedded within the DODAB (Carvalho et al., 2012, Ragioto et al., 2014, Carrasco LD de et al., 2016). This affects the ionic balance of the bacterial cells, such as that of *E. coli* and *S. aureus* (Carrasco LD de et al., 2016, Xavier and Carmona-Ribeiro, 2017).

22.10 Conclusion

This chapter elaborates the enormous potential of nanoparticles for wastewater treatment particularly the elimination of pathogenic microbes following various mechanisms (Fig. 22.1). Preparation of different composite material made from them and its use as combinatorial treatment options increase their efficacy. In addition to this, decontamination at the source itself will have better quality discharge and thus it will help in keeping aquatic ecosystem balanced. Furthermore, it will also reduce the eventual harmful impact of human and other life forms. Diversity in the engineered nanomaterial may cater to the needs for industrial and domestic water treatment applications. Also, technological advancements have applications in miniaturized household filtration units to extremely vast scale wastewater treatment plants. Further studies are required to overcome the logistic and procedural challenges, toxic impact on the beneficial microbiota involved in the decomposing organic and inorganic substances in water treatment processes and leaching of nanomaterials to natural waterbodies and making their way to living systems of different habitats. Thus the use of nanomaterials has very bright future in the field of wastewater treatment.

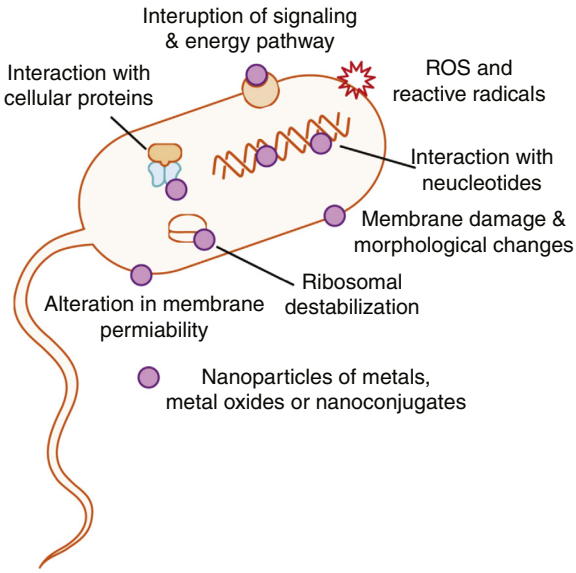

FIG. 22.1 Schematic depiction of mode of microbicidal actions mediated by different nanoparticles and nanoconjugates.

Abbreviations

AgNP	Silver nanoparticles
AOP	Advanced oxidation processes
AuNP	Gold nanoparticle
Cu-Alpill-MMT	Copper (II) doped aluminium pillared montmorillonite
CuONP	Cupric oxide nanoparticle
GO	Graphene oxide
IONP	Iron oxide nanoparticles
MBC	Minimum bactericidal concentration
MIC	Minimum inhibitory concentration
NP	Nanoparticle
PGA	Poly γ-glutamic acid
ROS	Reactive oxygen species
TNP	Titanium dioxide nanoparticles
ZnONP	Zinc oxide nanoparticle

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CHAPTER

23

Application of nanomaterial in wastewater treatment: recent advances and future perspective

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23.1 Introduction

Even though two third of the earth's surface is covered with water but, only 1% of it is fresh water, usable by human, trapped underground, rivers and lakes. There is an exponential increase of water demand in the agricultural field to sustain ever increasing global population. Furthermore, uneven world population distribution and unreliable climate change due to global warming, complicates this water scarcity even more. According to the UNICEF report, about 1.1 billion people lack fresh water, 2.4 billion people lack proper sanitation, and because of water borne diseases about more than 2.2 million children die every year. With this rate global water consumption to increase by 55% in 2050. Since, the main consumption of fresh water is in the agricultural field, the permanent solution relies in the advancement of agricultural methods such as drip irrigation, organic farming, Genome decoding, genetic improvement, etc. But very few countries can afford these both economically and technologically (Hedley et al., 2014). Basically, wastewater is the fresh water source that has been utilized and contaminated in various anthropogenic activities or any natural causes. Waste water generated from municipal waste contains dangerous levels of pathogens and high in biological oxygen demand, if untreated, can go septic or causes major eutrophication in the environment. Whereas effluent generated in industrial establishments are highly toxic in nature and there have severe acute and long-term detrimental effect on the environment and human. For these purposes, to protect public health and the environment, the prompt and nuisance-free elimination of wastewater from its generation sources, accompanied by storage, reuse, or dispersed into the atmosphere is very important. The overarching goal of wastewater engineering is to protect public health in a manner that is consistent with environmental, cultural, social, and political issues. To protect public health and the environmental

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ecosystem, knowledge of the constituents of interest in wastewater and the impacts of these components of wastewater is released into the environment is needed. The processing and long-term nature of these constituents in treatment procedures and treatment approaches that can be used to eliminate or alter components present in wastewater. Finally, treatment schemes for the effective use or disposal of solids.

Municipal waste is a significant source of diverse contaminants, including suspended particulate matter and dissolved solids (DS). They act as a rich source of persistent carbon and nitrogen nutrients in organic compounds, poisonous metals, and salts. It also contains colloidal particulates, contaminants, infectious pathogenic species and other harmful chemicals much higher than their approved acceptable limits (Chan et al., 2009).

Industrial facilities are the principal sources for producing wastewater and contaminating marine environments with large amounts of poisonous and hazardous waste that is harmful to our environment's safety and health. Industrial waste may be classified into two major groups, biodegradable and nonbiodegradable, composed of various poisons, and inflammable, corrosive, contagious, dangerous chemicals, pesticides, including agricultural hydrocarbon waste (Sikosana et al., 2019; Ranade and Bhandari, 2014).

Tannery used to turn raw skin and hides into useful products, but the manufacturing of raw skin / hides is an extremely water-consuming method that requires vast amounts of fresh water and discharges large quantities of this water as wastewater, which is a significant environmental problem. Tannery runoff contains large aggregates of sulphates, chlorides, suspended solids, poisonous metals (mainly chromium), diverse colors, and other contaminants. Tannery factories, however, are the most significant cause of chromium contamination, since chromium tanning is used to produce inexpensive and high-quality leather (Durai and Rajasimman, 2011).

Distilleries are a large fermentation industry, which produces the most effluent. Bioethanol is produced mainly by the fermentation of a solution of distilled cane molasses. During fermentation, distillation extracts, alcohol and discharges the remaining solvent as a Distillery Spent Wash as an effluent. This effluent is dark brown in color, low pH and includes all the molasses ingredients except fermentable sugar. The wastewater discharged from the distillery industries is generally high in biological oxygen demand (BOD), chemical oxygen demand (COD), total solids (TS), sulfate, phosphate, phenolics, and heavy toxic metals. On the ground, it causes seed germination inhibition and vegetation degradation by reducing the soil alkalinity and availability of manganese, and in aquatic settings, it reduces sunlight penetration and decreases both photosynthetic activity and dissolved oxygen content that damages aquatic fauna and flora both. About 12-15 liter of wastewater is formed during per liter of alcohol production during the course of alcohol production in distillery industries (Kanimozhi and Vasudevan, 2010).

Pulp and paper are the third largest industrial polluter in the air, water, and land and it releases well over 100 million kilograms of harmful waste per year. Chlorine and chlorine related products, mercury, hydrogen sulfide, and sulfur dioxide are the main components of the emissions associated with pulp mill. Mainly Chlorine and

chlorine containing compounds are exploited in wood pulp bleaching, in particular chemical pulps specified by the kraft method or sulfite process. Plants using elemental chlorine have created large quantities of dioxins which are persistent organic contaminants and are one of the most harmful pollutants released by humans. Pulp and paper mills discharged waste water containing high concentrations solids, nutrients and dissolved organic matter which are responsible for water pollution. Waste water can also be contaminated with organochlorine compounds. Some of these toxic materials are naturally present in the wood, but the chlorine bleaching of the pulp creates even greater amounts of toxins to be released. The disintegrations of chemical pulps release significant amounts of organic material into the environment, especially in water bodies (Toczyłowska-Mamińska, 2017).

The conventional method for treatment of wastewater consists of primary, secondary, tertiary steps whose nature depends on the specification of the discharged water and the contaminant level of effluent (Ramalho, 2013). The preliminary and primary treatment mainly consists of physical processes to remove settable and floating solids, oil, organic solids, etc. from effluent via sedimentation, filtration and skimming. In secondary treatment the target is the elimination of organic matter and likely nutrients (nitrogen and phosphorus) by pathways primarily biologic. The purpose of tertiary treatment is to eliminate particular pollutants (usually toxic or nonbiodegradable compounds) or to replace contaminants that have not been properly removed in the secondary treatment. In most of the developing countries, tertiary treatment is limited.

23.1.1 Physical treatment technologies

23.1.1.1 Sedimentation

Conventional treatment for the processing of surface water for drinking water usually consists of coagulation, flocculation, sedimentation and sand filtration. One of the key drawbacks of a modern method combining sedimentation and filtration is a very long duration of residence. This is primarily due to the flocculation and sedimentation processes. Sedimentation is a fundamental, physical pre-treatment of water preceding to the use of other purification techniques such as filtration and disinfection. It extracts damaging tiny suspended matter (sand, silt and clay) and certain biological pollutants from water under the control of gravity. The more the water stays undisturbed, the more dissolved solids and bacteria fall back to the bottom of the tank. Adding coagulants can accelerate the cycle of sedimentation. Three specific chemicals used for this reason are aluminum sulphate, polyaluminum chloride, and ferric sulphate (De Feo et al., 2012).

23.1.1.2 Adsorption

The adsorption process by solid adsorbents has promise as one of the most effective approaches for handling and eliminating organic pollutants in wastewater treatment, among other water treatment strategies. Adsorption has advantages over other approaches, which can entail low investment. The adsorption method is commonly

used to treat chemical wastewater from organic and inorganic contaminants. Adsorbents of various forms are categorized into natural adsorbents and synthetic adsorbents. Environmental adsorbents involve charcoal, clays, minerals in clay, zeolites, and ores. Activated carbons (AC) (both granular activated carbon (GAC) and powdered activated carbons (PAC)) are typical adsorbents used to extract unwanted odor, color, taste and other organic and inorganic impurities from domestic and industrial wastewater due to their wide surface area, nonpolar microporous structure and economic viability. Activated carbon adsorbent can be easily prepared exploiting sewage sludge (Smith et al., 2009). Activated carbon adsorbent prepared from sewage sludge has been identified as a potentially attractive wastewater material. The efficacy of the treatment with adsorption is determined by the form of a substance that will be removed. Natural carbon is best adsorbed with substances with high molecular weight and poor water solubility. Adsorption efficacy is often determined by the concentration of the extracted material, the presence of other organic elements, temperature, pH, and set-up architecture (Doke and Khan, 2013). One major downside of adsorption technology, especially when working with toxic substances and/or micropollutants, is that this mechanism accumulates and moves the contamination load from the aqueous phase to the adsorbent. A sequential treatment is often used initially by means of a chemical oxidation to remove toxic agents and adsorption as a next step (Huang et al., 1988).

23.1.1.3 Electrodialysis

Electrodialysis (ED) is a mechanism by which electrically charged membranes are used to isolate ions from aqueous fluids by means of electrical potential driving forces. Currently, owing to its isolation properties, electrodialysis is used for the manufacture of drinking water by desalination, for the recovery of water and precious metal ions from chemical effluents, for the removal of salts and acids from pharmaceutical fluids and for food processing and for the extraction of salts from seawater (Xu and Huang, 2008). The efficiency of ED depends on operational conditions and device configurations such as raw water ion content, current intensity, flow rate, membrane properties, feed concentration, and cell compartment configuration. The efficiency of ED systems is primarily dependent on the properties of ion exchange membranes. Fouling ion exchange membranes are one of the typical problems in ED processes. Fouling is primarily induced by accumulation of various materials such as organics, colloids and biomass on the membrane surface or within the membrane, and the issue of fouling limits the transfer of ions. Fouling issues are the reason to raise the resistance of the membrane, to decrease the selectivity of the membrane and to adversely affect the efficiency of the membrane. Membrane fouling results in high energy usage and low separation performance. Some techniques, such as feed solution pre-treatment, compartment turbulence, controlling zeta potential, pH and optimization of flow rate, membrane properties alteration, and pulsed voltage, have been considered to decrease fouling in ED systems. Many forms of elimination, such as mechanical processes, often require more materials, extra resources or equipment, and such factors raise operation and maintenance costs. Electrodialysis

reversal systems EDR also eliminated the fouling issue. EDR is closest to ED, but the path of the ion movement is changed regularly to break down foul momentum by changing the polarity of the generated electrical current (Allison, 1995).

23.1.2 Chemical treatment technologies

23.1.2.1 Coagulation/Flocculation

Turbid waters, having suspended, and colloidal particles, are usually purified by coagulation and flocculation followed by clarification; the procedure typically consists of prompt dispersion of the coagulant into the raw water after that extreme agitation commonly known as rapid mixing. Rapid mixing is controlled by chemical and physical factors, and the final product of the total procedure solely involves on this step. Iron(III) and aluminum(III) salts are the best regularly used coagulants. Coagulation treatment is dependent on the characteristics of raw water, temperature, pH, coagulant form, and dosage and the efficient mixing speed and duration. Coagulating agents are pH-specific and will also break down the emulsion at low pH levels.

23.1.2.2 Precipitation and filtration

Precipitation and filtration are primarily used for the separation of suspended and DS, sulphates, carbonates, phosphates, chloride impurities and metallic wastewater materials. Metals are typically precipitated as lime hydroxide (NaOH). Chemical precipitation usually contains metal salts such as aluminium sulphate and ferric chloride as precipitating agents that create a complex of polluted compounds. In addition, the precipitates are separated from the wastewater using a different filtration or clarification method.

23.1.2.3 Oxidation

Advanced oxidation processes (AOPs) usually imply the deployment of any advanced oxidation techniques utilizing UV/O_3, O_3/H_2O_2, UV/H_2O_2 or photo Fenton reactions (UV/H_2O_2/$Fe_2{}^+$ or $Fe_3{}^+$) (Neyens and Baeyens, 2003). Fenton's reagent was invented in 1894 by Fenton (Fenton, 1894). Fenton's reagent is a combination of H_2O_2 and ferrous iron that creates hydroxyl radicals. Ferrous iron (Fe^{++}) initiates and catalyzes the decomposition of H_2O_2, which results in the production of hydroxyl radicals. The development of such radicals requires a complicated series of reactions in an aqueous solution. H_2O_2 will serve as both an OH scavenger and an initiator. Generally, Fenton's oxidation cycle includes pH modification, oxidation, and neutralization and precipitation coagulation. Chemical compounds are also extracted after two levels of oxidation and coagulation. The oxidation method related to Fenton's reagent is gaining importance owing to the effective degradation of phenolic, chlorinated and organic pollutants that predominantly exist in industrial effluents. Fenton's oxidation cycle is a quick and desirable approach that improves the biodegradability of organic halides, polyphenols, total organic content and intractable contaminants owing to its ability to work at low pH rates. Fenton's procedure is used extensively for the possible de-coloration of clothing dyes, for the processing of lignocellulosic colors and for the extraction of wastewater.

23.1.3 Biological treatment

The treatment of wastewater by microorganisms such as algae, fungi, or bacteria under aerobic or anaerobic conditions during which organic matter in wastewater is oxidized or absorbed into cells that can be extracted by removal or sedimentation is called biological treatment (Wu et al., 2012). This treatment method utilizes naturally occurring microorganisms to convert dissolved organic matter. Wastewater is put into a specially built bioreactor, where under aerobic or anaerobic conditions, organic matter is used by microorganisms such as bacteria (aerobic or anaerobic), algae, and fungi (aerobic). The bioreactor provides sufficient bioenvironmental conditions for microorganisms to replicate and consumption of dissolved organic substances for their energy source. Given that oxygen and food are supplied to the microorganisms in the form of solid wastewater, the biological oxidation cycle of dissolved organic matter would be preserved.

As new compounds are being developed, new ways of avoiding environmental toxicity also have to design. New contaminants such as dyes, pharmacons, and activated sludge are processed by factories and disposed of in water bodies. Xenobiotic compounds, such as chlorinated organic matter. Hydrocarbons do not exist naturally in marine environments, among others, affecting the flora and fauna. In addition, some of those toxins in marine animals, plants and microorganisms are recalcitrant and bioaccumulate. The harm to wildlife created by these novel contaminants is not well understood, and since these are strange molecules, some are not metabolized by microorganisms (Crini and Lichtfouse, 2019). This current treatment, distribution and disposal of wastewater pollutants, which depend heavily on transportation and centralized systems, are no longer sustainable. The highly effective, scalable and multifunctional method made possible by nanotechnology is anticipated to deliver a huge-performance, economical wastewater treatment system that not dependent on large infrastructure. Developing an effective wastewater treatment technique is one of the greatest needs of the twenty-first century due to the lack of water supplies. In addition, identifying effective methodologies for the economic treatment of wastewater is of utmost importance. Recent developments in nanotechnology have drawn the attention of many wastewater treatment researchers. Although several research works have been published in this regard, there is very limited collective knowledge available. The main objective of this chapter is therefore to identify the recent developments in wastewater treatment systems based on nanomaterials.

Clean drinking water is turned into an inexorably constrained asset in numerous places of the world and as outcome water purifying advances are increasing significant consideration around the world. The modern pollution, alongside residential effluents, agricultural and urban spillover are contaminating water bodies and rivers and making it hard for regular water treatment to eliminate all the toxins. They also rely on centralized systems which are not sustainable in the distribution and discharge processes for the needs of today. Over the last decade nanomaterials have gained special interest in studies regarding water pollution control (Qu et al., 2013). Two critical properties make for highly lucrative nanoparticles as sorbents. Nanoparticle have greater surface area to mass ratio than macro particles. They can

also be reinforced with specific reactor groups to increase their chemical affinity to target compounds. Nanofiltration methods are now commonly used in the removal of various cations, normal organic substance, biological pollutants, chemical contaminants, nitrates and arsenic from groundwater and surface water (Schäfer et al., 2004). The nanomembranes are used through filtration or separation techniques to treat polluted water. Nanosorbents are commonly used in water purification as separation media for separating inorganic and organic contaminants from polluted water. Nanoparticles of titanium dioxide (TiO_2) have emerged as promising photocatalysts for water purification over the last decade (Bhatkhande et al., 2002). As a result, numerous researchers have implemented methods such as chemical precipitation, sol gel, vapor deposition, solvothermal, solid state reaction, etc. for the synthesis of certain nanostructured mixed oxides that can be used effectively for groundwater treatment. Nanomaterials are concentrated as a potential of purging salt from seawater, making it consumable. However, there is a need to clarify the possible hazards these nanomaterials can present a threat to the ecosystem. Nanoengineered materials, such as nanoadsorbents, nanometal oxides, nanomembranes, and nanophotocatalysts, give the potential for new water technologies which can be easily incorporated into customer-specific applications. Most can be compliant with current treatment systems and can easily be incorporated into standard modules. Retention and reuse of nanomaterials is a key aspect of system design allowed by nanotechnology, due to both cost and public health concerns.

23.2 Nano adsorption

Adsorption is a mechanism that adsorbs contaminants onto the solid surface. It is essentially a surface phenomenon and driven by physical forces, but often weak chemical bonding also engages in the process of adsorption. Owing to its special characteristics, nanoparticles have proved themselves to be excellent adsorbents. Small size, catalytic potential, high reactivity, large surface area, faster isolation, nontoxicity and large number of active sites for contact with different contaminants are the most important characteristics of these particles; which made them ideal adsorbents. These properties are responsible for high adsorption potential by increasing the nanoparticles ‘surface area, free active valences and surface energies. Nanomaterials are currently used in adsorption processes to extract heavy metals, dyes, synthetic organic chemicals and are also used in purification processes like water disinfection and microbial control (Santhosh et al., 2016). The key benefits of adsorption are that it is flexible; it does not need massive volumes of electricity, large amounts of water or extra chemicals. This easy and inexpensive solution can be a feasible choice in developing nations where access to large quantities of power and sufficient capital can be a problem. The mechanistic adsorption method allows for flexibility in the adsorbent configuration and use. Batch method and column or flow method are the two most common methods used for adsorption. The batch process is where the adsorbate is applied to the sorbent under constant mixing or agitation

in an aqueous suspension. A form of a column or flow uses a steady stream of water through the adsorbent fixed surface. The flux of the water through the stationary bed set a fixed limit. In industrial settings the flow approach is usually applied.

Generally, inorganic NMs are classified into transition metal / oxides / sulfides NMs, carbon based NMs such as graphene, silica based NMs, and associated nanocomposites. Because of their special properties, nanoparticles of transition metal or metal oxides (NMOs) are commonly used to extract heavy metal ions in wastewater, such as iron, silver, gold, magnetic ferric oxide, manganese oxide, titanium oxide, magnesium oxide, copper oxide, cerium oxide, etc. (Santhosh et al., 2016; Hua et al., 2012). They are found in different types, including particles, tubes and others. The size and shape of NMOs are both important factors which affect their performance in adsorption. Over the past decade, efficient synthetic methods have been widely studied to obtain shape-controlled, highly stable, and mono disperse metal oxide nanomaterials.

23.2.1 Iron oxide nanoparticles

Iron is one of the utmost natural elements on Earth. Ferric oxide nanoparticle (NFeOs) is the most useable low-cost adsorbents for toxic element separation due to its resource facility and simplicity in the synthesis process (Xu et al., 2012). NFeOs can be straightforwardly impelled to polluted locations with negligible ancillary pollution risks due to the environmentally friendly nature of elemental iron. The intensively researched NFeOs for water / wastewater removal of heavy metals include goethite (-FeOOH), hematite (-Fe_2O_3), amorphous hydrous Fe oxides, maghemite (-Fe_2O_3), magnetite (Fe_3O_4), and iron / iron oxide (Fe@FexOy) (Xu et al., 2012; F. Hasany et al., 2013). Rama Rao Karri group, formed iron oxide nanoparticles modified with the extract of tangerine peel (T-Fe_3O_4) and used to adsorb lead from aqueous solutions (Lingamdinne et al., 2019). It was found that 99 percent of the elimination of Pb(II) adsorption was done with 0.6 g/L of T- at an initial metal concentration of 10 ppm and 25°C room temperature. Using a low-cost template-free microwave assisted solvothermal process.

Wei-Guo Song group, developed a flowerlike nanostructures α-Fe_2O_3, which is an outstanding As(V) and Cr(VI) adsorption capacity due to its large surface area encompasses abundant hydroxyl ion (Cao et al., 2012). As an ion exchange between hydroxyl on the α-Fe_2O_3 surface and As(V) and Cr(VI) species was reported as the adsorption mechanism for As(V) and Cr(VI) on flowerlike α-Fe_2O_3 nanostructures. Due to the advantages, such as low cost, high surface area, and high adsorption power, these flower-like α-Fe_2O_3 nanostructures were an attractive adsorbent for removing both As(V) and Cr(VI) from water. Chunru Wang group, developed an α-FeOOH 3D chrysanthemum-like hierarchical structure through a simple, cost effective, and environmentally friendly process (Li et al., 2011). That approach did not employ surfactants, costly iron salts or alkali reagents. The hierarchical nanomaterials obtained with iron oxyhydroxide have high BET surface area and show excellent adsorption efficiency of heavy metal ions in water treatment.

Pengcheng Li group, synthesized hollow nestlike α-Fe_2O_3 nanostructures under microwave heating using a novel, template-free glycerol-assisted approach (Wei et al., 2013). In the reaction phase, the relative amount of glycerol has a major effect on the creation of hollow interiors in the products. The quasi- of glycerol used in this study provides a "template" for forming α-Fe_2O_3 interweaving nanorods on the surfaces of the hollow nanostructures. In water, the as- hollow nest like α-Fe_2O_3 spheres with meso porous structures exhibit excellent capacity of adsorption to As(V) and Cr(VI) ions and Congoredions.

23.2.2 Other metal oxide nanoparticles

Tentatively several other metal oxide NPs is used to remove contaminants from the water. For example, chemical alumina (Al_2O_3) NPs was prepared for selective solid phase extraction and pre-concentration of Cd^{2+} and Pb^{2+} ion trace quantities (Kumar and Chawla, 2014). The CeO_2 NPs had outstanding As(V) and Cr(VI) ion adsorption capacities (Yaseen and Yaseen, 2019). It was shown that CuO nanostructures are effective adsorbents for removing arsenic and Pb^{2+} ions from aqueous solutions (Mahdavi et al., 2014). For the ultrasonic-assisted simultaneous removal of Pb^{2+} ions from aqueous solution, copper oxide NP-loaded activated carbon was successfully applied. Extremely porous, nanostructured ZrO_2 spheres demonstrated extraordinary results on As(III) and As(V) removal (Hristovski et al., 2008). Additionally, binary metal oxides NPs is prepared, characterized and used for wastewater treatment. For example, polysaccharide-stabilized Fe–Mn oxide NPs have been used for soil and groundwater immobilization of As(III). Bimetal mixed oxide synthetic iron(III)–cerium(IV) had high As(III) and As(V) removal capability in engineered pH (7.0 ± 0.1) and temperature 30 (±1.0)°C (Gupta and Ghosh, 2009).

23.2.3 Polymer supported metal oxide nanoparticles

Synthetic organic polymers or biopolymers, i.e. cellulose and chitosan contains polyfunctional surface groups such as –NH2, –OH, –COOH, etc. adsorb heavy metals effectively in the water yet their use is constrained by the small surface area and sluggish adsorption rate (Zhao et al., 2011). Meanwhile, for chelating heavy metals, transition metal NPs or carbon NMs have a broad surface area but lack usable surface groups. The development and implementation of NMs and nanocomposites based on polymers offer an alternative possibility for the effective removal of heavy metals in water. Compared to transition metal or metal oxide NPs, activated carbon and organic polymers, polymer NMs and polymer-supported nanocomposites as nanosorbents have broad surface areas and multifunctional groups in the soil (White et al., 2009). The functional chelating group and the exchange of ions contribute primarily to the adsorption of heavy metals such as ions Pb^{2+}, Hg^{2+}, Cr^{3+}, and Cr^{6+}. Polymeric nanocomposites are often categorized as a polymer matrix for the integration of inorganic NPs. Polymer NMs include polymer NPs, polymer nanofibers, and polymer nanocrystals. Alginate has also been used as a biopolymer aid to create nanocomposites to extract poisonous materials from water. The nanochitosan and nanocellulose

adsorption process of heavy metals is primarily due to ion exchange, electrostatic interaction, metal chelation, surface and pores ion-pair adsorption, adsorption, and complexation reactions (Olivera et al., 2016).

23.2.4 Carbon-based nanoparticles for adsorption

The unique hybridization properties of carbon and the vulnerability of the carbon structure to deviations in the conditions of synthesis permit tailor-made modification to a degree not yet matched by inorganic nanostructures. Although inorganic nanomaterials are a promising field for future study, the science and application of carbonaceous nanostructures is being more thoroughly developed. Graphite surfaces on the nanoscale are thermodynamically more stable than three-dimensional structures. The strain energy produced by the planar graphite curvature is compensated by the reduction of unfavorable dangling bonds. The result is fullerenes and nanotubes that share many of the characteristics of graphite, but also exhibit a distinct and tunable range of properties due to nanoscale quantum effects, enhanced bonding sp^3 structure, quantity confinement of wave functions in one or more dimensions, and closed topology. Carbonaceous nanomaterials therefore have the same bonding properties as macroscopic carbon structures, but their features and composition are governed by the stability of specific resonance structures rather than by the bulk averages of their crystalline shapes. The adsorptive potential of traditional carbonaceous sorbents is constrained by the number of surface-active sites, the activation energy of adsorptive bonds, the slow kinetics and nonequilibrium of sorption in heterogeneous structures, and the rate of mass transfer to the sorbent surface. Studies of sorption using carbon-based nanomaterials report rapid equilibrium levels, high adsorption efficiency, broad pH effectiveness and compatibility with BET, Langmuir or Freundlich isotherms. Direct sorption of organic pollutants to the nanomaterial surface is guided by the same simple hydrophobic, dispersive and low dipolar forces in traditional systems that determine sorption energies. The higher equilibrium levels of carbonaceous nanosorbents over activated carbon are due to interactions with aromatic sorbates, decreased heterogeneity of adsorption energies, and loss of pore diffusion as an intermediate mechanism in adsorption. Given the high cost of synthesis, fast equilibrium rates and high sorbent ability are powerful qualities of carbonaceous Nanosorbents are merely incremental improvements on an existing model. Nanosorbents' true revolutionary potential lies in the numerous pathways for personalized modulation of fullerene and nanotube surface chemistry (Gupta and Saleh, 2013). Functionalized nanosorbents can provide an engineered method for handling different micropollutants, removing contaminants at low concentrations.

Rajeev Kumar et al. explores nanosorbents based on carbon that have been shown to be efficient adsorbents for separating cadmium ions from water (Kumar et al., 2015). Nanomaterials based on carbon include carbon nanotubes, oxidized carbon nanotubes, carbon-based fibers, graphene, nanocomposites of carbon and fullerene. CNTs are altered by oxidation, mixed with other metal ions or metal oxides, and coupled with organic compounds to improve the sorption capacities (Thines et al., 2017).

Fresh carbon-based nanomaterials and nanomaterials based on transforming carbon have been widely used to extract heavy metal ions from waste water. Metal-organic structures (MOFs) as models or precursors for the creation of novel magnetic porous carbon have recently drawn growing interest in the field of environmental health, owing to their different physical and chemical properties. For example, magnetic porous carbon from the Co-based organic metal structure have an excellent ability to adsorb aromatic contaminants from pesticides in aqueous environment (Jakubus et al., 2017). Additionally, magnetic porous carbon materials derived from Fe-MOFs may effectively extract organic dyes from aqueous solution (Banerjee et al., 2012). Porous carbon nanospheres prepared with spray pyrolysis have been tested as adsorbents in de-ionized (DI), pipe, and well water for the removal of arsenate and selenite (Li et al., 2015). Microporous carbon nanospheres demonstrated high surface-to-volume ratio and specific surface functional groups, which has a strong affinity to both metals in DI water, proficiently exploit as a commercial activated carbon for arsenate elimination at pH > 8.

23.3 Nanofiltration

Membrane processes such as nanofiltration (NF) arise as primary contributors to purification of the water. Nanofiltration is nothing but a pressure propelled membrane procedure that in terms of its capacity to discard molecular or ionic substances lies in-between ultrafiltration and reverse osmosis. Membrane nanofiltration, organic membranes, or ceramic membranes can be either rigid or porous. Nanofiltration membranes can have a greater free area, tiny pores, or nanovoids accessible for transport. The dimension of these nanovoids forms a modification among microporous and condensed membranes that can be in the size range of 0.5–1 nm. Nanofiltration membranes are generally considered to be capable of exhibiting nominal cutoff between 1000 and 200 Da (Mohammad et al., 2015). The removal of turbidity, microorganisms and inorganic ions such as Ca and Na has been shown by NF membranes. They are very useful for groundwater hardness lessening, elimination of liquefied organic substances and trace impurities from surface water, disposal of wastewater (removal of organic and inorganic chemicals and organic carbon) and pretreatment in the desalination of seawater. For water treatment applications, carbon nanotube filters are now gaining popularity (Upadhyayula et al., 2009). These innovative filtration membranes comprise of hollow cylinders with centrifugally spaced carbon nanotube barriers. The filters have been effective in filtering infected water from the bacteria (*Escherichia coli* and *Staphylococus aureus*) (Brady-Estévez et al., 2008). Ultrasonic and autoclaving cleanse the carbon nanotube filters readily.

The basic characteristics of the nanofiltration membranes are primarily the combination of excessive rejections of multivalent ions (> 99%) with low to moderate eliminations of monovalent ions (~70%) and very good rejection (> 90%) of organic substances with a molecular weight exceeding the membrane's molecular weight (Childress and Elimelech, 2000). The mechanism of mass transport is highly

dependent on the configuration of the membrane and on the interactions between the membrane and the molecules that are transported. Separation effectiveness can be coordinated by the sieving effect or by the solvent molecules and diffusion characteristic. NF membrane rejection can be due to a combination of steric, Donnan, dielectrical, and transportation effects. The transportation of neutral solutes is through the steric mechanism (size-based exclusion) and is well known via numerous UF membrane studies. The classical Donnan effect describes the possible interactions of equilibria and membrane between a charged species and the charged membrane interface. The membrane charge arises from the dissociation of ionizable groups at the surface of the membrane and inside the structure of the membrane pore. NF membranes have a low ion exchange capacity in addition to the ionizable surface groups, and in some cases ions from the contacting solution can adsorb to the membrane surface causing a slight modification of the membrane charge. Electrostatic repulsion or attraction occurs according to the valence of the ion and the fixed membrane charge which may differ depending on the localized ionic environment as a result of the above mentioned phenomena. The dielectric exclusion phenomena are still less known, and there are two key conflicting theories about the exact existence of the interaction. Solutes moving in free solution encounter drag forces exerted across the confined pore structure of the solvent. The flow of solutes in this confined space is significantly influenced by the local environment, and the solution transport is considered to be impeded. Hindered transport can be expressed both as a convective and diffusive factor which contributes to the overall effect of transport. The fact that the dimensions of the NF active layer are similar to atomic length scales, coupled with limitations in current measurement technologies, has delayed thorough knowledge of the physical structure and electrical properties of real NF membranes, leading to confusion and considerable debate about the true nature of the separation mechanisms and the function of dielectric exclusion.

In membrane systems, two flow types are generally distinguished; Cross-flow with concentrate recycling (CFCR); and Flow with a dead end system. Cross-flow filtration (also known as tangential flow) is done by using a high-pressure feed water flow through the membrane. The solution is split into two parts, one part passes through the membrane or is filtered, which is called permeate, and the rest only flow marginally to the surface of the membrane without separation or filtration, which is called the reject or concentrate. The concentrate is composed of all the salts rejected and is typically combined with all the discarded materials. Membrane types are categorized into isotropic microporous, nonporous, solid, electrically charged, asymmetric, ceramic, and liquid membranes according to the composition of the membrane and the form of the pore. NF is marked by calcium and magnesium ion removal resulting in water softening and no addition of sodium ions during filtration relative to ion exchange units (Hilal et al., 2004). To minimize hardness, NF doesn't require additional chemical treatment. For example, NF will not require heating or cooling of feed such as distillation, which will effectively reduce separation costs. Furthermore, no mechanical stirring is needed to ensure gentle separation of the molecules. NF has the significant benefit of handling a relatively high volume of feed and a

steady permeate flow rate. NF has, however, a limited use in the industry due to the membrane pore size that is restricted to nano-porous size. RO and ultrafiltration are preferred because they can easily cover the ultrafiltration spectrum due to high initial, operating and maintenance costs without the cost constraint of NF (Rautenbach et al., 1997). Using NF systems, energy requirements for water treatment have risen by 60–150 percent, low-energy systems are a big demand. Green energy can serve as an effective means of rising energy demand. One way of reducing NF energy requirements is to use more permeable NF which decreases the pressure and energy requirements which may affect the activity of the membrane. High pressure driven process NF membrane is capable of processing significant volumes of high quality water. Excellent contaminant removal capacity, lower membrane costs, lower energy consumption, and increased membrane life compared to RO have resulted in NF being widely accepted and popular around the world. NF is used by many researchers for the treatment of groundwater, surface water, and wastewater reclamation in environmental applications. In addition to the traditional function of removing divalent salts and small organics, recent studies have shown that NF has been increasingly used for many new, interesting applications, such as the removal of arsenic (As), persistent organic contaminants (POPs), pharmaceutical active compounds (PhACs), and hormones (Van der Bruggen and Vandecasteele, 2003).

23.3.1 Inorganic membranes

Inorganic membranes are asymmetric, thick, porous ceramic support materials which include alumina, silica, zirconia, mullite, mixtures of oxides, and metals that are sintered. The main aim of ceramic membrane production is to form ultrafilter membranes with water permeability along with nanofilter and reverse osmosis membranes selectively similar to solute. Following the introduction of nanotechnology in membrane technology for water purification applications, zeolite-coated ceramic membranes are extensively studied for brackish water and wastewater desalination through reverse osmosis (Goh and Ismail, 2018). Ceramic membranes with a wide variety of insoluble oxides showed intriguing properties for isolation and refining. Out of these, zirconia and titania mesoporous membranes were introduced throughout the industry. Usually, a ceramic membrane based on porous metal oxide is distinguished by a multilayered asymmetric structure composed of a thicker support layer with fairly wide pores (~0.5 μm) to provide mechanical stability for membrane structures, an intermediate layer to minimize pores to mesoporous dimensions (2–5 nm) and a much thinner top layer with minimal and narrow pores (< 1 nm) (Kim and Van der Bruggen, 2010).

Mesoporous γ-alumina membrane, one of the most commonly researched ceramic membranes, was typically used as interlay for ceramic NF membranes (Schaep et al., 1999). A standard mesoporous γ-alumina membrane is distinguished by an average pore size of 3–5 nm corresponding to a 3000–10,000 Da molecular weight cutoff. Also attempted was the alumina membrane, with a typical pore size of around 1 nm. Due to the close pore structure, however, the membrane permeance has been usually

less than 5 L m^{-2} h^{-1} bar^{-1} thus inadequate to fulfill the industrial standards. Unlike conventionally prepared ceramic membranes centered on metal oxide comprising three layers, several recent studies suggested an enticing approach to serving the mesoporous interlayer as the top layer as a separate medium for pervaporation desalination. This groundbreaking approach decreases the preparation costs for the membrane by eliminating the need for additional top layers. Furthermore, the decreased thickness of the membrane will therefore help decrease water diffusion resistance across the membrane and improve water flux. In general, most ceramic membranes of porous metal oxide achieve separation dependent on through size via hydration and electrostatic effects at the pore entrance (Vandezande et al., 2008). For the treatment of standard industrial wastewater consisting of a mixture of metallic ions, organic and inorganic substances, the rejection is controlled primarily by the intense electrostatic interactions formed between the multivalent cations and the positively charged metal oxide ceramic membranes. This rejection function is highly based on the pH of the feed solution and the membrane surface charge alteration. Membrane surfaces play an important role in affecting certain membrane properties such as hydrophobicity, surface charges, hydrodynamics and fouling rate. As such, the surface characteristics of ceramic membrane were investigated in order to better understand and improve their filtration efficiency. Another prominent consequence of the surface modification of metal oxide ceramic membrane is the fouling resistance of the membranes, especially in the treatment of water-in-oil (W / O) emulsions. By careful selection of a surface modifying agent, the diameter and composition of the membrane pore remain unmodified to preserve the efficiency of the separation. Self-assembled alcoxysilane monolayer such a hexadecyltrimethoxysilane can effectively minimize water droplet adsorption on the membrane surface while reducing membrane fouling as well as significantly improving oil flux and water rejection based on enhanced surface oleophilicity. In the traditional filtration of W / O emulsions, the ceramic membrane is ideally designed to exhibit hydrophilic surface to prevent connecting W / O emulsion droplets to the membrane surface or reaching the membrane pores, thereby reducing the fouling phenomena. For this purpose, a wide variety of hydrophilic nanomaterials such as TiO_2, Fe_2O_3 and graphene oxide were incorporated (Cheng et al., 2014).

Zeolites are porous crystalline aluminosilicates with a well-defined molecular-dimensional channel structure. They accept different mono- and divalent cations (Na^+, K^+, Ca^{2+}, Mg^{2+}) and can therefore be easily exchanged in a contact solution. The zeolite membranes have certain exceptional properties which traditional polymeric membranes cannot satisfy. Several of these properties include thermal and chemical stability, tunable pore sizes and a low propensity to foul (Al-Amoudi, 2010). In recent decades, substantial progress has been made on zeolite membrane synthesis approaches that have resulted in various membrane morphologies, compositions, and separation characteristics. To date, there are still some questions and doubts about the transport mechanism and the rejection of ions via the vicinity of zeolite frameworks. It was widely accepted that zeolite membrane separation mechanism is based on size exclusion and ion interactions in order to reject the hydrated

ions (Han et al., 2015). As such the efficiency of separation usually increases with ion valence. In principle, in order to reject Na^+ and Cl^- with a hydrated size of 0.72 nm and 0.66 nm, respectively, the intercrystalline interconnection and pore size must be regulated well below 0.66 nm to ensure high ion rejection.

MOFs are a fairly new class of functional porous material that consists of an interaction of coordination between metal-containing clusters and organic multitopic connections. This particular approach has brought flexibility to customizable structures and chemical functionalities. All MOFs are structurally composed of secondary building units (SBUs) consisting of metal ions and oxygen atoms. The organic linkers therefore serve as the bridging agent connecting these SBUs to form the MOF assembly. A wide variety of organic linkers with different functionalities, ranging from bidentate to polydentate aromatic carboxylates, have been used to synthesize different features of MOFs. MOFs have a wide surface region of 6000 m^2/g and a porosity of 90 percent. Thanks to their crystalline properties, MOFs are physically stable and versatile in many industrial applications, preserving integrity and withstanding strong external pressures.

23.3.2 Carbon nanotubes

Carbon nanotubes CNT membranes have been identified as a groundbreaking method for solving global water issues and water contamination problems (Upadhyayula et al., 2009; Han et al., 2015). As one of the fullerene family members, CNTs are structurally made of cylindrical graphite sheets which are rolled up into a smooth tube shape form of nanometer scale diameter and lattice fencing appearance. CNTs can be further categorized as single-walled carbon nanotubes, double-walled carbon nanotubes, and multiwalled carbon nanotubes, based on the layers of graphene shells. The nanotubes 'properties are generally correlated with their atomic structure, shape, nanotube diameter, and length. The particular interest in CNT membrane design resides in the capacity of the lightweight and the thick CNT network to have excellent water flux and the provision of tips or tube openings for convenient functionalization (Fig. 23.1).

Ideally, a CNT membrane would be a well-grafted CNT structure with standardized nanopores spread uniformly on the surface of the membrane. To guarantee the efficiency of the CNT membranes the inner diameter of the CNT should be precisely regulated within a very limited range. In addition, the output of the CNT membrane is not only assessed by the efficiency of separation in terms of water flux and salt (or ion) discharge, but also focused on its ability to provide synergistic antimicrobial properties to minimize biofouling of membranes, chemical resistance to harsh filtration environments and convincing mechanical strength for functional pressure-separation process. CNT's quick and frictionless movement of fluid is largely due to the smooth and hydrophobic nonpolar surface of hollow CNT structures. At the water-CNT interface, the development of organized hydrogen bonds introduces a vapor phase barrier between the inner walls of the channel and the water molecules line, thereby enabling the water molecules to flow resistant free. The presence of COOH and OH functional groups on the plasma treated CNT membrane has greatly enhance

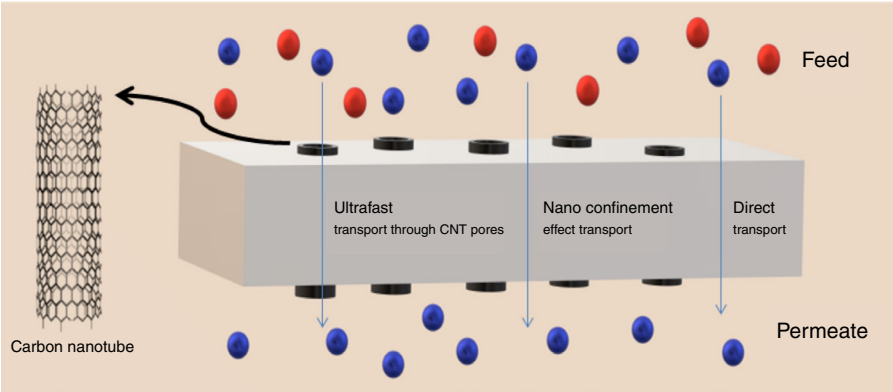

FIG. 23.1 Nano filtration through carbon nanotubes.

the surface hydrophilicity and ion binding properties. As a result, the desalination of the CNT membranes could be barely driven by the free energy of adsorption and only a small pressure drop was required to sustain water flux.

23.4 Nanocatalyst

Nanoparticles have greater surface area due to smaller sizes and enhanced exposed active sites. Nanoparticles thus have greater areas of interaction with the reactants, and are catalytically more active than traditional heterogeneous catalysts. Variations in nanocatalyst arrangement and composition offer access to diverse natures of catalytic positions. A particular type of site shows greater selectivity for a specific reaction pathway. Therefore, nanocatalysts from the perspective of increased activity and selectivity have properties that correspond to those of homogeneous catalysts. Additionally, nanocatalysts are comparatively simpler to isolate from the reaction compositions, and are heterogeneous facilitators in that context. Furthermore, reactant(s) adsorption on the nanocatalyst surface is an essential requirement for every nanocatalyzed reaction. Nanocatalysts with better operation, stability and selectivity can therefore be engineered and synthesized by regulating their scale, shape and nanomaterial composition. The unusual physical and chemical properties of NPs introduced with the Nanoscience technology make them very promising candidates for various applications, including catalysis (Garrido-Ramírez et al., 2010; Bethi et al., 2016). The valence electrons form continuous bands in bulk metals. When a bulk material is reduced to the nanometer scale in a certain direction, the energy of the electrons is subjected to confinement in this direction. NPs exhibit significantly larger total exposed surface areas and different combinations of surface structures compared to bulk metals, and the effects of electronic containment within NPs can cause significant changes in an electronic structure. The effect increases the likelihood of catalytic process tuning. Nanotechnology can provide an efficient means of regulating

the surface structure and electronic properties of nanocatalysts efficiently and quantitatively, without altering their composition. Adsorption and catalytic reactions can be controlled by continuous nanometer-scale modification of the size of catalysts. Nanocatalytic substances such as zero valent metal, semiconductor materials and bimetallic nanoparticles are commonly used in water treatment due to high surface-to-volume ratio and shape-dependent properties, as they increase the catalytic activity at the surface. It increases the reactivity and oxidation of environmental toxins such as organochlorine pesticides, azo dyes of halogenated herbicides, polychlorinated biphenyls, and nitro aromatics. For environmental contaminant elimination, generally used catalytic nanoparticles are semiconductor substance, zero-valence metal and bimetallic nanoparticles, for example, PCBs (polychlorinated biphenyls), azo dyes, halogenated aliphatic agents, organochlorine pesticides, halogenated herbicides, and nitro aromatics. Silver (Ag) nanocatalysts, AgCCA catalysts, N-doped TiO2, and ZrO2 nanoparticles catalysts are highly effective in the degradation of microbial pollutants which can be used in water purification system (Chaturvedi et al., 2012). Using modern nanocatalytic operations, wastewater with unique toxins, such as traces of halogenated organic compounds (HOCs) can be selectively biodegraded.

23.4.1 Photocatalysis

Photocatalysis can be described as a photo- reaction that is accelerated by a catalyst present. When a semiconductor photocatalyst is irradiated photons whose energy is equal to or huger than its band difference, electrons are excited from the valence band to the conductive band, leaving positively charged gaps in the valence band, resulting in a splitting of the charge. Using electron acceptors such as O_2 adsorbed on the catalyst surface, the photo generated electrons can react or dissolve in water to give O^{2-} • radicals. Photocatalysts either accept an electron or migrate the charge to another substrate to quench the excited state. Photocatalysis effectiveness varies on how well one can inhibit recombination of this charge. The use of photocatalysis for the wastewater management has been of great interest. Several kinds of nanoparticles, including TiO_2, ZnO, CdS, andWO_3, have been researched as photocatalysts until now (Ahmed and Haider, 2018). There are many ways to enhance the catalysts dependent on TiO_2. TiO_2 sensitization with a second dimension to improve activity and transfer the wavelength of irradiation to the visible region is an enthusiastically sought goal (Mondal and Sharma, 2014). There are several ways to accomplish this goal, including doping TiO_2 nanomaterials with other elements, combining two semiconductor structures, organic-inorganic nanostructured composites, and nanocrystalline film dye sensitization.

The primary process in photocatalysis is given by as follows (Baruah et al., 2012)

$$MO + h\nu \rightarrow MO(e^- + h^+)$$

where MO symbolizes a metal oxide photocatalyst similar to TiO_2, ZnO etc. Photo-induced electrons lead to the development of superoxide anions ($\cdot O^{2-}$),

hydrogenperoxide molecules (H_2O_2), hydroxyl radicals (·OH), hydrogen dioxide anion (HO_2^-) and the hydroperoxy radicals (·HO_2)

$$MO(e^-) + O_2 \rightarrow MO + \cdot O_2^-,$$

$$MO(e^-) + \cdot O_2^- + 2H^+ \rightarrow MO + H_2O_2,$$

$$MO(e-) + H_2O_2 \rightarrow MO + \cdot OH + OH^-,$$

$$\cdot O_2^- + H_2O_2 \rightarrow \cdot OH + OH^- + O_2,$$

$$\cdot O_2^- + H^+ \rightarrow \cdot OH_2,$$

$$MO(e^-) + \cdot OH_2 \rightarrow MO + HO_2^-,$$

$$HO_2^- + H^+ \rightarrow H_2O_2,$$

$$2 \cdot OH_2 \rightarrow O_2 + H_2O_2.$$

While the oxidation reactions started by the photogenerated holes are:

$$MO(h^+) + H_2O \rightarrow MO + \cdot OH + H^+,$$

$$MO(h^+) + H_2O \rightarrow MO + \cdot OH + H^+,$$

$$MO(h^+) + OH^- \rightarrow MO + \cdot OH.$$

The reactions are finished as:

$$\cdot OH + H^+ + 2e^- \rightarrow H_2O,$$

$$1/2O_2 + 2H^+ + 2e^- \rightarrow H_2O.$$

Nano-sized TiO_2 is an excellent candidate for a multipurpose photocatalyst due to its optical properties, including a high refractive index resulting in shielding strength and whiteness, as well as chemical stability, relatively low cost of production and high performance. In the case of photodegradation, one of the most important subjects is the enhancement of the interface charge-transfer reaction. This can be achieved by implanting, doping and depositing into the structure of TiO_2 suitable transition metal ions, noble metals, semiconductor metal oxides, or nonmetal ions. The industrial scale use of nanoparticles, such as TiO_2 and ZnO in water purification process poses challenges due to problems in their separation and rescue after treatment. Moreover, the use of both metal oxide nanoparticles for water treatment has some drawbacks, such as, greater colloidal stability in aqueous solution, agglomeration of nanomaterials at high concentrations, and difficulty in separating and recovering the nanomaterial after usage. Nevertheless, steps were taken to overcome those shortcomings.

Those include doping and co-doping nanomaterials from metal oxide, and immobilizing nanomaterials on suitable mattresses. The appropriate substrate could act as a help to resolve the post-separation and recovery difficulties. In addition, supporting nano-sized semiconductor materials on matrices may help increase their behavior as opposed to ordinary nanomaterials. Numerous clay matrices such as kaolinite, montmorillonite, and bentonite have been used as support in this regard successfully (Chong et al., 2010). TiO_2 and ZnO nanoparticles immobilizing and anchoring on the clay mineral surface creates more active surface sites, decreases nanoparticles agglomeration and prevents the release of nanoparticles into the surrounding environment. Clay nanocomposites have become major components of clay with metallic nanoparticles used in recent time in addressing contaminants from the environment.

Water purification agents should be able to eliminate not only chemical contaminants, but also microbial pollutants such as bacteria, fungus, virus, molds, etc. Photocatalytic inactivation of microorganisms is a dynamic process and the inactivation rate varies with the form, concentration and physiological state of the microbes. The existence, composition, concentration and condition (slurry or immobilized) of the catalyst content can have a significant effect on the microbial inactivation rate. *Escherichia coli* (*E. coli*), which causes diarrhea, has been extensively studied for optimizing photocatalytic processes as well as for testing newly designed photo reactors among the different bacterial species.

23.4.2 Catalytic ozonation

Ozone is the most active organic oxidant required for treating water. Ozonation implementation started with drinking water treatment in the early 1990s, has expanded around the world and is that today in the area of industrial wastewater treatment. In this region, full-scale plants use ozone treatment to recover marina aquaria waters, obtain cyanides in the metal finishing industry, to reuse washwaters in the production of electronics, to reduce color and surfactant concentrations in wastewater from textile dyeing plants, to dissolve phenols oxydrocarbons in wastewater petroleum refinery, and remove COD in wastewater chemicals (Kasprzyk-Hordern et al., 2003). If dissolved in water, ozone can react in two ways to other organic compounds mainly by direct reaction with molecular ozone or by the creation of secondary oxidants with indirect reaction to the formation of free radical species. On action, both processes can occur depending on the chemical composition of the emissions from water. Because of its high reactivity, treatment lines for agricultural wastewaters usually require ozone after biological treatment as an end solution for significant COD elimination.

23.4.3 Advanced oxidation processes

Advanced oxidation processes (AOPs) are other alternative methods for treating wastewater and can degrade organic bioactive chemicals. AOPs usually work with less energy consumption than direct oxidation. AOPs are similar to atmospheric temperature and water treatment methods requiring adequate concentrations of hydroxyl radicals to impact water purification (Fig. 23.2).

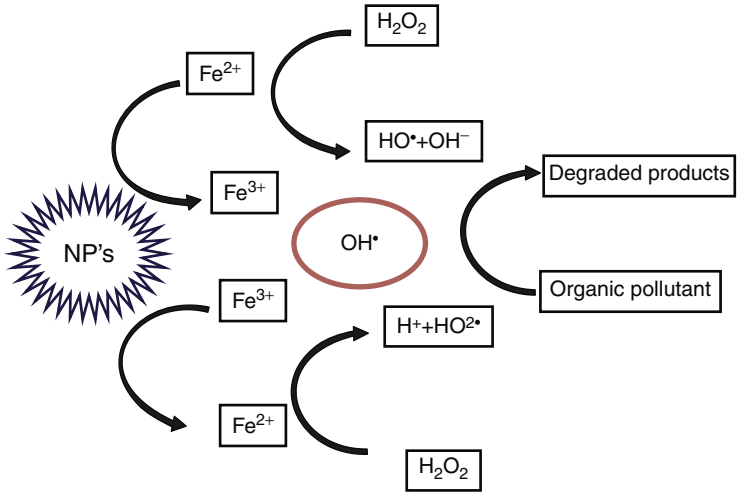

FIG. 23.2 Advance oxidation process.

The hydroxyl radicals are highly reactive species, which typically targets the majority of organic molecules with rate constants in the range of 10^6–10^9 L mole^{-1}s^{-1}. Further improving the flexibility of AOPs is the fact that they provide various potential ways for radical hydroxyl development, thereby allowing greater compliance with the particular treatment needs. The hydroxyl radical is the second strongest oxidant followed by fluorine, and it interacts 10^6–10^{12} times faster than ozone depending on the substrate to be treated. AOPs are categorized by reactive (homogenous and heterogeneous) or hydroxyl radical (chemical, electrochemical, sonochemical, and photochemical) methods. Identification of traditional AOPs depends on the source used for hydroxyl radical production. It introduces the processes involving a combination typical and nonconventional AOPs such as photo-electro-Fenton and sonoelectro-Fenton (Bethi et al., 2016). Pulsed plasma, ionizing radiation, and microwaves methods are the main example of the nonconventional AOPs. Additionally, solar-irradiated technologies are being researched to reduce the costs involved with the use of energy from nonnatural sources. Nanoparticles display a higher catalytic activity compared with their micro sized counterparts. The benefit of using nanoparticles as catalysts for Fenton-like reactions would more than outweigh the downside of accelerating the reaction by allowing UV radiation (Oliveira et al., 2012).

23.5 Nano biocides

While the methods of disinfection commonly used in drinking water treatment can effectively disinfect microbial pathogens, study in recent decades has uncovered a problem between successful disinfection and the creation of dangerous by-products

of disinfection (DBP). Chemical disinfectants widely used by the water industry such as free chlorine, chloramines, and ozone can interact with natural water to form DBPs with different components, many of which are carcinogens. It reported more than 600 DBPs in the literature. Given the DBP formation processes, it was expected that DBPs would be formed while chemical oxidants are used in water treatment (Richardson and Kimura, 2016). Due to its large specific surface area and high reactivity, nanomaterials are excellent adsorbents, catalysts and sensors. In a recent report, numerous natural and engineered nanomaterials such as chitosan, silver nanoparticles, photocatalytic TiO_2, fulllerol, aqueous fullerene nanoparticles, and carbon nanotubes, have been shown to be strong antimicrobial properties. Such antimicrobial nanomaterials, unlike traditional chemical disinfectants, are not heavy oxidants, and are relatively inert in soil. Therefore, it is not anticipated that they would contain harmful DBPs. We have the ability to substitute or improve traditional disinfection approaches if properly integrated into treatment processes. Nanoparticles exert antimicrobial action using a multitude of mechanisms that can vary with individual properties such as size, morphology, electrical charge, surface coatings, etc. empowering scientists to devise novel antimicrobial composite agents for different applications. The antimicrobial activity, especially of heavy metal nanoparticles and carbon-based nanoparticles can provide a solution to the current challenges of antimicrobial resistance to traditional methods of treatment.

23.5.1 Antimicrobial peptides and chitosan

Chitin and other peptides, which exist naturally, have long been known for their antimicrobial properties. It is only recently that nanoparticles were engineered with these materials. They are promising for applications for low-cost and low-tech disinfections, especially in developing countries. Antimicrobial peptides were initially synthesized based on recognizing protein structures. The ability to synthesize these peptides enables creating tailor-made antimicrobial nanostructures. Engineered peptides are engineered for different antimicrobial uses in terms of duration, composition, coatings, derivatization, and other properties. Chitosan, obtained from chitin in arthropod shells, has previously been reported for its antibacterial activity; this polymer has only been converted into nanoparticles more recently (Hossain et al., 2014). As well as its relatives, nano-scale chitosan exhibits antimicrobial activity against bacteria, viruses and fungi. Chitosan inhibits bacteriophage replication in bacteria, and causes plant resistance to viral diseases. Depending on the organism, pH, molecular weight, degree of polymerisation, and presence of lipids and proteins, a wide range of minimum inhibitory concentrations (MICs) were recorded from 18 to 5000 ppm.

23.5.2 Silver nanoparticle

Because of their unique properties, silver nanoparticles have been widely used for different applications which facilitate numerous antimicrobial applications. This has been demonstrated that both chemically synthesized and biosynthesized silver nanoparticles inhibit Gram negative and Gram positive bacteria, as well as yeasts

(Marambio-Jones and Hoek, 2010). Stronger antimicrobial activity has been demonstrated against Gram negative bacteria and can be due to Gram positive bacteria's thicker cell wall composition. The bactericidal activity of silver NPs is attributed to a variety of pathways.

23.5.3 Titanium oxide nanoparticles

It is well known that TiO_2NPs have antimicrobial activity against both Gram negative and Gram positive bacteria. Increased bactericidal behavior results in further alteration of the TiO_2NPs with plant extracts. In conjunction with the endogenous antimicrobial activity and photo catalytic function the antimicrobial nature of plant extracts enhances the ability of TiO_2NPs as microbicidal agents (Pelaez et al., 2012). Because of its photocatalytic character, TiO_2 NPs can kill microorganisms in the presence of light. TiO2NPs-generated, reactive oxygen species will oxidize the cell membrane components contributing to degradation. TiO_2 antimicrobial activity observed in the absence of light suggests that apart from photocatalytic activity, direct contact and adsorption of cells onto TiO_2 nanoparticles that result in a loss of membrane integrity.

23.5.4 Carbon nanostructures

Fullerene, carbon nanotubes (CNTs), graphene and diamond-like carbon (DLC) are the example of carbon nanostructures (CNSs), have significant broad-spectrum bactericidal properties. There is a complex process by which CNSs induce bacterial lysis. Fullerene causes degradation of the cell membrane, damage to DNA and inhibits the mitochondrial energy pathways to inactivate microorganisms (Al-Jumaili *et al*., 2017). It also has photochemical activity that leads to antimicrobial activity by producing ROS upon exposure to light. According to recent research, single and multiwalled Carbon nanotubes have a stronger antimicrobial function than fullerenes. Antimicrobial efficacy of CNTs varies in length, diameter, residual catalyst, electronic structure, functional surface group, surface chemistry, and coatings (Maleki Dizaj et al., 2015). During antimicrobial activity, CNTs having a length of more than 50 μm can wrap around the bacterial cell. Long nanotube aggregates in liquid media are known to be more bioactive and have powerful antibiofilm activity, especially during the early stage of biofilm formation. Carbon nanostructures can cause physical abrasions and structural damage to the walls and membranes of bacterial cells. Several types of graphene nanoparticles were documented, including nanosheets of graphene oxide (GO), reduced graphene oxide, graphite, and graphene. GO is usually highly antibacterial (Perreault et al., 2015). The antimicrobial mechanisms and behavior are affected by numerous factors, including sheet sizes, layer number, nanopores, shapes and the presence of functional groups. Chemical interactions between the nanomaterial and the bacterial cell surface will lead to reactive oxygen species production. The transfer of electrons from the microbial surface into the carbon nanomaterial is also suggested as a source of oxidative stress that is independent of ROS.

23.6 Future prospect

The world faces daunting challenges in meeting growing demands for clean water as fresh water sources are steadily depleting with increasing population. Nanomaterials have numerous substantial features which make them exclusively attractive for water decontamination as separation media. They have much higher surface areas than particles in bulk and have a high potential / selectivity in aqueous solutions for hazardous substances. These developments range from the direct application of synthesized nanoparticles as adsorbents for extracting harmful contaminants, or as catalysts for oxidizing and breaking down noxious pollutants in wastewater, to the incorporation of nanoparticles into traditional treatment technologies, such as the photocatalytic composite membrane that incorporates separation technology with photocatalytics. As growing amounts of nanomaterials are manufactured and used water treatment, these substances are also increasingly likely to find their way into the potable water supply. While the risks associated with nanomaterials remain largely unknown, aggressive steps are being taken to recognize the potential to extract engineered nanomaterials in our existing treatment technologies. This includes a deeper understanding of the processes that control the transport of nanomaterials in both natural and engineered systems. Recent studies discuss the transport of nanomaterials in porous media, the aggregation of nanoparticles and the chemical processing of nanomaterials during water and wastewater treatment. Potential nanomaterial risk assessment is the subject of many articles suggesting toxicity of nanomaterials. Such aspects of nanomaterial applications, risk assessment and risk control cover the full spectrum of environmental nanotechnology topics, and highlight the new technology development. Technological progress will lead to an ever-expanding range of innovative approaches to address our water management problems, even generating new challenges for themselves. The environmental engineering community's current efforts to use nanomaterials responsibly to develop new technologies while monitoring over their future impacts should serve as a blueprint for a pragmatic approach to analyzing emerging technologies and placing them on a path to sustainability.

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CHAPTER

24 Photocatalytic removal of emerging contaminants in water and wastewater treatments: a review

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24.1 Introduction

Water scarcity is nowadays one of the major global concerns. Attempts have been done in order to convert wastewater into water that can be reused for other purposes. However, traditional methods are not suitable for water reclamation as not all contaminants present in wastewater are easily removed. A group of contaminants that have raise researchers' attention are emerging contaminants (ECs). ECs are synthetic or naturally occurring chemicals, and their transformation products, or any microorganisms (virus as SARS-CoV-2 could be included) which are not commonly monitored in the environment but have a high potential to enter the environment causing known or suspected harmful effects on human health and ecosystems (Rosenfeld and Feng, 2011; Yap et al., 2019). ECs are commonly present in wastewater, surface water, ground water, and drinking water at trace concentration levels ranging from ng/L to mg/L. ECs include pharmaceuticals and personal care products (PPCPs), endocrine disrupting chemicals (EDCs), perfluorinated compounds (PFCs), surfactants, pesticides, flame retardants, industrial additives and viruses such as human polyomaviruses, hepatitis E virus, and human adenoviruses (Ahmed et al., 2017; Philippe et al., 2016; Rosenfeld and Feng, 2011; Zhao et al., 2018). ECs are biologically active compounds that pose great risks to human health and natural ecosystems mainly due to their recalcitrance, low biodegradability and short- and long-term toxicities. ECs may cause ecological risk such as interference with the normal endocrine functions of living organisms, microbiological resistance, and bioaccumulation. ECs tend to accumulate in lipid-rich tissues being active across the food chain (Abdel-Maksoud et al., 2018; Arfanis et al., 2017; Mirzaei et al., 2016).

Current treatment technologies for ECs include biological processes, chemical, or physical treatments. ECs removal will depend on their physicochemical properties,

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biological persistency and operational conditions. Physical processes as adsorption, filtration or reverse osmosis, have shown to be unable to break down ECs and only transfer the pollutants from one phase to another. In addition, regardless biological oxidation being the most widely used for ECs removal and one of the most advantageous technologies to cope with wastewater remediation, some ECs can inhibit biodegradation owing to their toxicity and microbial growth resistance (Ahmed et al., 2017; Mirzaei et al., 2016; Zhao et al., 2018). From this perspective, advanced oxidation processes (AOPs) such as ozonation, Fenton oxidation, electrochemical degradation, photolysis and photocatalytic processes can effectively eliminate ECs avoiding the production of secondary waste in the environment. AOPs are based on the generation of reactive oxygen species (ROS) particularly hydroxyl radical (OH•) which are highly reactive and non-selective, able to oxidize pollutants into less harmful and more biodegradable compounds, even some organic compounds are fully oxidized into carbon dioxide (CO_2) and water (H_2O) (Arfanis et al., 2017; Fast et al., 2017; Mirzaei et al., 2016; Yap et al., 2019).

Among AOPs, photocatalytic processes attracted considerable attention due to its non-toxicity, high stability, lack of mass transfer limitation, and operation at ambient temperature (Lofrano et al., 2017; Mirzaei et al., 2016). Photocatalysis is the interaction between a semiconductor and light source to produce ROS that can inactivate microorganisms and transform pollutants. Photocatalytic oxidation is initiated upon UV illumination of a semiconductor catalyst, anyhow using sunlight radiation as the light source would significantly reduce electric power required and therefore water treatment costs. Its main drawbacks are catalyst fouling and recovery; which can be overcome by doping or immobilization. The main photocatalysts include single metal oxides as titanium dioxide (TiO_2), zinc oxide (ZnO), zirconia (ZrO_2) iron (III) oxide (Fe_2O_3), vanadium (V) oxide (V_2O_5) and tungsten trioxide (WO_3); a combination of them or combined with graphene oxide (GO) or carbon nanotubes (CNT) (Aoudj et al., 2019; Fast et al., 2017; Gomes et al., 2019).

This chapter compiles some of the most relevant knowledge about photocatalytic processes in their application for the removal of emerging contaminants in wastewater treatment. Photocatalysis mechanisms will be assessed (Section 24.2) considering the most important aspects for the performance of the process (Section 24.3). The most common photocatalysts will be analyzed giving special attention to TiO_2 and ZnO (Section 24.4), as well as the different strategies for improving photocatalysis processes (Section 24.5). Finally, wastewater treatment applications (Section 24.6) and the future challenges of this technology (Section 24.7) will be reviewed.

24.2 Photocatalysis mechanisms

Photocatalytic reactions are initiated through the excitation of a semiconductor photocatalyst (SP) by irradiation of photons with an equal or higher amount of energy than its band gap (Fig. 24.1). The photo-generated electrons in the conduction band excite electrons from the valence band to the conduction band producing holes (h^+)

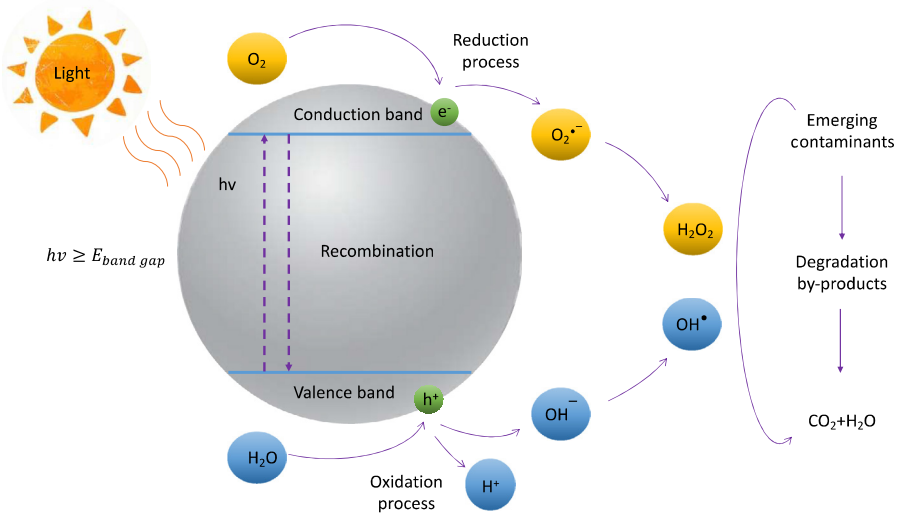

FIG. 24.1 Photocatalysis mechanism for emerging contaminants removal. Source: own elaboration based on Nguyen et al. (2020).

in the valence band (Eq. 24.1). The produced electron holes can directly oxidize organic matters or react with either water or hydroxyl ions to generate hydroxyl radicals ($OH^\bullet$) which are strong oxidants, highly reactive, and nonselective (Eqs. 24.2–24.3). The conduction band electron can reduce dissolved oxygen species to form superoxide radical anions (Eq. 24.4). Then, superoxide radical anions can react with water to produce hydrogen peroxide and hydroxyl ions (Eq. 24.5). In addition, further hydroxyl radicals and hydroxyl ions are generated by the cleavage of hydrogen peroxide (Eq. 24.6) (Lofrano et al., 2017; Mirzaei et al., 2016; Nguyen et al., 2020).

$$SP + hv \rightarrow SP(e^- + h^+) \tag{24.1}$$

$$SP(h^+) + H_2O \rightarrow H^+ + OH^\bullet \tag{24.2}$$

$$SP(h^+) + OH^- \rightarrow OH^\bullet \tag{24.3}$$

$$SP(e^-) + O_2 \rightarrow O_2^{\bullet -} \tag{24.4}$$

$$O_2^{\bullet -} + H_2O + H^+ \rightarrow H_2O_2 + OH^- \tag{24.5}$$

$$H_2O_2 + e^- \rightarrow OH^\bullet + OH^- \tag{24.6}$$

Photocatalytic degradation of organic substances such as EC can be achieved directly by electron transfer between the pollutant and the positive holes or indirectly via oxidizing species generation. In real wastewater, some other species such as Cl–, HCO_3–, CO_3^{2}– and/or SO_4^{2}– are present, which can be reduced and produce radicals improving the degradation of pollutants. In addition, several authors have

described the recombination of photo-generated electrons and holes causing a pread-sorption of substrate onto the photocatalyst enhancing the photocatalytic degradation (Aoudj et al., 2019; Gomes et al., 2019; Lofrano et al., 2017; Nguyen et al., 2020).

24.3 Impact of operating and process parameters

The efficiency of ECs photocatalytic degradation strongly depends on certain para meters, including pH, light source, contaminant concentration, presence of oxidants, presence of ions, dissolved oxygen, temperature, catalyst characteristic and catalyst concentration. The following section briefly presents the impact of these parameters.

24.3.1 pH

pH is one of the most significant operating parameters in ECs photocatalytic degradation. It plays a crucial role in the size of catalyst aggregates, the surface charge properties of the catalyst, the adsorption of organic pollutants on the catalyst surface, the position of conduction and valence bands, as well as the ionic forms of the pollutants, the hydrophobicity, and the amount of generated hydroxyl radicals and other oxidants (ClO^-/HClO, O_3, H_2O_2 and $S_2O_8^{-2}$) (Ahmed and Haider, 2018; Aoudj et al., 2019; Mirzaei et al., 2016; Nguyen et al., 2020; Zhao et al., 2018).

Regarding to the surface charge properties and particle size of the catalyst, the zero-point charge (ZPC) is the pH at which the catalyst surface is globally neutral, consequently the electrostatic attraction between the photocatalyst particles and water pollutants is minimal. Below ZPC value, the catalyst surface is positively charged and exerts an electrostatic force towards the negatively charged compounds. In contrast, beyond this value, catalyst surface is negatively charged and repels the anionic compounds. Additionally, particle size of the catalyst becomes larger when pH is close to ZPC on account of zero surface charge which impedes the interactive rejection needed to separate the particles (Ahmed and Haider, 2018; Nguyen et al., 2020; Zhao et al., 2018).

As an example, the ZPC of TiO_2 can be found in the pH range of 4.5 to 7.0 as reported by many authors. Several researchers have observed different results about the effect of pH on the photocatalytic degradation of ECs using TiO_2 as photocatalyst. Chinnaiyan et al. (2019) worked with a synthetic hospital wastewater containing amoxicillin (AMX) and metformin (MTF) on a pH range of 3 to 11, and an increase in pharmaceuticals removal was observed as pH increase. Similarly, Zúñiga-Benítez et al. (2016) evaluated benzophenone-3 removal in the pH range from 3 to 9 and results portrays an increase in compound removal percentage by increasing the pH. Likewise, Delnavaz et al. (2015) observed a highest removal efficiency at pH of 9 to 12 on phenol degradation in pH range of 4 to 12. Although, Cai and Hu, (2017) investigated sulfamethoxazole (SMX) and trimethoprim (TMP) degradation with four pH conditions (3, 5, 7 and 9), and their results showed an easier decomposition of SMX in acidic condition, while for TMP the effect of pH was no significant. In addition, Ounnar et al. (2016) performed over the pH range 2.85 to 9.92 the degradation of

spiramycin macrolide (SPM) obtaining a maximum SPM removal at pH values of 6.09 and 8. This discrepancy on the optimum pH might be a function of other operational parameters that influence the photocatalytic process. However, there is a tendency showing a better performance of the photocatalytic process at high pH values.

24.3.2 Light source

Light source has a significant effect on the photocatalytic reaction rate according to both the wavelength and light intensity, which are affected by the type of photocatalysts used. As for instance, the photoactive phase of TiO_2 is only activated under UV radiation, which only represents the 5% of solar spectrum. In this sense, in order to use solar light to reduce operational costs, photocatalysts research has been focused on improving the photocatalytic response of TiO_2 and other semiconductors to visible light. Some of the developed approaches include doping the semiconductors with metal or nonmetal compounds (Ahmed and Haider, 2018; Belver et al., 2020; Zhao et al., 2018).

Ghosh et al. (2018) studied the photocatalytic degradation of acesulfame K (ACK), an artificial sweetener, with TiO_2 photocatalyst using a solar simulator. By using five different light intensities, their goal was to find a correlation between light intensity and ACK degradation rate. Results showed that as light intensity increased (20 to 100 mW/cm^2), degradation rate increases too (10 to 35 mg/L min). Similarly, Oseghe and Ofomaja, (2018) evaluated the photocatalytic performance of carbon modified TiO_2 under five different light levels for tetracycline hydrochloride degradation. The intensities were classified into Level 1, Level 2, Level 3, Level 4 and Level 5 with their corresponding units at 5. 64, 27.06, 46.00, 61.6, and 76.4 W/m^2 respectively. An increase in degradation rate was observed as light levels increased up to level 3. However, from level 4 light intensity might have been too high, hence promoting high electron-hole recombination which slows degradation rate. In addition, an inverse relationship between emission wavelength and degradation rate was observed.

24.3.3 Contaminant concentration

Contaminant concentration is an important factor that affects photocatalytic efficiency, kinetics removal and optimum catalyst dosage. In general, there is a consensus among researchers on the inverse relationship between contaminant concentration and degradation rate. Low contaminants concentration favor high yields of photocatalytic processes as there are sufficient amounts of radicals and holes for degradation to occur. While, degradation removal is diminished at high contaminant concentration as catalyst surface will be saturated by the contaminant and its intermediates, reducing the generation of oxidizing ROS since there are fewer active sites for the adsorption of H_2O, OH^-, and O species onto the catalyst. In addition, an increase in the initial concentration of contaminants will demand a prolonged irradiation time increasing operational costs (Ahmed and Haider, 2018; Aoudj et al., 2019; Cai and Hu, 2017; Mirzaei et al., 2016; Nguyen et al., 2020).

Choina et al. (2015) observed a higher adsorption of tetracycline and ibuprofen to ZnO nanoparticles when using low contaminant concentration. Likewise, Pirilä et al. (2015) determined that degradation efficiency decreases when increasing the pollutant concentration while working with TiO_2 in the degradation of diuron, p-coumaric acid, bisphenol A and phthalic anhydride. As well, using TiO_2 as catalyst, Cai and Hu (2017) observed that the time required for the maximum degradation of sulfamethoxazole and trimethoprim depends on their initial concentration; the final removal rates of both antibiotics decreased with higher initial concentrations. Similarly, spiramycin macrolide maximum degradation with TiO_2 was observed at low concentrations (Ounnar et al., 2016). Due to the importance of adsorption in the photocatalytic process Ounnar et al. (2016) suggested a three step reaction mechanism for photocatalysis kinetic model which includes adsorption, chemical reaction and desorption.

24.3.4 Presence of oxidants

The addition of external oxidants could assist photocatalytic degradation. Hydrogen peroxide (H_2O_2) is the most common oxidant used in photocatalytic processes. H_2O_2 has proved to increase the removal efficiency of organic pollutants by three mechanisms: reducing the electron-hole recombination, generating other oxidizing species and contributing to the generation of powerful hydroxyl radicals (Aoudj et al., 2019). Several researches on EC degradation by photocatalytic processes have concluded that contaminant degradation efficiency is enhanced with the increase of H_2O_2 concentration until a certain point. However, an excess addition of H_2O_2 may be detrimental to the process as H_2O_2 may act as hydroxyl radicals and holes scavenger (Cai and Hu, 2017; Mirzaei et al., 2016).

Many authors have reported the enhancement of TiO_2 photocatalysis with the addition of H_2O_2. Cai and Hu, (2017) observed a higher sulfamethoxazole and trimethoprim removal when a small amount of H_2O_2 (332.9 ppm) was added into the system. Similarly, Zúñiga-Benítez et al. (2016) reported a boost in benzophenone-3 degradation by increasing H_2O_2 concentration up to an optimal concentration of 128.1 mg/L. Both researches remark that the excess of H_2O_2 scavenges the hydroxyl radicals generated by photocatalytic reactions and form hydroperoxyl radical which is a much weaker oxidant (Cai and Hu, 2017; Zhao et al., 2018; Zúñiga-Benítez et al., 2016).

Regarding to other types of oxidants, Eskandarloo et al. (2014) proved that inorganic oxidants (HSO_5^-, IO_4^-, ClO_3^-, $S_2O_8^{2-}$, H_2O_2, and BrO_3^-) have a positive effect on the photocatalytic degradation rate of acid Fuchsin, a triphenylmethane dye pollutant, by using TiO2/NiO coupled nanoparticles. Likewise, Eskandarloo et al. (2016) studied the influence of various oxidants including hydrogen peroxide, peroxymonosulfate, peroxydisulfate, and periodate for phenazopyridine degradation. The optimum concentration of oxidants to obtain phenazopyridine degradation as higher as 90% were 0.61 g/L of H_2O_2, 1.12 g/L of $S_2O_8^{2-}$, 0.46 g/L of HSO_5^- and 0.68 g/L of IO_4^-. This research determined that all of the employed oxidants

have a positive influence on the sonocatalytic activity of samarium doped ZnO nanoparticles.

24.3.5 Presence of ions

The presence of ions in water has a significant impact on the effectiveness of photocatalytic processes. They can improve the efficiency of organic contaminants degradation due to the generation of highly reactive radical species. However, at high concentrations beyond the optimum value they have a detrimental effect on the photocatalytic process acting as electron scavengers (Eskandarloo et al., 2016, 2014; Mirzaei et al., 2016).

Radical species react with organic molecules, mainly by three different ways: hydrogen abstracting from saturated carbon, hydrogen addition to unsaturated or aromatic hydrocarbons, and electron removing from anion. Radical species improve the photocatalytic reaction by reducing electron-holes recombination. In addition, they initiate the production of highly reactive hydroxyl radicals (Eskandarloo et al., 2016, 2014; Mirzaei et al., 2016).

The most common ions found in water are chloride, bicarbonate and sulfate. Bicarbonate ions absorb light energy and act as radical scavengers decreasing the rate of degradation (Eq. 24.7).

$$CO_3^{2-} + OH^{\bullet} \rightarrow CO_3^{\bullet -} + OH^- \tag{24.7}$$

Chloride ions act as hydroxyl radical (Eq. 24.8) and holes (Eq. 24.9) scavenger which inhibit the removal of contaminants.

$$Cl^- + OH^{\bullet} \rightarrow Cl^{\bullet} + OH^- \tag{24.8}$$

$$Cl^- + h^+ \rightarrow Cl \tag{24.9}$$

Sulfate ions also can inhibit the photocatalytic degradation trapping holes (Eq. 24.10) and hydroxyl radical (Eq. 24.11). In addition, organic contaminants degradation decrease owing to the reaction with sulfate ions formed on the catalyst surface which contribute to the deactivation of catalyst sites (Eskandarloo et al., 2016, 2014; Mirzaei et al., 2016; Saadati et al., 2016).

$$SO_4^{2-} + h^+ \rightarrow SO_4^{\bullet} \tag{24.10}$$

$$SO_4^{2-} + OH^{\bullet} \rightarrow SO_4^{\bullet -} + OH^- \tag{24.11}$$

Sodium chloride, sodium phosphate, sodium sulfate or surfactants are usually present in wastewater. The presence of these salts inhibits photocatalytic degradation on account of the competitive reaction of ions with the generated holes on the surface of the catalyst. Surfactants affect contaminant degradation due to the preferential adsorption of the cationic or anionic surfactant molecules on the catalyst surface (Eskandarloo et al., 2016, 2014; Mirzaei et al., 2016; Saadati et al., 2016).

Eskandarloo et al. (2014) analyzed the effects of inorganic anions (CO_3^{2-}, NO_3^-, Cl^-, $H_2PO_4^-$, and SO_4^{2-}), and transition-metal ions (Co^{2+}, Zn^{2+}, Fe^{2+}, Cu^{2+}, Ni^{2+},

and Mn^{2+}) on the photocatalytic degradation of acid fuchsin (AF) dye by using TiO_2/NiO coupled nanoparticles. Results showed that transition-metal ions (2 to 10 mg/L) have a positive effect on the photocatalytic degradation rate of AF, while with the increasing concentration of inorganic anions (0.1 to 1 g/L), the photocatalytic degradation of AF becomes slower. Likewise, Kanakaraju et al. (2015) studied the effect of water matrix, anions and diclofenac on the degradation rate of naproxen (NPX) by using TiO_2 photocatalysis. NPX degradation rate was reduced in river water spiked with phosphate and chloride ions. However, the addition of chloride to drinking water enhanced NPX degradation rate.

24.3.6 Dissolved oxygen

Dissolved oxygen (DO) was found to be a key parameter in photocatalytic degradation as it contributes to the stabilization of radical intermediates, direct photocatalytic reactions and mineralization of contaminants. DO may induce the cleavage mechanism for aromatic rings in organic pollutant. As well, it acts as an electron scavenger, trapping photogenerated electrons preventing charge carrier recombination. This enable the formation of superoxide and ROS. Furthermore, DO supplies the necessary force to have an adequate suspension of catalyst particles in photocatalytic reactors (Ahmed and Haider, 2018; Fotiou et al., 2015; Malato et al., 2016).

Fotiou et al. (2015) using a TiO_2 photocatalyst investigated the degradation of cyanobacterial toxin microcystin-LR and off-odor causing compounds (geosmin, 2-methylisoborneol) under air (2.5×10^{-4} M of O_2), oxygen saturated (1.2×10^{-3} M of O_2) and nitrogen (0 M of O_2) atmosphere. Results showed a more efficient degradation as the concentration of DO increases in the solution. Likewise, López-Serna et al. (2017) demonstrated that the quantum efficiency of a reaction is highly related to the DO content, by using TIO_2 for the photocatalytic degradation of bisphenol A. This research emphasizes the importance of measuring and maintaining DO concentration in order to have a complete mineralization.

24.3.7 Temperature

Photocatalytic reaction rate is strongly dependent on temperature. High temperatures above 80°C have been found to decrease the adsorption of reactants and benefit charge carrier recombination. Additionally, at high temperatures the oxygen concentration in water decreases. While, it has been observed that low temperatures increase the activation energy limiting final reaction products desorption. Hence, optimum reaction temperature shall be in the range of 20°C to 80°C (Ahmed and Haider, 2018; Malato et al., 2016).

Oseghe and Ofomaja, (2018) observed a higher degradation rate for tetracycline hydrochloride due to photocatalytic and thermal decomposition when temperature increased from ≤ 30°C to 35°C. Likewise, Baalbaki et al. (2017) determined that naproxen, ibuprofen and carbamazepine require the effect of light and temperature combined to have a significant degradation. These researches proved that temperature play an important role in improving thermal degradation.

24.3.8 Catalyst characteristic

In order to achieve an adequate conversion and selectivity, it is important to control the morphology and surface properties of the catalysts. Catalyst characteristics, such as shape, size, structure, and surface area have a significant impact on the photocatalytic performance owing to the number of active facets, distinct active sites, and associated adsorption–desorption ability to reactant (Ahmed and Haider, 2018; Nguyen et al., 2020).

Particle size, morphology, porosity, crystallinity and oxygen vacancy are the most important characteristic for a catalyst. Smaller particles are more active than larger ones due to increased specific surface area; the contact area between the reactants and the photocatalyst affects the rate of reaction. In addition, nanoparticles have more oxygen vacancies on the surface enhancing the production of unpaired electrons which acts as donor and change the tendency of O_2 and H_2O adsorption on the catalyst surface (Ahmed and Haider, 2018; Choina et al., 2015; Mirzaei et al., 2016; Nguyen et al., 2020).

Nanomaterial catalysis have demonstrated high efficiency on ECs removal due to larger surface area, smaller size and more active sites. Different catalyst structures have been studied such as nanowires, nanorods, nanosheets, nanofibers, nanoparticles, among others. Rokhsat and Akhavan, (2016) studied methylene blue dye photocatalytic degradation with a ZnO nanorod film acquiring 90% of degradation; Zhu et al. (2017) used Fe_3O_4@Bi_2O_3–RGO photocatalyst nanocomposites to achieve 98.3% of ciprofloxacin degradation; Choina et al. (2015) consider ZnO nanoparticles for tetracycline and ibuprofen removal obtaining 85% degradation. Each one of these researches agree that nanocomposites are promising catalysts for ECs photocatalytic degradation in wastewater treatment.

24.3.9 Catalyst concentration

Catalyst loading will have a great impact on the photocatalytic process efficiency. In addition, the relatively high cost of the catalyst and its separation from water after treatment makes catalyst dosage an important parameter to consider. The increase of catalyst dosage offers a larger number of active sites and a higher electron-hole formation leading to boosted hydroxyl and superoxide radicals production, which facilitate the degradation of contaminants (Ahmed and Haider, 2018; Mirzaei et al., 2016; Nguyen et al., 2020).

It has been observed that the reaction rate and removal efficiency of the process has a direct relationship with the amount of catalyst used. The increase in the catalyst initial concentration results in a higher pollutant degradation rate, up to a limiting value where the reaction rate becomes independent of the catalyst concentration. This value depends on many factors such as reactor geometry and working conditions (Ahmed and Haider, 2018; Aoudj et al., 2019; Malato et al., 2016). Ounnar et al. (2016) observed that the rate constant of spiramycin macrolide (SPM) degradation on TiO_2 increases with increasing the catalyst dose. However, further increase in TiO_2 dose (>1 g/L) does not improve the SPM degradation. Likewise, benzophenone-3

degradation initially rises by increasing the catalyst concentration. While, when TiO_2 concentration exceeds 1.20 g/L substrate removal decreases (Zúñiga-Benítez et al., 2016). In addition, Pirilä et al. (2015) noted a higher bisphenol A (BPA) removal as TiO_2 initial concentration increases. Although, above a certain level (200 mg/L), the addition of TiO_2 does not affect anymore BPA degradation.

Consequently, the catalyst dose should be carefully adjusted in order to avoid excessive catalyst dosage which will increase turbidity, impede light penetration, shield contaminants from direct radiation and raise operational costs. As well as, catalyst particles agglomeration may decrease the number of surface active sites reducing contaminant removal (Ahmed and Haider, 2018; Aoudj et al., 2019; Malato et al., 2016).

24.4 Common photocatalysts

24.4.1 TiO_2

TiO_2 is the most widely investigated photocatalysts due to its cost effectiveness, earth abundance, photo stability, low-toxicity, and good performance. TiO_2 is considered the most efficient photocatalyst in the removal of bacteria and organic contaminants. As well, it can operate at natural pH, ambient temperature, and pressure (Ahmed et al., 2017; Ahmed and Haider, 2018; Arfanis et al., 2017; Davididou et al., 2017; Philippe et al., 2016). Since the 1970s TiO_2 has been used for environmental purposes. However, the application of TiO_2 on emerging contaminants photodegradation dates form 2000s (Belver et al., 2020). For instance, Cai and Hu, (2017) obtained 90% removal of sulfamethoxazole (SMX) and trimethoprim (TMP) within 20 min with the initial concentration of 400 ppb for both antibiotics. Ounnar et al. (2016) achieved 98% removal of spiramycin macrolide antibiotic (SPM) determining its optimum conditions at low UV power, small SPM concentrations, natural pH and catalyst dose of 1g/L. Eskandarian et al. (2016) analyzed the photolytic decomposition of acetaminophen (ACT), diclofenac (DCF), ibuprofen (IBP), and sulfamethoxazole (SMX) and determined that the decomposition kinetics followed SMX > DCF > IBP > ACT with removals from 26% to 58% in three hours operation. More research remains to be done as some discordant results have been observed between authors (Table 24.1); N-TiO_2 was used for the removal of methylene blue, Than et al. (2017) obtained 99.4% within 90 min while Liu et al. (2016) after 180 min achieved only 71.1% removal, even though N-TiO_2 was coupled with graphene to improve its performance. Likewise, for the removal of bisphenol A López-Serna et al., 2017 obtained just 50% using visible light after 3 hours while Davididou et al., 2017 achieved 99% in 90 min with UV irradiation.

One of the major drawbacks of TiO_2 is that it can only utilize the UV spectrum. In addition, in real wastewater treatment processes the higher concentration of contaminants and the presence of other ions and oxidants can cause catalyst deactivation, slow kinetics, and low photo-efficiencies. However, these disadvantages can be overcome by coupling with other semiconductors oxides or by doping the catalyst

Table 24.1 Comparative review from the last five years on the application of TiO_2 for the removal of emerging contaminants.

Catalyst	Contaminant	Water matrix	Light source	Irradiation time	Degradation efficiency (%)	pH	References
1 g/L N-TiO_2 C-TiO_2 C,N co-doped TiO_2	100 mg/L 2-chlorophenol	Deionized water	Visible light	30 min	70 80 95	7	(Ananpattarachai et al., 2016)
0.1 and 1 g/L N-doped TiO_2	150 and 900 μg/L Ethyl paraben	Ultrapure water, water spiked with humic acids or bicarbonates, drinking water and secondary treated wastewater	Solar and visible light	120 min	up to 100	3-9	(Petala et al., 2015)
2 g/L Sm-TiO_2 N-TiO_2	50 mg/L 4-Acetamidophenol	Double distilled water	UV and visible light	180 min	60 63	6.8	(Rajoriya et al., 2019)
1 g/L Graphene oxide-TiO_2 composites	100 mg/L Diphenhydramine	Synthetic solution	UV/Vis radiation	60 min	92–94	-	(Pedrosa et al., 2018)
0.5 g/L N-TiO_2	5 mg/L Clopyralid, triclopyr and picloram	Milli-Q water	Black light	180 min	95	4	(Solís et al., 2016)
0.05 g/L TiO_2	400 μg/L Sulfamethoxazole and trimethoprim	Milli-Q water	UVA/LED	20 min	90	5.6	(Cai and Hu, 2017)
0.8 g/L TiO_2/SnO_2	20 mg/L Diclofenac	Synthetic solution	UV irradiation	300 min	90	5	(Mugunthan et al., 2019)

(continued)

Table 24.1 Comparative review from the last five years on the application of TiO_2 for the removal of emerging contaminants. *Continued*

Catalyst	Contaminant	Water matrix	Light source	Irradiation time	Degradation efficiency (%)	pH	References
10 mg TiO_2/SnO_2	10 mg/L Rhodamine B	Synthetic solution	UV irradiation	15 min	100	-	(Yuan et al., 2015)
1 g/L TiO_2	10 mg/L Spiramycin macrolide antibiotic	Synthetic solution	UV irradiation	300 min	98	6.68	(Ounnar et al., 2016)
0.5 g/L TiO_2	20 mg/L Acetaminophen Diclofenac Ibuprofen Sulfamethoxazole	Milli-Q water	UV-LED	3 hours	26 50 35 58	natural pH	(Eskandarian et al., 2016a)
150 mg N-TiO_2	10 mg/L Methylene blue	Synthetic solution	Visible light	90 min	99.4	-	(Than et al., 2017)
80 mg TiO_2/G N-TiO_2/G N-TiO_2/NG	10 mg/L Methylene blue	Synthetic solution	Visible light	180 min	59.8 71.1 87.9	-	(C. Liu et al., 2016)
100 mg N–TiO_2	30 mg/L Bisphenol A	Synthetic solution	Visible light	3 hours	50	5.5	(López-Serna et al., 2017)
0.1 g Cu, N co-doped TiO_2	3×10^{-5} M Methyl orange	Synthetic solution	Visible light	6 hours	92	6	(Reda et al., 2020)
TiO_2 nanotubular films	15 mg/L Caffeine 17.3 mg/L Salicylic acid	Synthetic solution	UV irradiation	240 min	50	Natural pH	(Arfanis et al., 2017)

Table 24.1 Comparative review from the last five years on the application of TiO_2 for the removal of emerging contaminants. *Continued*

Catalyst	Contaminant	Water matrix	Light source	Irradiation time	Degradation efficiency (%)	pH	References
50 mg/L N-TiO_2	5 mg/L Saccharin Bisphenol-A	Synthetic solution	UV irradiation	90 min	98 99	4.6 6.4	(Davididou et al., 2017)
1.5 g/L N,F-TiO_2	10 mg/L Acid red B	Synthetic solution	Visible light	4 hours	100	5.6	(Guo et al., 2017)
300 mg/L carbon modified TiO_2	5 mg/L Tetracycline hydro-chloride	Synthetic solution	White-LED light	2 hours	74	7	(Oseghe and Ofomaja, 2018)
100 mg NeTiO_2	20 mg/L Rhodamine B dye	Synthetic solution	Sunlight irradiation	300 min	97.36	7	(Barkul et al., 2016)
250 mg/L TiO_2/AC[a]	5 mg/L Acetaminophen	Synthetic solution	Simulated sunlight	6 hours	100	6.9	(Peñas-Garzón et al., 2019)
1 g/L Bi-TiO_2 / PAC[b]	20 mg/L Sulfamethazine	Ultra-pure water	Visible light	300 min	81.18	6	(Wang et al., 2019)
0.43 g Zeolite-TiO_2	20 mg/L Reactive black 5, cefiximetrihydrate, and phenazopyridine	Synthetic solution	UV-LED	40 min	60	7	(Eskandarian et al., 2016b)
0.5 mg/L TiO_2–RGO[c]	10 mg/l Bisphenol A	Simulated wastewater	UV	45 min	98.4	-	(Liao et al., 2016)

[a]*AC: Activated carbon.*
[b]*PAC: Powder activated carbon.*
[c]*RGO: Reduced graphene oxide.*

(Abdel-Maksoud et al., 2018; Fast et al., 2017; Gomes et al., 2019; Rizzo et al., 2014). Ioannidou et al. (2017) determined that WO_3 modifies the properties of TiO_2 and enhances its photocatalytic activity towards the degradation of sulfamethoxazole. Ananpattarachai et al. (2016) showed that co-doping TiO_2 with carbon and nitrogen had higher formation rate of $OH^{\bullet}$ and photocatalytic activity than those only doped with carbon or nitrogen. C,N co-doped TiO_2 achieved 95% of 2-chlorophenol degradation compared to 80% for C-doped TiO_2 and 70% for N-doped TiO_2. Petala et al. (2015) proved the efficiency of nitrogen-doped TiO_2 obtaining up to 100% removal of ethyl paraben in different water matrices including ultrapure water, water spiked with humic acids or bicarbonates, drinking water and secondary treated wastewater.

24.4.2 ZnO

ZnO is after TiO_2 the most studied catalyst for photocatalytic removal of ECs in wastewater. ZnO is an environmental friendly material as it has low toxicity, environmental stability and it is compatible with living organisms. Moreover, ZnO is a good semiconducting material due to its high photocatalytic capability, rapid carrier transport, direct and wide band gap, strong oxidation ability, a large free-exciton binding energy and low cost (Belver et al., 2020; Lee et al., 2016; Sin and Lam, 2018). Several researchers have studied the use of ZnO for the removal of ECs (Table 24.2). Haroune et al. (2014) studied the degradation of carbamazepine (CBZ) under UV irradiation obtaining a 35% removal. Ghosh et al. (2018) obtained 65% of acesulfame K degradation using solar light. Choina et al. (2015) achieved 85% of tetracycline and ibuprofen removal under UV irradiation. León et al. (2017) proved that under simulated sunlight radiation ZnO can degrade 89.5% of cefotaxime.

The major drawbacks of ZnO are the wide band gap energy and photocorrosion. The light absorption of ZnO is limited in the visible light region affecting the utilization of sunlight and producing a fast recombination of photogenerated electron-hole pairs which cause a low photocatalytic efficiency. To overcome this problem doping zinc oxide, with transition metals, rare earth, or noble metals, and also by coupling with other semiconductors oxides, is a promising way to enhance ZnO performance (Belver et al., 2020; Lee et al., 2016; Sin and Lam, 2018). Kaneva et al. (2015) found that lanthanide modified ZnO photocatalyst achieves contaminants mineralization within a short irradiation time while degrading reactive black 5 in a 100%. Calza et al. (2017) evaluated the photocatalytic performance of Ce doped ZnO versus ZnO for acesulfame K degradation in ultrapure and river water obtaining a higher degradation of 70% for Ce-ZnO vs 30% for ZnO in ultrapure water and 40% for Ce-ZnO vs 10% for ZnO in river water. Lam et al. (2015) showed excellent sunlight photocatalytic activities and an enhanced degradation for 2,4-dichlorophenoxyacetic acid (2,4-D) with WO_3/ZnO nanorods compared to pure ZnO nanorods.

24.4.3 Others

Tungsten trioxide (WO_3) is a promising photocatalyst with a narrow band gap. It can be used for optoelectronic applications, solar cells, phototransistors, photodiodes and

Table 24.2 Comparative review from the last five years on the application of ZnO for the removal of emerging contaminants.

Catalyst	Contaminant	Water matrix	Light source	Irradiation time	Degradation efficiency (%)	pH	References
4 cm^2 of ZnO NRs[a]-1 wt% GO[b]	3M Methylene blue	Synthetic solution	UV irradiation	450 min	90	-	(Rokhsat and Akhavan, 2016)
20 mg/L ZnO NP[c]	10 mg/L Tetracycline and ibuprofen	Synthetic solution	UV irradiation	180 min	85	9	(Choina et al., 2015)
1 g/L Sm-ZnO	10 mg/L Phenazopyridine	Synthetic solution	Ultrasonic irradiation	30 min	59	6.1	(Eskandarloo et al., 2016)
0.1 g ZnO, La-ZnO NP[c]	5 mg/L Paracetamol	Synthetic solution	Visible light	180 min	80	9	(Shakir et al., 2016)
100 mg/L Ce-ZnO	20 mg/L Acesulfame K	Ultrapure water River water	UV-Vis and visible light	90 min	70 40	Natural pH	(Calza et al., 2017)
100 mg Nd- ZnO NRs[a]	20 mg/L Resorcinol	Synthetic solution	Natural sunlight	60 min	98	6.8	(Sin and Lam, 2018)
0.125 g Ln-ZnO	20 mg/L Reactive black 5	Distilled water, sea water	UV-light	30 min	100	5.8–6 7.9–8.3	(Kaneva et al., 2015)
1g/L WO_3/ZnO NRs[a]	20 mg/L 2,4-dichloro phenoxyacetic acid	Deionized water	Natural sunlight	7 min	91.7	4.7	(Lam et al., 2015)
250 mg/L ZnO/Sep[d]	10 mg/L Antipyrine Acetaminophen Ibuprofen	Ultra-pure deionized water	Solar light	10 hours	70 85 100	-	(Akkari et al., 2018)

[a]*NRs: Nanorods.*
[b]*GO: Graphene oxide.*
[c]*NP: Nanoparticle.*
[d]*Sep: Sepiolite Others.*

gas sensors (Lam et al., 2015). Fakhri and Behrouz, (2015) determined that WO_3 possess excellent photocatalytic properties under visible light (VL) and sunlight (SL). It degraded 95.5% (VL) and 97.5% (SL) of lidocaine. Bismuth oxide (Bi_2O_3) has been widely studied thanks to its low cost and band gap. Aditionally, it is stable at ambient temperature and active under irradiation with visible light. Sánchez-Martínez et al. (2016) obtained removals of 40% for rhodamine B, 13% for indigo carmine and 72% for tetracycline hydrochloride while using Bi_2O_3, as well Bao et al. (2017) achieved a 72% degradation of sulfamethoxazole. Bismuth oxybromide (BiOBr) has received special attention for its high visible light photocatalytic activation. Zhang et al. (2015) attained a complete ciprofloxacin removal and Yi-Zhu et al. (2016) achieved 97% degradation for acetochlor. Ai et al. (2015) in the degradation of tetracycline obtained a removal efficiency of 100% with a 2.5 g/L In_2S_3 dosage and under solar radiation.

24.5 Strategies for improving photocatalysis

ECs degradation could be enhanced by improving the photocatalytic activity of the catalysts via the prevention of the electron-hole recombination rate, increasing the adsorption capacity of the catalyst, and reducing the band-gap energy. Various strategies have been adopted including using chemical oxidants, reduction of particle size to the nanoscale, doping the catalyst and combining semiconductor photocatalysis with other AOPs (Ahmed and Haider, 2018; Nguyen et al., 2020).

24.5.1 Doping

The recombination of photogenerated electron-hole is the major drawback in semiconductors photocatalysis. Metal doping could reduce the chances of electron-hole recombination by enhancing the charge separation between electrons and holes. Additionally, by doping it is possible to maximize the solar light utilization of the catalyst. To improve the absorption ability of the catalyst in the visible light region the electronic structure of the catalyst is modify by introducing metal or non-metal dopants with different energy levels between the valence and conduction band (Ahmed and Haider, 2018; Gomes et al., 2019).

24.5.1.1 Metal dopants

Noble metals such as Ag, Au, Pd, and Pt allow the catalyst to absorb the visible light due to the surface plasmon resonance. Although, the high cost associated with these materials make it difficult to use them in wastewater treatment processes. Doping with transition metal ions such us Cu, Zr, Zn, Co, Ni, Cr, Mn, Mo, Nb, V, Fe, Ru, W, Sb, Sn, and some lanthanides like La, Ce, Er, Pr, Gd, Nd, or Sm increase the charge carriers lifetime inhibiting electron-hole recombination as the dopants may trap electrons (Belver et al., 2020; Lofrano et al., 2017).

Mugunthan et al. (2019) observed that the addition of small amount of Sn could enhance the photocatalytic activity of TiO_2 allowing the complete mineralization of

diclofenac. Using the same type of catalyst, (Yuan et al., 2015) obtained complete removal of rhodamine B. TiO_2/SnO_2 exhibited significantly enhanced photocatalytic activities, with respect to bare SnO_2 and TiO_2. Besides, TiO_2/SnO_2 presented good recyclable photocatalytic activities. Rajoriya et al. (2019) achieved 50% degradation of 4-acetamidophenol (4-AMP) using TiO_2, while doping it with samarium (Sm) degradation increased to 60%. Likewise, Eskandarloo et al. (2016) found that Sm doped ZnO nanoparticles achieve higher phenazopyridine degradation (59%) than pure ZnO (51%). Shakir et al. (2016) proved that La can greatly enhance the photocatalytic activity of ZnO nanoparticles for paracetamol degradation. Li et al. (2016) proved the efectiveness of Ga doped ZnO for the degradation of rhodamine B. ZnO showed an enhanced electronic band gap absorption and an increases specific surface area after Ga doping.

However, metal dopants leaching behavior leads to the fast deactivation of the catalyst. In general, there is an increasing concern in using metal-doped photocatalysts due to photocorrosion phenomena and the possibility of toxic metals leaching (Ahmed and Haider, 2018; Gomes et al., 2019).

24.5.1.2 Nonmetal dopants

The low-cost and environmentally friendly characteristics of nonmetal dopants make them a suitable choice for improving photocatalysts. The main objective of doping catalyst with nonmetal ions, such as carbon, boron, sulfur, and some halides (F, Cl, Br, I), consists on altering both the electronic and structural properties of the catalyst, narrowing the band gap (Ahmed and Haider, 2018; Belver et al., 2020; Gomes et al., 2019; Lofrano et al., 2017).

Nitrogen has been the most used nonmetal species in TiO_2 doping. It has drawn attention because of its atomic size, small ionization ability, and high stability. The photocatalytic activity of N-doped TiO_2 varies depending on the method of synthesis. A wide range of preparation methods for successful doping of nitrogen in TiO_2 can be found in the literature including ion implantation, sintering at high temperature, plasma process, hydrothermal method, sol-gel method and hydrolysis (Barkul et al., 2016; Gomes et al., 2019; Nguyen et al., 2020).

Ion implantation consists of ion bombardment on the catalyst. The ion implantation promotes a significant decrease in the band gap. However, its main drawback is the increase in catalyst production cost due to the need of an ion implanter, a calcination step and higher energy requirements (Gomes et al., 2019). Yamashita and Li (2016) used metal ion implantation of TiO_2 to design photocatalysts that can operate under visible light irradiation.

Sintering at high temperature is the conventional method to produce N-TiO_2 by using high temperatures in the presence of N_2 and NH_3. This process produces a significant reduction in the band gap. However, the high temperatures produce agglomeration and pore structure collapse reducing the active surface area of the catalyst. In addition, NH_3 is erosive and toxic which may contribute to air pollution (Gomes et al., 2019). Lee et al. (2018) determined that after TiO_2 photocatalyst powders were treated with ammonia at 725°C they could utilize visible light photoelectrochemically. However, their incident photon to current efficiency was small.

Plasma process work at high temperatures and uses a gas stream which may cause a high operational cost for its high energy consumption and reactor special conditions (Gomes et al., 2019). However, Chen et al. (2019) achieved a simple, fast, inexpensive, and highly efficient method, which enhanced visible light photocatalyst by synthesizing N-TiO_2 through a cold atmospheric plasma. Via changing the concentration of NH_3 in the plasma or the applied power, the nitrogen concentration in the N-TiO_2 coatings could be adapted. After the NH_3/Ar plasma treatment the band gap of N-TiO_2 was significantly reduced. Photocatalytic activity tests were done with methylene blue as the target contaminant, results showed that the degradation rate constant for N-TiO_2 was improved more than 1.4 times compared with the undoped TiO_2.

Hydrothermal method allows the doping of high amounts of nitrogen. It requires high temperature and pressure conditions. Hydrothermal method does not only substitute oxygen atoms by nitrogen, it can also substitute titanium by nitrogen due to the high pressure applied, though this process demands high-energy consumption. Hydrothermal method has been widely used to prepare zeolite catalysts in industry and has been adapted to produce high yields of TiO_2 and titanate nanotubes with vast pore and unique nanotubular structures (Gomes et al., 2019; Liu et al., 2014). Liu et al. (2016) demonstrated that N doping by a simple hydrothermal method to fabricate N-doped TiO_2 nanowires (N-TiO_2 NWs) and N-doped graphene heterostructures (N-TiO_2/NG) permits the use of visible light by TiO_2, while for N-doped graphene (N-TiO_2/G) it improves the separation and transportation of photogenerated electron–hole pairs which generates a higher photocurrent. Methylene blue (MB) was used to determine the photocatalytic activity of these doped catalysts. It was found that N-TiO_2 NWs, N-TiO_2/NG and N-TiO_2/G reduce MB concentration by 32.9%, 87.9% and 71.1%, respectively.

Sol-gel method is the most used technique due to the simplicity of the process, short processing periods, fast heating rates, product homogeneity, high purity, controlled stoichiometry, and low power requirements (Reda et al., 2020; Rizzo et al., 2014). Than et al. (2017) produced nitrogen-doped TiO_2 nanoparticles via sol–gel method using $TiCl_4$ and NH_3. The benefits they found by using this technique were an easy manipulation, high purity and photoactivity of the produced catalyst, and level of nitrogen doping controllable. Guo et al. (2017) suggest that N,F co-doped TiO_2 nanoparticles (N,F-TiO_2) prepared using sol-gel method is a promising photocatalyst for wastewater treatment of dye using solar light. N,F-TiO_2 achieved a complete removal of acid red B in four hours operation.

Hydrolysis is based on the incorporation of N into the TiO_2 lattice after hydrolysis during the crystallization step. It is similar to sol–gel method, the main difference is the absence of an aging step. In addition, it has the advantages of working at low temperatures and fast production (Gomes et al., 2019). Chen et al. (2019) synthesized a cationic S-doped TiO_2 (S-TiO_2)/SiO_2 catalyst with visible-light response by a co-hydrolysis precipitation method. Its catalytic activity was assessed over the degradation of nitrobenzene, p-chlorophenol, and phenol under ultraviolet, artificial visible and solar light irradiations. Complete degradation under visible light was achieved in 100 min for phenol, in 80 min for nitrobenzene and in 120 min for p-chlorophenol.

This research showed that the advantages of doping the catalyst were highly active photocatalytic activity in visible and UV light response, easy separation from contaminants, and durable reusability.

24.5.2 Immobilization

Photocatalytic processes in which the semiconductor is suspended in the aqueous phase achieve high degradation rates due to high solid to liquid contact area. Nevertheless, the fine photocatalyst particles have limited adsorption capacity, due to its low surface area, which also cause an expensive particle-separation processes after treatment. This drawback can be overcome by supporting the semiconductor on a surface. To be a suitable support, the substrate should present special properties such as chemical inertness, high specific surface area and transparency to UV radiation. Therefore, semiconductors have been immobilized on larger particulates such as activated carbons, graphene, clays, zeolites, and silica among others (Belver et al., 2020; Gomes et al., 2019; Lofrano et al., 2017).

The high adsorption capacity of activated carbon (AC) improves the removal of ECs by generating a synergistic effect of adsorption and photocatalytic degradation. Immobilization over a porous material prolong the separation time of electrons and holes and increase the concentration of organic molecules close to the semiconductor active sites, enhancing the photocatalytic activity. Residues such as forestry, agricultural, and biomass industrial wastes, can be used as precursors of carbonaceous substrates (Belver et al., 2020; Peñas-Garzón et al., 2019; Wang et al., 2019). Peñas-Garzón et al. (2019) used lignin as a precursor for AC, which was used as a support for TiO_2 on the degradation of acetaminophen. The reaction rate was lower than the one obtained with pure TiO_2, although complete removal was observed and TiO_2/AC present higher settling velocity, being easier to recover after the process. Wang et al. (2019) used Bi-doped TiO_2 nano-composites supported by powdered activated carbon (PAC) for sulfamethazine removal reaching 81.2% degradation. Bi-Ti/PAC showed smaller crystal size, larger specific surface area and pore size, stronger light absorption and lower band gap energy than bare TiO_2.

Graphene is an excellent material for applications in photocatalysis due to its high surface area, high chemical stability, superior electrical conductivity and mechanical properties (Liu et al., 2016; Pedrosa et al., 2018). Pedrosa et al. (2018) using graphene oxide-TiO_2 composites presented very high catalytic activities for the degradation of diphenhydramine (92–94%). Liu et al. (2016) obtained removal efficiencies of 50% for sulfamethoxazole and 100% for methylene blue using cuprous oxide-reduced graphene oxide (Cu_2O/rGO-x). Cu_2O nanoparticles supported on the surface of graphene oxide (GO) sheets can enhance absorption of visible light during photocatalysis. Liu et al. (2016) proved that the photocatalytic activity of TiO_2 and graphene hybrids were higher than pure TiO_2 catalysts. N-doped TiO_2 nanowire/N-doped graphene (N–TiO_2/NG) showed the highest methylene blue degradation of 87.9% followed by N-TiO_2/G (71.1%) and TiO_2/G (59.8%), compared to TiO_2 nanowires (19.8%) and N-TiO_2 nanowires (32.9%).

Clay minerals are good adsorbents due to their cation-exchange capacity, high surface area and chemical stability. They have raised research interest owing to their high availability and low cost (Belver et al., 2020). Akkari et al. (2018) inmobiliced ZnO nanoparticles on the surface of sepiolite (Sep) fibrous clay mineral obtaining high removal efficiencies for ibuprofen (100%), acetaminophen (85%) and antipyrine (70%). Additionally, the catalyst was modified with magnetite (Fe_3O_4) nanoparticles. ZnO/Fe_3O_4-Sep showed superparamagnetic character and photocatalytic activity, permitting an easy recovery by the application of an external magnetic field improving its reusability.

Pumice rock and zeolites have become of great interest as catalyst supports on account of their high porosity, high surface area and low cost (Gomes et al., 2019). Eskandarian et al. (2016) studied the degradation of reactive black 5, cefiximetrihydrate, and phenazopyridine using zeolite-TiO_2 composite. Enhancement in the photocatalytic degradation was observed when persulfate and UV-LED was used compared to bare TiO_2. Moreover, the improvement was more significant when zeolite was used as a support. Zeolite-TiO_2 proved to be reusable. However, these solids can become an environmental problem due to their leaching behavior since some of the metals in its composition can be toxic to aquatic organisms (Gomes et al., 2019).

Silica is an interesting support owing to its transparency, porosity, mild hydrophobicity, light diffraction properties and neutral framework. The combination of SiO_2 with different catalyst allowed the photodegradation of pollutants at a higher concentration, improved the catalyst separation properties and permited some catalyst to operate under visible light irradiation (Belver et al., 2020; Chen et al., 2019; Yamashita and Li, 2016). Chen et al. (2019) analized the influence of immobilizing S-doped TiO_2 on silica for the degradation of nitrobenzene, p-chlorophenol, and phenol. S-TiO_2/SiO_2 had good reusability, presented excellent activity under UV, artificial, visible and solar light irradiations and was easily separated after the photocatalytic process.

Other substrates have been studied as catalyst support such as sand and concrete. Sand has unique characteristics as it is cheap, mechanically resistant, chemically inert, abundant in various particle sizes and has high density (Abdel-Maksoud et al., 2018). Abdel-Maksoud et al. (2018) immobilized TiO_2 in sand using epoxy, this method worked at room temperature, achieved high phenol degradation and showed to be resistance to abrasion and cost-effective. Concrete preset several advantage such as absence of toxicity, porosity, natural abundance and low price (Delnavaz et al., 2015). Delnavaz et al. (2015) obtained over 90% of phenol removal while immobilizing TiO_2 on concrete.

24.5.3 Combined methods

Fast and complete mineralization of refractory organics was difficult to attain by a single advanced oxidation process (AOP). Coupled AOPs turned out to be an efficient way to improve ECs removal. Ultrasonic and ultraviolet (UV) irradiations have

raised great attention due to their reduced chemical usage, simple operation and an extensive variety of applications in pollutants removal. Combining ultrasonic and UV irradiations with a catalyst can generate powerful oxidizing agents such as $OH^{\bullet}$ and other oxygen species which would degrade ECs rapidly and non-selectively (Yap et al., 2019). Khalegh and Qaderi (2019) improved the photocatalytic efficiency of ZnO nanoparticles using ultrasound waves in the treatment of methylene blue. Results showed that as the ultrasonic power increased, dye removal occurred faster. Rajoriya et al. (2019) obtained 60% and 63% degradation of 4-acetamidophenol (4-AMP) using a Sm and N doped TiO_2 catalyst. Aditionally, combining the photocatalyst with ultrasound (US) and hydrodynamic cavitation (HC) the photocatalityc oxidation of 4-AMP was enhanced to 87% and 91% for US and HC, respectively.

Recently, coupling ozonation with photocatalysis has been considered an efficient process for ECs removal. Photocatalytic ozonation accelerates the photocatalytic reaction by the inhibited recombination of photogenerated charges and allows the decomposition of ozone into $OH^{\bullet}$. The dissolved ozone can get photo-generated electrons from photocatalyst and form $OH^{\bullet}$ (Liao et al., 2016; Ling et al., 2019). Solís et al. (2016) proved that N doping improves TiO_2 photoactivity for clopyralid, triclopyr and picloram removal. Moreover, photocatalytic process was associated with ozonation which considerably improved herbicide and TOC abatement (95% in 3h) compared with photocatalytic oxidation (50% in 3h) or single ozonation (10% in 3h) and no significant loss of activity was observed after five runs. Liao et al. (2016) used TiO_2–reduced graphene oxide (TiO_2–RGO) for the degradation of Bisphenol A (BPA) by means of photocatalysis and ozonation combined system. The combination of TiO_2 with RGO made the catalyst very stable after five consecutive runs, enhanced the separation efficiency of photo-generated charges and enabled the electrons trapping by ozone and improved $OH^{\bullet}$ yield. Ling et al. (2019) acquired 83.1% acetaminophen removal by using Ag-g-C_3N_4 (Ag-doped graphitic carbon nitride) photocatalytic ozonation. The addition of Ag to graphitic carbon nitride (g-C_3N_4) boost the transfer of photogenerated electrons and enhanced the utilization efficiency of ozone, which reinforced the synergistic effect between photocatalysis and ozonation.

24.6 Wastewater treatment applications

Photocatalysis has been widely used for water and wastewater purification. It has been successfully used for the treatment of many types of ECs on actual water samples and even for the treatment of seawater in case of oil spills, for the removal of water-soluble fractions of crude oil. Photocatalysis turned to be a suitable choice for the removal of emerging contaminants from water, safeguarding ecosystems and human health (Ahmed and Haider, 2018; Gomes et al., 2019; Nguyen et al., 2020). A comparative review from the last six years on the application of photocatalysis for the removal of emerging contaminants is shown in Table 24.3.

Table 24.3 Comparative review from the last six years on the application of photocatalysis for the removal of emerging contaminants.

Catalyst	Contaminant	Water matrix	Light source	Irradiation time	Degradation efficiency (%)	pH	References
250 mg/L WO_3/ TiO_2	350 µg/l Sulfamethoxazole	Wastewater and drinking water and pure water	Solar light	5 min	50	Inherent pH	(Ioannidou et al., 2017)
0.1 g Fe - TiO_2, N,C	30 mg/L Amoxicillin Streptomycin Diclofenac	Synthetic antibiotics solution	Visible light	300 min	69.15 58.49 72.3	3.5 8 5	(Aba-Guevara et al., 2017)
20 mg Cu_2O/ RGO[a]	5 mg/L Sulfamethoxazole Methylene blue	Synthetic solution	Visible light	120 min 40 min	50 100	-	(S. H. Liu et al., 2016)
2.5g/L In_2S_3	20 mg/L Tetracycline	Synthetic solution	Solar radiation	40 min	100	7	(Ai et al., 2015)
563 mg/L TiO_2	10 mg/L Amoxicillin trihydrate Metformin HCl	Synthetic hospital wastewater	UV irradiation	150 min	90 98	7.6	(Chinnaiyan et al., 2019)
24 mg/L TiO_2	40mg/L Sulfamethoxazole	Milli-Q water	UVC light	120 min	95	6	(Yuan et al., 2019)
0.1 g/L TiO_2	30 mg/L Naproxen	Distilled water, unfiltered river water and drinking water	UV irradiation	10 min	99	7.8	(Kanakaraju et al., 2015)
1 g/L TiO_2	55 mg/L Tetracycline	Ultrapure water, drinking water and secondary effluent	UV irradiation	90 min	82.6	5	(Safari et al., 2014)
1.184 g/ L TiO_2	mg /L Benzophenone-3	Milli-Q water	Photo simulator	300 min	67	9	(Zúñiga-Benítez et al., 2016)
500 mg/L TiO_2 ZnO	10 µg/mL Carbamazepine	Synthetic solution	UV irradiation	6 hours	63 35	6.4	(Haroune et al., 2014)

Table 24.3 Comparative review from the last six years on the application of photocatalysis for the removal of emerging contaminants. Continued

Catalyst	Contaminant	Water matrix	Light source	Irradiation time	Degradation efficiency (%)	pH	References
200 mg/L TiO_2	15 mg/L Diuron P-coumaric acid Bisphenol A Phthalic anhydride	Synthetic solutions, industrial wastewater	UV irradiation	3 hours	85-99 89-98 72-92 73-96	10	(Pirilä et al., 2015)
1 g/L ZnO	40 mg/L Acesulfame K	Synthetic solution	Solar light	30 min	65 89	6	(Ghosh et al., 2018)
1 g/L TiO_2							
2.5 g/L TiO_2	20 mg/L Cefotaxime	Ultra-pure deionized water	Simulated sunlight	8 min	84.2 89.5	7 6	(León et al., 2017)
1.5 g/L ZnO							
5 mg WO_3 NPs[b]	50 mg/L Lidocaine	Synthetic solution	Visible light Sunlight	60 min	95.48 97.5	6	(Fakhri and Behrouz, 2015)
200 mg Bi_2O_3	20 mg/L Rhodamine B 30 mg/L Indigo carmine 20 mg/L Tetracycline hydrochloride	Synthetic solution	Simulated sunlight	24 hours	40 13 72	6	(Sánchez-Martínez et al., 2016)
1 g/L Bi_2O_3	10 mg/L Sulfamethoxazole	Deionized water	Simulated sunlight	60 min	72	-	(Bao et al., 2017)
0.02 g BiOBr	5 mg/L Ciprofloxacin	Synthetic solution	Visible light	140 min	100	-	(Zhang et al., 2015)
1.5 g/L BiOBr	10 mg/L Acetochlor	Double distilled water	Visible light	10 hours	97	natural pH	(Yi-Zhu et al., 2016)
0.25 g/L Ag-g-C_3N_4	10 mg/L Acetaminophen	Deionized water	Simulated solar light	120 min	83.1	7	(Ling et al., 2019)

[a]*RGO: Reduced graphene oxide.*
[b]*NRs: NanorodsConclusions and future challenges.*

For instance, Aba-Guevara et al. (2017) proved the effectiveness of Fe-TiO_2,N,C in the degradation of amoxicillin (AMX), streptomycin (STR) and diclofenac (DCF). AMX had a degradation efficiency of 69.2%, DCF of 72.3% and STR of 58.5%. Safari et al. (2014) obtained complete tetracycline degradation and observed an enhancement in degradation rate and a substantially reduction in the time required to degrade tetracycline when hydrogen peroxide was added. Chinnaiyan et al. (2019) suggested the effectiveness of UV/TiO_2 system for the pre-treatment of hospital wastewater and determined that photocatalytic effect plays a major role in the removal of amoxicillin trihydrate (90%) and metformin HCl (98%) when compared with adsorption and photolytic processes. Yuan et al. (2019) determine the inhibitory effects of ions and natural organic matter (NOM) present in water for the removal of sulfamethoxazole obtaining a degradation of 95%. Zúñiga-Benítez et al. (2016) obtained 67% removal of benzophenone-3 with a reduction in toxicity and an increase in biodegradability when H_2O_2 was added.

Some researchs have been focussed on the utilization of different water matrices to determine the influence of different parameters in ECs removal. Ioannidou et al. (2017) studied the degradation of sulfamethoxazole in three different water matrices. Degradation in wastewater and drinking water was slower than in pure water due to the presence of non-target organics and anions. However, the presence of hydrogen peroxide or sodium persulfate improves significantly removal rates. Likewise, Kanakaraju et al. (2015) studied the removal of naproxen in distilled water, unfiltered river water and drinking water, and demonstrated high degradation efficiency (99%) in all the conditions studied with an enhacement of photocatalytic degradation when chloride was present. Pirilä et al. (2015) studied the removal of diuron, p-coumaric acid, bisphenol A and phthalic anhydride using a synthetic solution and industrial wastewater. Diuron was removed the most efficiently while bisphenol A was the most difficult to remove. Additionally, industrial wastewater was observed to negatively affect the removal results.

24.7 Conclusions and future challenges

The increasing concern on ECs in the environment has raised researchers' attention on environmentally friendly processes which can be cost effective for the removal of these organic pollutants. Among AOPs, photocatalytic processes has shown to be a suitable choice since catalysts can present good activity under sunlight radiation, reducing operational costs. This chapter mainly focused on the different parameters affecting photocatalytic processes and the ways to overcome its drawbacks. Additionally, it shows the recent advances in the application of photocatalysis on ECs removal. As it stands now, different catalysts have been used in a wide range of ECs obtaining high mineralization percentages. However, most of the studies focused on a single contaminant. Further efforts shall be done to investigate the effect of combined ECs in real wastewater samples. Additionally, little has been done in the field of combining photocatalysis with other AOPs or biological process to enhance ECs degradation.

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CHAPTER

Biologically synthesized nanoparticles for dye removal

25

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25.1 Introduction

Environmental pollution due to the discharge of hazardous dye contaminated industrial effluents has become a major concern threatening human health and biodiversity. Synthetic dyes are widely used as coloring agents in various industries associated with paper, plastic, pharmaceuticals, dyeing, leather, and printing. It is estimated that more than 1000 different dyes and pigments are used worldwide in different industries and the annual production of synthetic dyes amounts to approximately 7×10^5 tons (Ghosh et al. 2015a).

Dyestuff compounds are considered as priority hazardous compounds due to their high toxicity, carcinogenicity, teratogenicity, and environmental persistence (Mumjitha and Raj, 2015).

Exposure to azo dyes can lead to bladder cancer, splenic sarcomas, hepatocarcinomas, nuclear alterations, chromosomal aberrations, and liver nodules. Dyes can be taken up by aquatic animals like fish, which enter the food chain and accumulate in higher amounts. The consumption of such food may lead to severe physiological disturbances that include hypertension, sporadic fever, and renal failure. Dye contamination reduces the quality of the irrigational water as well which adversely affects seedling germination, survival, growth, and the yield of crop plants (Luikham et al. 2018). Thus, methods like chemical oxidation, ultrafiltration, adsorption, coagulation, microbial degradation, electrochemical, and photocatalytic degradation are commonly employed for the decolorization and degradation of dyes during treatment of industrial effluents.

Nanotechnology driven solutions to address several challenges in the field of medicine, agriculture, catalysis, sensors, photonics, and also environmental remediation have received global attention and acceptance (Kale et al. 2017; Ghosh et al. 2018a; Kitture et al. 2019; Ghosh et al. 2019a; Ghosh, 2019). Nanoscale structures associated with resin, bentonite, biopolymer, kaolin, rectorite, montmorillonite, cellulose, biochar, and clinoptilolite can enhance dye removal efficiency due to their

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superior biosorption capacity. Recently, metal and metal oxide nanoparticles have gained wide attention in dye removal due to their promising photocatalytic activity. Gold, silver, platinum, palladium, copper, zinc, iron, and titanium-based nanostructures have potential use for dye degradation (Karmakar et al. 2020). However, chemical procedures for the synthesis of these nanoparticles, involve extensive use of toxic and hazardous chemicals which compromise the biocompatibility of the nanostructures (Robkhob et al. 2020; Adersh et al. 2015). Hence, rapid, efficient, cost effective, and environmentally benign biological routes for the synthesis of metal and their oxide, nanoparticles has emerged as a promising strategy.

Several bacteria, fungi, algae, and plants have been reported for the synthesis of nanoparticles with potential catalytic activity. These biogenic nanoparticles with exotic shapes and sizes are reduced and stabilized by cellular metabolites like reducing sugars, proteins, ascorbic acid, citric acid, polyphenols, flavonoids, polysachharides, and surfactants (Ghosh, 2018b; Joshi et al. 2019). In this chapter, we discuss various methods for the green synthesis of metal nanoparticles and their promises in dye degradation.

25.2 Bacteriogenic nanoparticles

Various metal tolerant or resistant microbes have been employed to synthesize nanosized metal and metal oxides owing to their cellular machinery to utilize, grow and survive in toxic, high metal concentration environments. In this section, different processes for the fabrication of bacteriogenic nanoparticles with dye degrading ability are discussed in detail.

Khan and Fulekar (2016) isolated Bacillus amyloliquefaciens from the effluent of the dairy industry in Mehsana, India and placed them on nutrient agar medium (10 g peptone, 10 g meat extract, 0.5 g NaCl, 15 g agar, in 1000 mL distilled water) plates incubated at 37°C for 24 h. The bacterium was inoculated in fresh diluted nutrient medium (100 mL) and co-incubated with 0.025 M titanyl sulfate at 37°C under shaking conditions (120 rpm) for 72 h. The resulting insoluble white precipitate was recovered by centrifugation, washed, and calcined at 500°C for 3 h in order to ensure complete removal of associated organic contents from the biomass eventually giving titanium dioxide nanoparticles (TiO_2NPs). The yield of the bacteriogenic nanoparticles was found to be time and pH dependent. After 16 h, 0.276 g of TiO_2NPs was obtained. Similarly, a maximum 0.28g of nanoparticles was recovered when the synthesis was carried out at pH 5. The biogenic nanoparticles were spherical with a size range of 22.11–97.28 nm as seen in Fig. 25.1. TiO_2NPs exhibited efficient photocatalytic degradation of Reactive Red 31 (RR31) dye in an aqueous solution. TiO_2NPs (0.4 g) were added per 100 mL of dye solution (75 ppm) and stirred for 20 min in darkness followed by exposure to UV radiation (working intensity approx. of 305 μWcm^{-2}) under constant stirring (340 rpm) and aeration. Decolorization efficiency of the photocatalyst was evaluated by recording the absorbance of RR31 at 545 nm. It is important to note that dye degradation efficiency of bacteriogenic

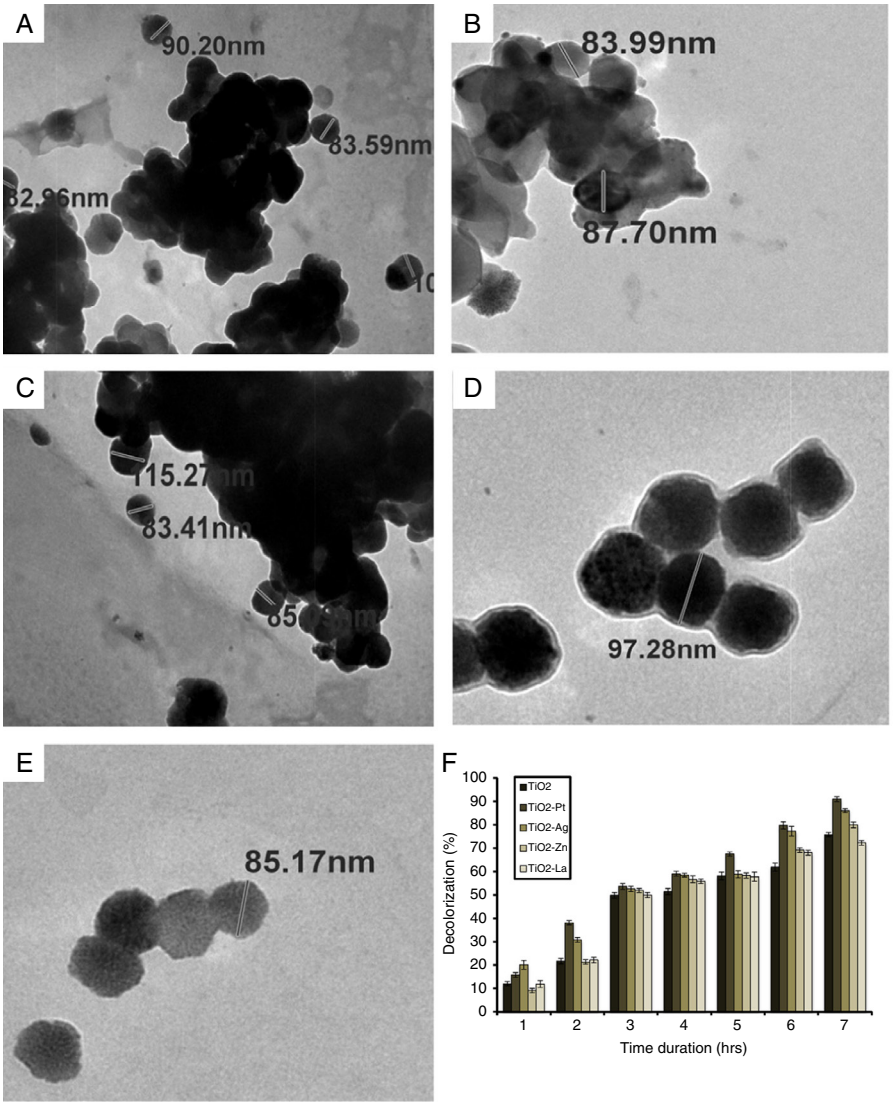

FIG. 25.1 TEM image of biosynthesized TiO_2NPs nanoparticles synthesized by Bacillus amyloliquefaciens.

(A) Pt-TiO_2; (B) Ag-TiO_2; (C) Zn-TiO_2; (D) La-TiO_2; (E) TiO_2; and (F) Percentage of dye decolorization at different time intervals using doped and undoped titanium dioxide nanoparticles. Reprinted with permission from Khan, R., Fulekar, M.H., 2016. Biosynthesis of titanium dioxide nanoparticles using *Bacillus amyloliquefaciens* culture and enhancement of its photocatalytic activity for the degradation of a sulfonated textile dye Reactive Red 31. J. Colloid Interface Sci.475:184-191.

TiO_2NPs could be significantly enhanced by doping of metals. As seen in Fig. 25.1f, platinum doping of TiO_2NPs exhibited the highest RR31 degradation potential of 90.98% followed by silver, zinc and lanthanum, which was notably higher compared to undoped TiO_2NPs (75.83%).

Bacillus marisflavi YCIS MN 5 isolated from the estuarine water at Dabhol, India synthesized gold nanoparticles (AuNPs) upon the reaction of its cell free extract with a gold chloride solution at room temperature within 96 h. The FTIR analysis indicated a peak at 3121 cm^{-1} specific to N-H bending vibrations in amines while the peak at 2889 cm^{-1} was due to C-H stretching vibrations in aldehydes. The peaks at 1639 and 1523 cm^{-1} were attributed to N-H bending vibrations in primary and secondary amines, respectively. Another peak at 1332 cm^{-1} was due to stretching vibrations of C-N aromatic functional group of proteins. Thus, it was confirmed that the bacteriogenic AuNPs were capped by conjugation with aldehydes and functional groups of proteins as represented in Fig. 25.2A. As seen in Fig. 25.2B, the resulting AuNPs were spherical with a size of 8-30 nm. Mostly, AuNPs were in the size range of 10–20 nm with an average particle size of 13.5± 0.2 nm (vol.73.21%). However, a few AuNPs were also in the range of 20–50 nm with average particle size of 41.6± 9.7 nm (vol. 26.79%). These biogenic AuNPs were further assessed for the catalytic reduction of Congo Red by adding 500 μL of AuNPs (50 μg/mL) in 3 mL of a reaction mixture containing 1 mL of a freshly prepared $NaBH_4$ (0.150 M) solution with 1 mL of a Congo Red dye solution (1 mM). Similarly, catalytic degradation of methylene blue was initiated by the addition of 200 μL of AuNPs (50 μg/mL) in a reaction mixture containing 5.77 mL of distilled water, 30 μL of 0.01 M Methylene Blue and 200 μL of 0.1 M $NaBH_4$. Figs. 25.2C and 25.2D show the time-dependent reduction of dyes as indicated by the UV-visible spectra in the range of 500–800 nm recorded at an interval of 1 min. The Congo Red solution became colorless within 20 min of reaction due to 98% degradation following a pseudo-first-order kinetics with a rate constant of 0.0013 min^{-1}. Similarly, 88% of Methylene Blue degradation was achieved within 10 min following a pseudo-first-order kinetics with a rate constant of 0.2484 min^{-1}. The change in colour might be due to the reduction of Methylene Blue (blue in an oxidized state) to a colourless compound called leuko methylene blue (Nadaf and Kanase, 2019) (see Fig. 25.3).

Erwinia herbicola was reported to synthesize exotic stannic oxide nanoparticles (SnO_2NPs) when the bacterial biomass (0.4 g) was incubated with 100 mL of an aqueous solution of 1 mM $SnCl_2$•$2H_2O$ at 30°C for 48 h under shaking conditions (120 rpm). The biogenic nanoparticles were recovered by centrifuging at 12000 rpm for 10 min which were further washed in distilled water and acetone followed by vacuum drying at 60°C and annealing at 150°C for 2 h. Bacteriogenic SnO_2NPs were mostly spherical with a diameter of 10–42 nm. Reduction and stabilization was brought about by carboxyl, amide, and amine groups of the bacterial proteins. Initially, the Sn^{2+} ions might be trapped by the extracellular bacterial enzymes or by surface associated membrane proteins which were further reduced by enzymes such as NADH dependent reductase or NAD-linked dehydrogenases. NADH/NAD^+ undergoes reversible oxidation and reduction by accepting or losing

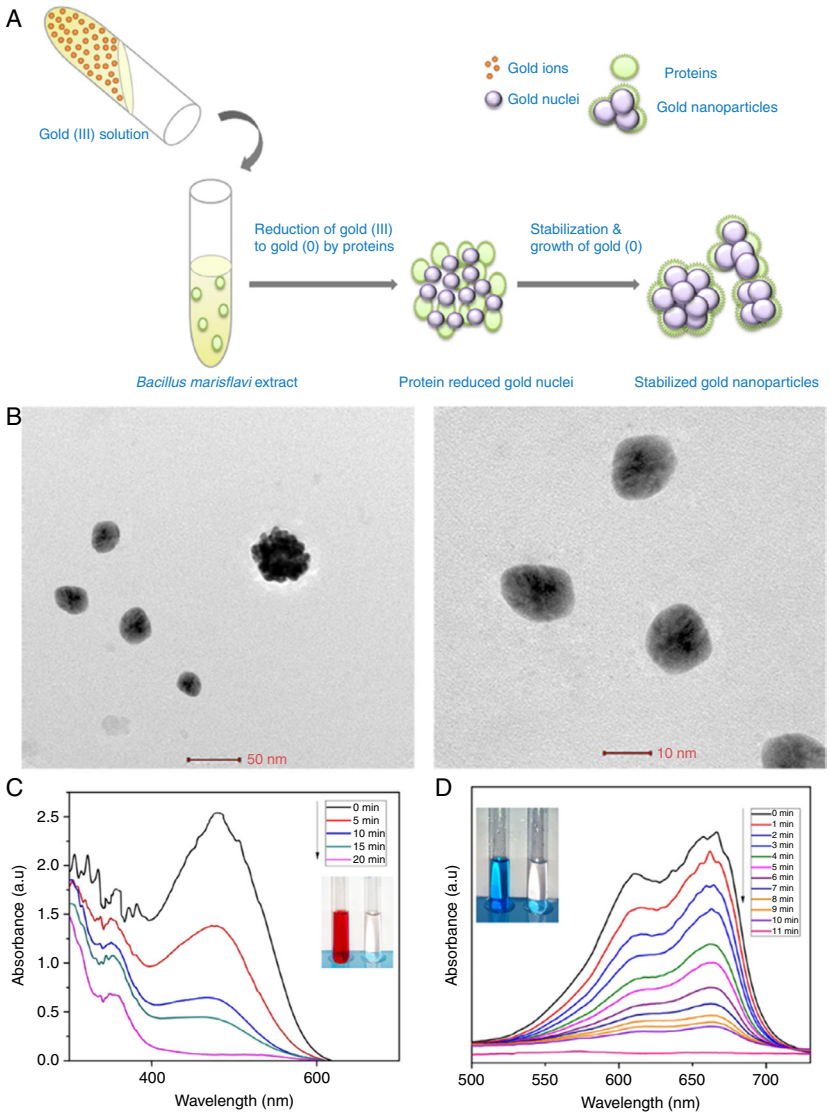

FIG. 25.2 ***B. marisflavi*** **mediated synthesis of AuNPs with catalytic dye degrading properties.**

(A) A plausible mechanism of the formation and stabilization of AuNPs by the proteins present in the extract of *B. marisflavi*; (B) TEM images of biosynthesized AuNPs under different magnifications; (C) UV-Visible absorbance spectra showing the degradation of Congo red using $NaBH_4$ in the presence of AuNPs; and (D) UV-Visible absorbance spectra for the degradation of methylene blue using $NaBH_4$ in the presence of AuNPs. Reprinted with permission from Nadaf, N.Y. Kanase, S.S., 2019. Biosynthesis of gold nanoparticles by *Bacillus marisflavi* and its potential in catalytic dye degradation. Arab. J. Chem. 12:4806–4814. Copyright 2016 The Authors. Production and hosting by Elsevier B.V. on behalf of King Saud University.

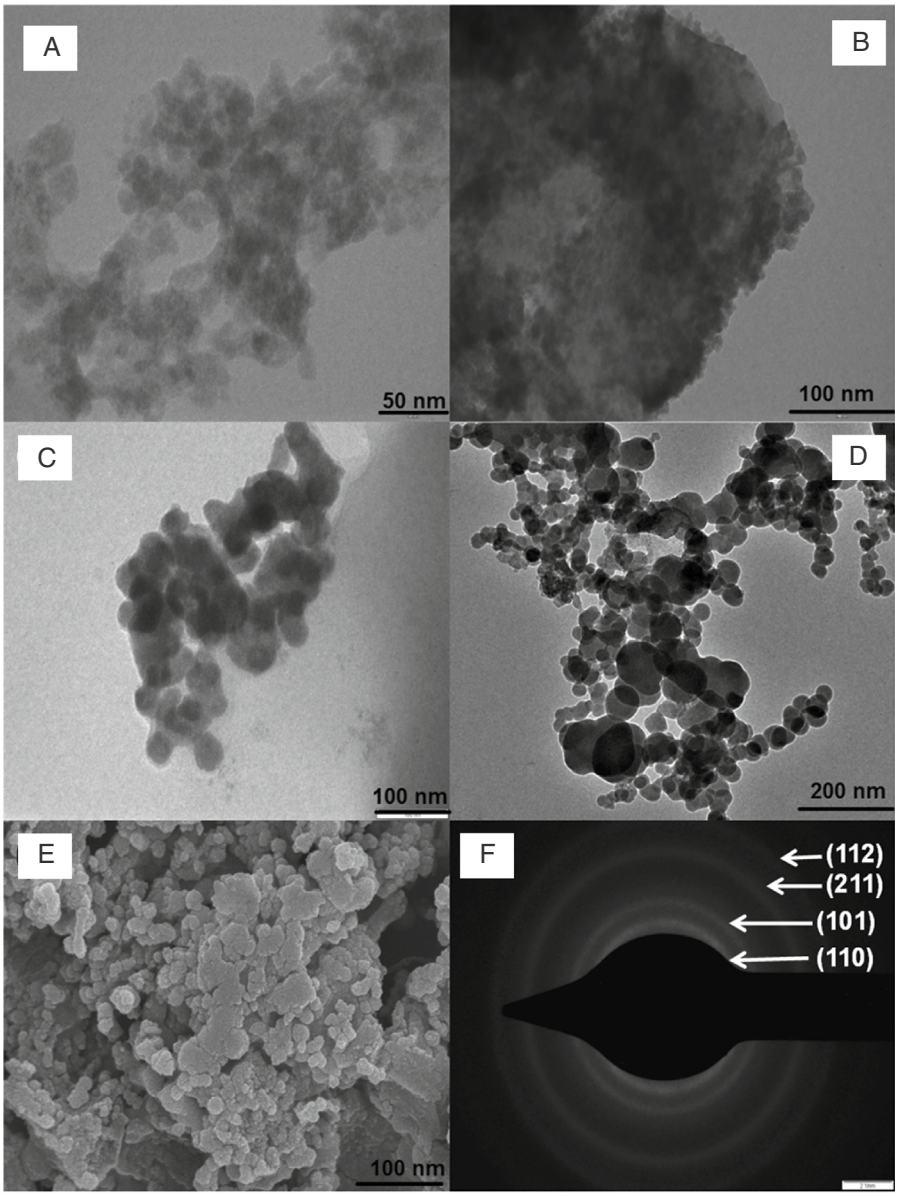

FIG. 25.3 TEM micrographs of *Erwinia herbicola* biosynthesized SnO_2NPs at:

(A) 50 nm scale; (B) 100 nm scale; (C) after annealing at 150°C at 100 nm scale; and (D) 200 nm scale. (E) SEM micrographs showing a cluster of spherical nanoparticles at 100 nm scale and the (F) SAED pattern. Reprinted with permission from Srivastava, N., Mukhopadhyay, M., 2014. Biosynthesis of SnO_2 nanoparticles using bacterium *Erwinia herbicola* and their photocatalytic activity for degradation of dyes. Ind. Eng. Chem. Res. 53(36): 13971-13979. Copyright 2014 American Chemical Society.

electrons and protons in several electron transfer reactions. Hence, gaining two electrons may have reduced Sn^{2+} ion with the simultaneous oxidation of NAD^+ to NADH eventually forming SnO_2NPs which could effectively degrade methylene blue, erichrome black T, and methyl orange dyes up to 93.3, 97.8, and 94.0%, respectively. It is important to note that the catalytic dye degradation was associated with a gradual blue shift of the absorption peaks (λ max) with time marked by the disappearance of the absorption peak of the respective dyes due to cleavage in the aromatic ring of the dye molecules. Degradation of methylene blue, erichrome black T, and methyl orange in the presence of bacteriogenic SnO_2NPs followed the pseudo-first-order reaction kinetics with rate constants (k_{app}) corresponding to 0.00566 s^{-1}, 0.01152 s^{-1} and 0.00751 s^{-1}, respectively. Further, an easy recovery of SnO_2NPs from the reaction mixture after termination of the photocatalytic degradation reaction by a simple centrifugation strongly rationalized its reusability and recyclability (Srivastava and Mukhopadhyay, 2014).

Escherichia sp. SINT7, isolated from wastewater samples collected from the Parahang drain, Faisalabad, Pakistan could synthesize copper nanoparticles (CuNPs) upon reaction with 5 mM $CuSO_4$ at 28 ± 2°C and 150 rpm for 24 h. The biosynthesis of CuNPs was associated with a change of colour from bluish green-to dense green. Bacteriogenic CuNPs were recovered by centrifugation at 8000 g for 5 min followed by drying in an oven at 100°C for 72 h. The resulting CuNPs were spherical in shape ranging from 22.33 to 39 nm in size. CuNPs could degrade Congo red, malachite green, direct blue-1, and reactive black-5 up to 97.07%, 90.55%, 88.42% and 83.61%, respectively, with an initial dye concentration of 25 mg L^{-1} when exposed to sunlight for 5 h. However, with a 100 mg L^{-1} dye concentration, the degradation percentage was found to be 83.90%, 31.08%, 62.32% and 76.84% for Congo red, malachite green, direct blue-1, and reactive black-5, respectively. Further, a significant reduction in pH, electrical conductivity, turbidity, total suspended solids, total dissolved solids, hardness, chlorides, and sulphates was observed when the textile effluents were treated with the bacteriogenic CuNPs (Noman et al. 2020).

Leuconostoc lactis KC117496, isolated from idli batter (an acidic fermented food) exhibited an exopolysaccharide (EPS) mediated synthesis of AgNPs capable to degrade hazardous azo-dyes (Saravanan et al. 2017). Initially, 9 mM of the $AgNO_3$ solution was mixed with a 10 mL solution containing the partially purified bacterial EPS (10 mg) followed by incubation at room temperature in darkness for 24 h. The development of yellow color indicated the synthesis of polymeric AgNPs. After 1 month of incubation, AgNP concentrations increased which was recovered from the solution by centrifuging at 19200 x g for 15 min. The resulting spherically shaped nanoparticles with an average size of 35 nm showed a size variation in a the range from 30 to 200 nm. Significant catalytic efficiency of EPS-stabilized AgNPs using $NaBH_4$ as a reducing agent was seen against methyl orange and Congo red. The rate of degradation increased with an increase in the amount of EPS-stabilized AgNPs up to 5 mg beyond which no further enhancement was observed. The degradation rate constants were 11.31×10^{-3} min^{-1} and 12.57×10^{-3} min^{-1} for Methyl Orange and

Congo Red, respectively. Saravanan et al. (2017) stated that the enhanced degradation observed with our nanocatalysts could be attributed to the following reasons: (i) high surface area of the EPS could adsorb azo-dyes; (ii) $NaBH_4$ was expected to act as a hydride source and the AgNPs catalysts were expected to activate the azo nitrogen bond and also to bind with the sulphur and oxygen atoms of the dyes resulting in weakening of azo double bonds via conjugation; (iii) a large number of oxygen atoms of the EPS could assist in increasing the number of AgNPs; and (iv) EPS networks containing more hetero atoms were expected to exhibit hydrophilic interactions with azo-dyes, which facilitated the movement of the dye molecules near the catalytic sites.

A marine selenite-reducing bacterium *Lysinibacillus* sp. ZYM-1 was isolated as red colonies using sterilized Luria-Bertani media supplemented with 2 mM Na_2SeO_3 and incubated at 30°C, 150 rpm for 7 days. The biosynthesis of selenium nanomaterials (SeNMs) took place upon the addition of 0.1 to 150 mM of the substrate (Na_2SeO_4 or Na_2SeO_3) to 20 mL of LB or TSB media containing 200 μL of the bacterial suspension incubated for 48 h at 30°C under a shaking condition (150 rpm). Red colored SeNMs were formed by the reduction of selenite by *Lysinibacillus* sp. ZYM-1 under both aerobic and anaerobic conditions. More than 88% of the selenite reduction took place within 48 h between pH 5.0 to 9.0, the optimal being pH 7.0. Various metals like Cu^{2+}, Mn^{2+}, Co^{2+}, Cd^{2+}, and Zn^{2+} inhibited the selenite reduction in different levels even at the 0.1 mM concentration. Fig. 25.4 shows the TEM images of selenium nanocubes (SeNCs) formed with the 1 mM selenite concentration and selenium nanospheres (SeNSs) formed with higher selenite concentrations. SeNSs in different selenite concentrations were in the range of 100–200 nm. The effects of different reaction parameters like pH, temperature, and reaction time was determined using 5 mM selenite as the initial concentration. Fig. 25.5 shows the comparison of the SeNSs synthesized at pH 7.0 with those irregular SeNMs generated at pH 5.0 and bowl-like SeNMs at pH 9.0. On incubation at 50°C, the *Lysinibacillus* sp. ZYM-1 synthesized much smaller monodispersed SeNSs with a size distribution of 3.8 ± 1.8 nm (Fig. 25.5l). Two genes in the *Lysinibacillus* sp. ZYM-1 genome, namely, *dedA* and *cysA*, were possibly responsible for selenate and selenite transport. Also, a gene-encoding sulfite reductase located at the downstream of *cysA*, plays a critical role in selenite reduction. Additionally, five thioredoxin reductase encoding genes are involved in selenite reduction, as well. The bacteria employs an export system for the secretion of selenium atoms in the form of Se(0) nanoparticles, and a protein named Se factor A (SefA) was involved with the assembly of selenium nanostructures. Bacteriogenic SeNSs exhibited significant visible light-driven photocatalytic activity on Rhodamine B (RhB) with H_2O_2 having a reaction rate constant of 0.0011 min^{-1}. The predominant degradation products were N-deethylation intermediates and phthalic acid as identified using liquid chromatography-high resolution mass spectrometry (LC-HRMS), confirming the coexistence of chromophore cleavage and the N-deethylation pathway (Che et al. 2017).

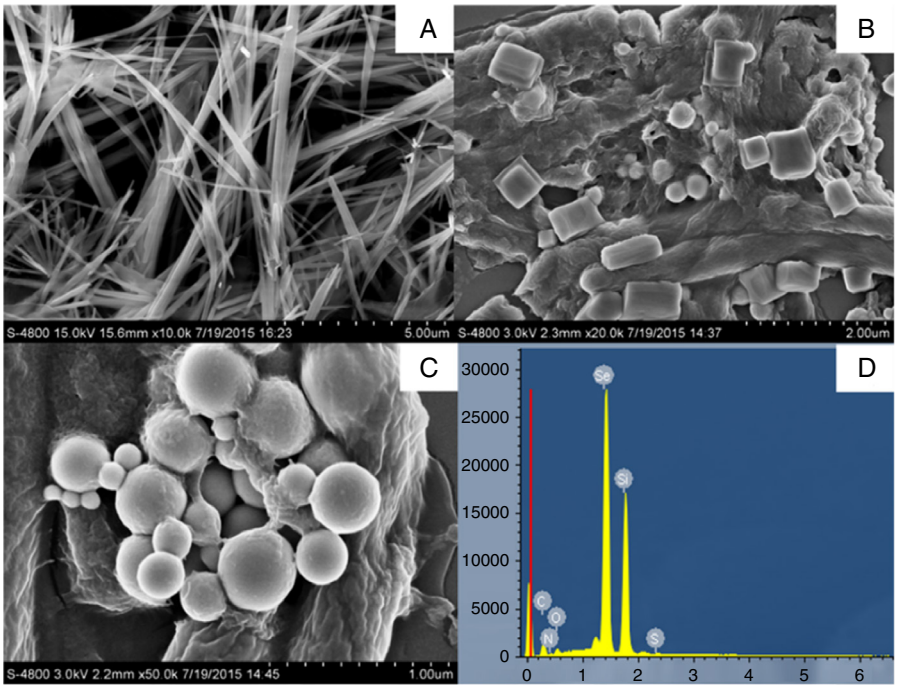

FIG. 25.4 Morphology control of *Lysinibacillus* sp. ZYM-1 synthesized by SeNMs by the concentration of selenite in LB media:

(A) 1 mM selenite; (B) 2.5 mM selenite; and (C) 5 mM selenite; and (D) Energy dispersive X-ray (EDAX) analysis of SeNSs generated at 5 mM selenite where X and Y axis represent energy (KeV) and counts, respectively. Reprinted with permission from Che, L., Dong, Y., Wu, M., Zhao, Y., Liu, L., Zhou, H., 2017. Characterization of selenite reduction by *Lysinibacillus* sp. ZYM-1 and photocatalytic performance of biogenic selenium nanospheres. ACS Sustainable Chem. Eng. 5:2535–2543. Copyright 2017 American Chemical Society.

25.3 Mycogenic nanoparticles

Economically viable and eco-friendly methods for the synthesis of nanoparticles have been developed using various fungal isolates. The cell-free extracts of fungi can serve as reducing, capping and stabilizing agents during the synthesis of nanostructures with exotic shapes like spheres, triangles, hexagons and rods. Mycogenic synthesis is advantageous due to its simplicity of operation without complicated down-stream processing.

Elegbede et al. (2018) reported efficient dye removal capability of AgNPs synthesized by xylanases from *Aspergillus niger* L3 and *Trichoderma longibrachiatum* L2. Crude xylanases (1 mL) synthesised by non-aflatoxigenic fungal strains of

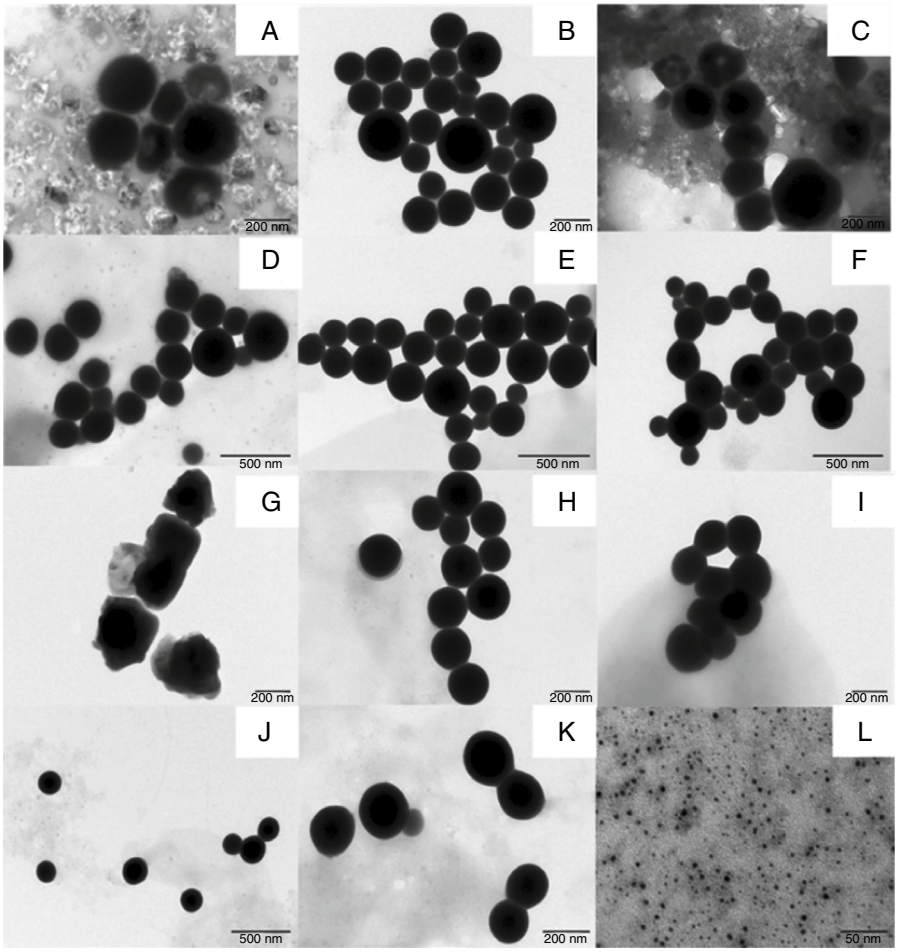

FIG. 25.5 TEM images of SeNMs generated by *Lysinibacillus* sp. ZYM-1 in TSB media at different conditions:

(A) pH 9.0; (B) pH 7.0; (C) pH 5.0; (D) 48 h; (E) 96 h; (F) 240 h; (G) 1 mM selenite; (H) 5 mM selenite; (I) 25 mM selenite; (J) 30°C; (K) 40°C; and (L) 50°C. The scale bar for each image was 200 nm (A), 200 nm (B), 200 nm (C), 500 nm (D), 500 nm (E), 500 nm (F), 200 nm (G), 200 nm (H), 200 nm (I), 500 nm (J), 200 nm (K), and 50 nm (L). Reprinted with permission from Che, L., Dong, Y., Wu, M., Zhao, Y., Liu, L., Zhou, H., 2017. Characterization of selenite reduction by *Lysinibacillus* sp. ZYM-1 and photocatalytic performance of biogenic selenium nanospheres. ACS Sustainable Chem. Eng. 5:2535–2543. Copyright 2017 American Chemical Society.

A. niger L3 (28.69 U/mL) and *T. longibrachiatum* L2 (22.13 U/mL) was reacted with 50 ml of a 1 mM $AgNO_3$ solution for the synthesis of AgNPs at ambient temperature (30 ± 2°C). The resulting AgNPs were spherical, cylindrical and oval shaped. The size of the mycogenic AgNPs were in a range of sizes of 18.11–77.49 nm and

15.21–54.03 nm for *A. niger* L3 and *T. longibrachiatum* L2, respectively. The AgNPs exhibited antimicrobial, antioxidant, anticoagulant, thrombolytic as well as catalytic dye degrading activities. AgNPs could degrade Malachite Green (78.97%) better compared to Methylene Blue (25.30%).

AuNPs with catalytic activity were synthesized employing cell-free extracts of *Aspergillus* sp. WL-Au isolated from activated sludge using Modified Martin Broth (MMB, pH 7), containing $(NH_4)_2SO_4$, 1 g/L; KH_2PO_4,1 g/L; $MgSO_4 \bullet 7H_2O$, 0.5 g/L and glucose, 2 g/L. Initially the fungus was grown aerobically at 30°C for 4 days followed by recovery of the mycelium by filtration. Washed fungal mycelium was then re-suspended in phosphate sodium buffer (50 mM, pH 7) and subjected to ultrasonication for 40 min for lysis. The cell-free extract was collected by centrifugation and filtration of the supernatant. The addition of a $HAuCl_4$ solution to the cell-free extracts initiated the synthesis of AuNPs which was completed upon incubation in darkness at 30°C after 9 days. The bioreduced AuNPs were mostly uniform and spherical with an average size of 4 nm to 29 nm as illustrated in Fig. 25.6. The size of the AuNPs formed after 12 h ranged from 2.5 nm to 6.7 nm and the average size was 4.4 nm which gradually became larger with an incubation time until 5 days. At day 5, the size of the AuNPs was mostly in the range of 25–35 nm with an average size of 29 nm. The AuNPs synthesized after 5 days had a similar size distribution (25–35 nm). The biogenic AuNPs efficiently catalyzed the reduction of 4-nitrophenol which is often used as a precursor for dye manufacturing. The reaction rate constant was linearly correlated with the concentration of AuNPs, which increased from 0.59 min^{-1} to 1.51 min^{-1} with the amount of AuNPs increasing form 1.46×10^{-6} to 17.47×10^{-6} mmol (Shen et al. 2017).

Bhargava et al. (2016) reported the extracellular synthesis of AuNPs using a high metal tolerant fungus *Cladosporium oxysporum* AJP03 isolated from rhizospheric soil samples of a plant, *Calotropis procera*, growing in the Sonshi mining region of the Bicholim-Pale area located in the North Goa district of Goa, India. The fungus was isolated on Rose Bengal Agar medium (pH 7.2) supplemented with chloramphenicol (30 mg mL^{-1}) by incubating for 5-6 days at 28°C in darkness. The fungal biomass was prepared by inoculating a loopful of spore from the isolated fungi in 80 mL of MGYP medium (0.3% malt extract, 1.0% glucose, 0.3% yeast extract, and 0.5% peptone; pH 7.0) followed by incubation at 28°C for 72 h under shaking conditions (120 rpm) in darkness. The mycelia mat was then separated by centrifugation at 5000 rpm for 15 min at 4°C followed by washing with autoclaved Milli-Q water. A fungal cell-free filtrate containing extracellular metabolites was prepared by resuspending 20 g of this washed biomass in 100 mL of autoclaved Milli-Q water and incubating it for 72 h followed by vacuum filtration using Whatman filter paper no. 1. AuNPs were synthesized using aqueous gold (III) chloride trihydrate (0.5 mM) mixed with 100 mL of a fungal cell-free filtrate incubated at 28°C under dark conditions. The resulting AuNPs were quasi-spherical in shape with an average particle size of 72.32 ± 21.80 nm. The majority of the AuNPs were between 40-60 nm. The maximum synthesis of AuNPs was achieved using a biomass:water ratio of 1:5 and a 1 mM precursor salt concentration at physiological pH (7.0). Mycogenic AuNPs

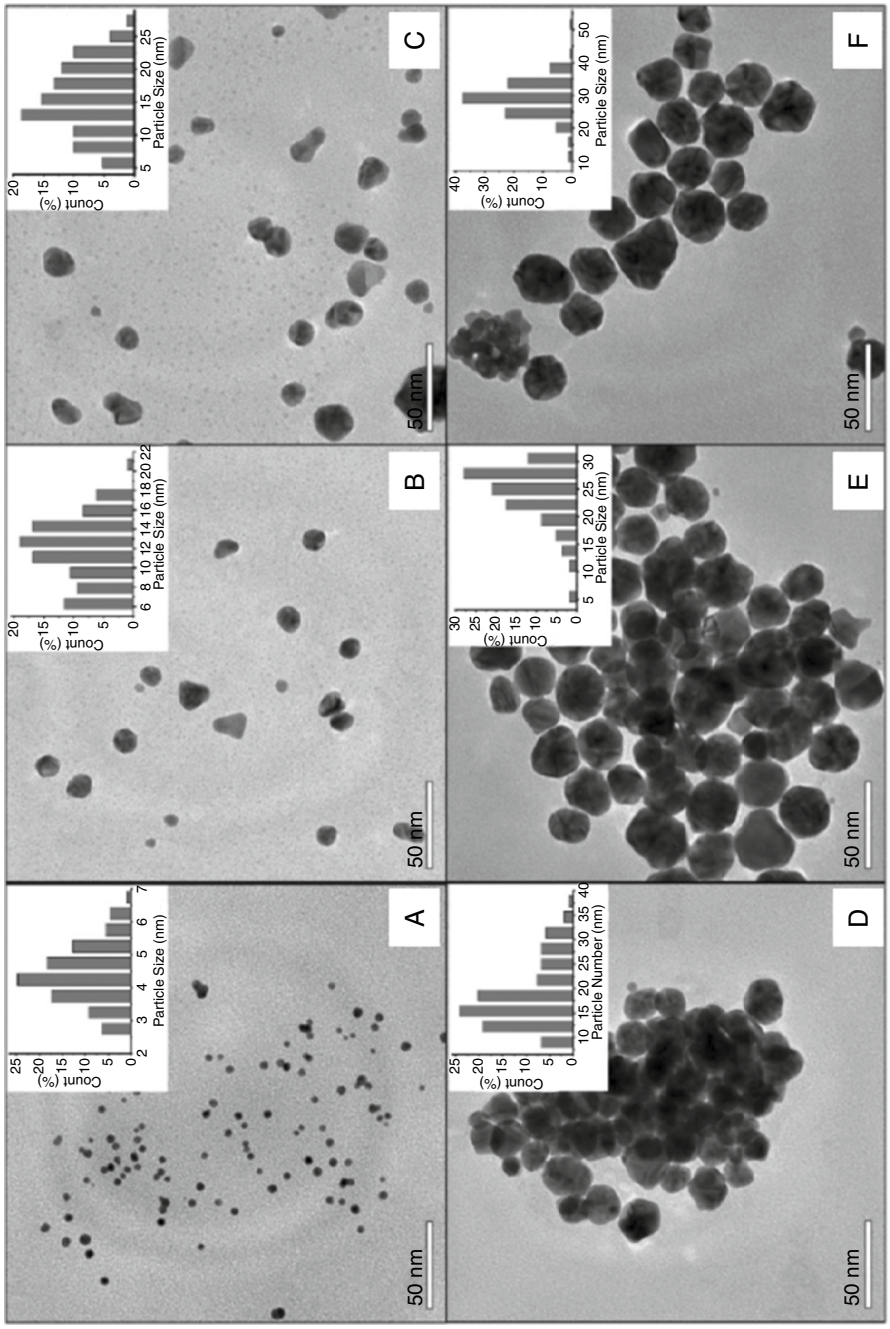

FIG. 25.6 The size and morphology of AuNPs in the synthesis process.

(A) 0.5 day, (B) 1 day, (C) 2 day, (D) 3 day, (E) 4 day, and (G) 5 day. Reprinted with permission from Shen, W., Qu, Y., Pei, X., Li, S., You, S., Wang, J., Zhang, Z. and Zhou, J., 2017. Catalytic reduction of 4-nitrophenol using gold nanoparticles biosynthesized by cell-free extracts of *Aspergillus* sp. WL-Au. J. Hazard. Mater. 321: 299-306. Copyright 2016 Elsevier B.V.

exhibited excellent catalytic efficiency towards sodium borohydride mediated reduction of Rhodamine B (2.5×10^{-5} M) within 7 min of reaction time under experimental conditions. Superior catalytic efficiency was attributed to the presence of proteins as a capping material on the surface of the AuNPs.

Mycogenic zinc oxide nanoparticles (ZnONPs) synthesized by *Cordyceps militaris* fungus showed excellent photocatalytic degradation against methylene blue dye. Laboratory grown *C. mellitus* was collected, washed, dried and crushed to make a fine powder, 5 g of which was suspended into 100 ml of distilled water and autoclaved in high pressure and 100°C for 1 h. The autoclaved extract was filtered and used for the synthesis of ZnONPs using a co-precipitation method which was achieved by mixing it with 0.1mM $Zn(NO_3)_2$•6 H_2O at 70°C followed by the addition of NaOH (0.2M) dropwise with continuous stirring at 500 rpm. The appearance of a milky white color indicated the completion of the nanoparticle synthesis, which was allowed to settle for 2 h. The resulting nanoparticles were recovered by centrifuging at 5000 rpm for 15 min followed by washing and drying at 60°C for complete conversion of $Zn(OH)_2$ to ZnONPs. The flower like ZnONPs with a size of about 10.15 nm as illustrated in Fig. 25.7 degraded the hazardous dye Methylene Blue by about 97% in the presence of UV-radiation (Li et al. 2019).

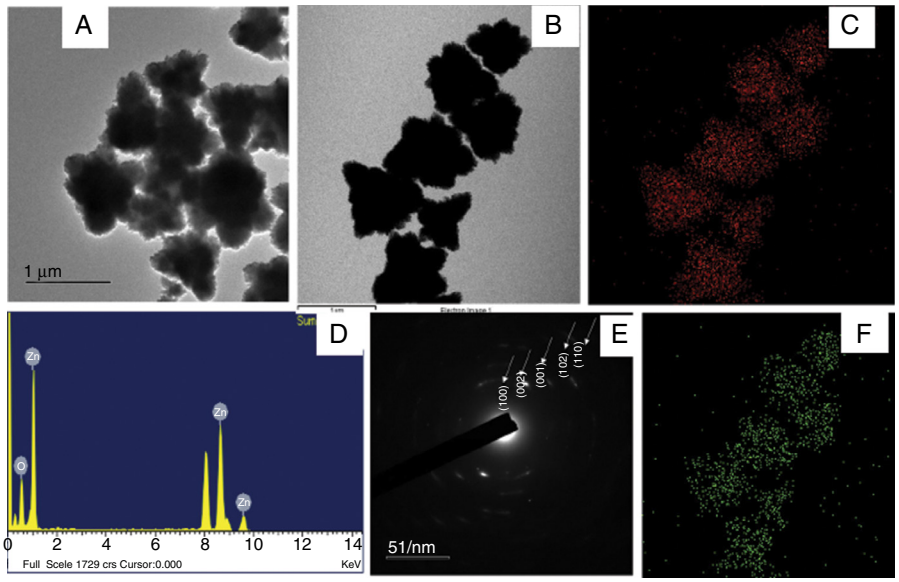

FIG. 25.7 FE-TEM image of ZnONPs synthesized by *Cordyceps militaris*:

(A) and (B) for the shape and size of ZnONPs; (C), (D), and (E) Elemental distribution; and (F) the SAED pattern. Reprinted with permission from Li, J.F., Rupa, E.J., Hurh, J., Huo, Y., Chen, L., Han, Y., chan Ahn, J., Park, J.K., Lee, H.A., Mathiyalagan, R., Yang, D.C., 2019. *Cordyceps militaris* fungus mediated zinc oxide nanoparticles for the photocatalytic degradation of methylene blue dye. Optik 183:691-697. Copyright 2019 Elsevier GmbH.

25.4 Phycogenic nanoparticles

Several marine and fresh water algae contain proteins, minerals, fibers, polyunsaturated fatty acids, vitamins, and bioactive antioxidants that can play a critical role in the bioreduction of ions to stable nanoparticles with chemoctalytic potential. Hence, cell free aqueous extracts of algae have been applied for the development of efficient and rapid phycogenic routes for the synthesis of metal nanoparticles with superior dye degrading potential.

The marine algae *Caulerpa racemosa* is rich in metabolites like ceramides, sesquiterpenes, caulerpin (alkaloid), reducing sugars (galactose, glucose, arabinose, xylose, mannose and rhamnose) and amino acids (leucine, aspartic acid, glutamic acid, serine, valine, glycine, alanine, isoleucine, lysine and phenylalanine). It also has reducing sugars which can play an important role in the synthesis of metal nanoparticles which can be further stabilized due to the capping effect of alkaloids and amino acids. *C. racemosa* was collected from coastal areas of Mandapam, Tamil Nadu, India. Algal biomass was washed, dried and converted to a fine powder, 5 g of which was suspended in 100 mL of double distilled water and heated at 80°C for 30 min followed by recovery of the aqueous extract by filtration. The AgNPs were synthesized at room temperature by reacting the aqueous extract of algae (1, 3 and 5 mL) with 0.01 M $AgNO_3$ (24, 22 and 20 mL) at 25°C for 24 h when a brown color developed. Fig. 25.8 illustrates the distorted spherical shaped AgNPs with an average size of 25 nm as evident from HR-TEM analysis. The phycogenic AgNPs exhibited greater catalytic activity towards the degradation of Methylene Blue dye by $NaBH_4$ with a rate constant of 1.114×10^{-3} s^{-1} (Edison et al. 2016).

In another study, *Caulerpa serrulata*, collected from the Red Sea coast, Egypt, showed the efficient synthesis of stable colloidal AgNPs by its aqueous extract. Various reaction parameters like extract concentration, contact times, pH values, and temperature were optimized. Increased concentration of the extract from 5 to 20% resulted in a decrease in AgNP mean diameter as indicated by an increase in the intensity of the SPR bands and shifting to a lower wavelength (435 nm). The phycogenic AgNPs were found to be stable with no precipitation even after 5 months of synthesis. The akaline pH of the medium resulted in an enhanced reducing power and stabilizing ability of the *C. serrulata* extract. Increases in reaction temperature from 27 to 95°C enhanced the reduction rate of silver ions and thereby the synthesis of AgNPs, with a maximum being after 1 h. The biogenic AgNPs were spherical with an average particle size of 10 ± 2 nm. Excellent catalytic reduction of the Congo Red (CR) dye from aqueous solutions was exhibited by the AgNPs which could be further accelerated by increasing either the $NaBH_4$ concentration or catalytic dosage. The AgNPs synthesized at 95°C using a 10% (v/v) extract concentration showed the highest catalytic activity with pseudo first order kinetics (Aboelfetoh et al. 2017).

Cadmium sulphide nanoparticles (CdSNPs) with a dye degrading property were reported from *Chlamydomonas reinhardtii*. The algae were grown as a suspension in 225 mL of Bolds Basal Medium (BBM) with a twelve-hour photoperiod at 25°C for a week followed by centrifugation at 12,000 rpm for 20 min at 4°C. The supernatant,

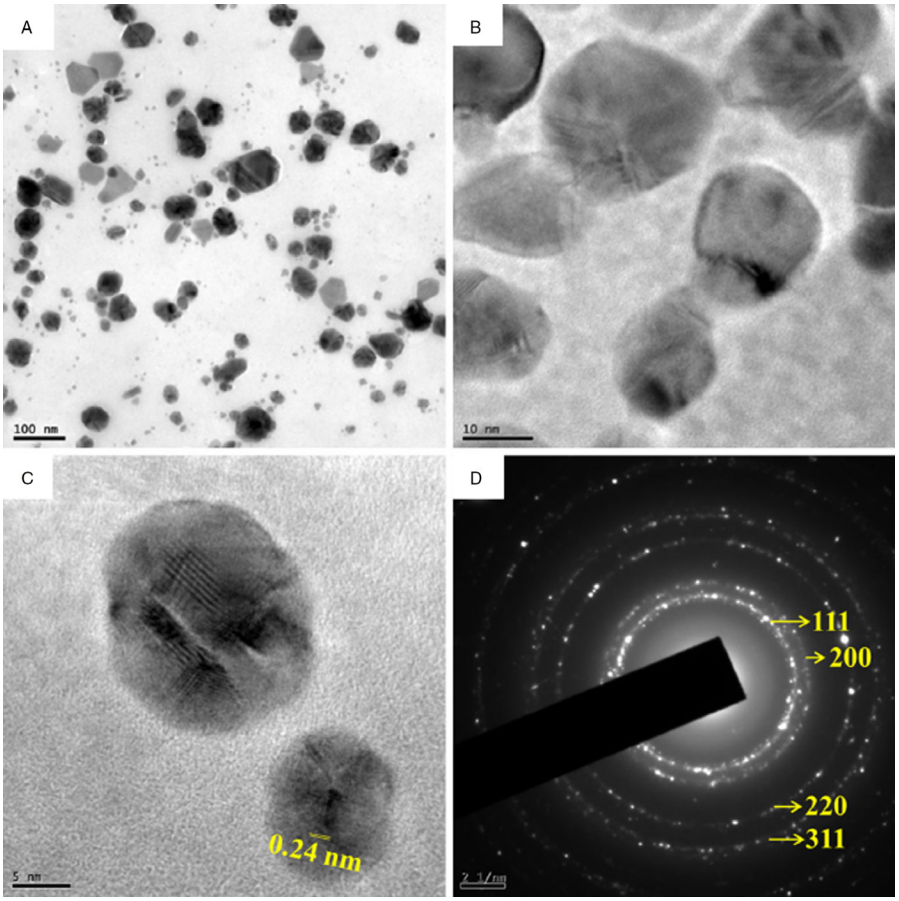

FIG. 25.8 AgNPs synthesized by the *C. racemosa* extract.

(A–C) HR-TEM images at different scales and the (D) SAED pattern of the synthesized AgNPs. Reprinted with permission from Edison, T.N.J.I., Atchudan, R., Kamal, C. and Lee, Y.R., 2016. *Caulerpa racemosa*: a marine green alga for eco-friendly synthesis of silver nanoparticles and its catalytic degradation of methylene blue. Bioprocess Biosyst. Eng. 39(9):1401-1408. Copyright © 2016 Springer-Verlag Berlin Heidelberg.

such as the cell free extract, was collected and appropriately diluted to make it react with cadmium chloride and sodium sulphide with a final concentration of 1 mM. After 20 min, the synthesis of CdSNPs was completed. The resulting nanoparticles were recovered by centrifuging at 8720 g. CdSNPs were spherical measuring approximately 5 nm and were capped with algal proteins. Further, these phycogenic CdSNPs exhibited excellent photocatalytic ability against Methylene Blue under UV light degrading 90% of the dye within 90 min with a rate constant of 0.018 min^{-1}. However, an increase in the concentration of the dye resulted in a decrease in the

photocatalytic efficiency from approximately 86% to 71%. On the other hand, an increase in catalyst dosage could significantly augment photodegradation of methylene blue from 74% to 90% (Rao and Pennathur, 2017).

In another interesting study, Ag-ZnO nanoparticles (AgZnONPs) were synthesized by using a *Padina gymnospora* seaweed extract designated as the chemical co-precipitation method. The AgZnONPs were synthesized using a multi step process where one part of the seaweed extract was reacted with 25 mL of a 0.05 M $AgNO_3$ solution at 60°C. Another part of the seaweed extract was mixed with 25 mL of 0.1 M $Zn(NO_3)_2$ and was reacted by continuous stirring for 2 h at 60°C. Finally, the two reaction mixture solutions were combined together and mixed well by continuous stirring for 30 min. A freshly prepared 0.2 M NaOH solution was gradually added into the capped Ag, Zn colloidal solution resulting in a brownish white colored precipitate, which was allowed to settle for 24 h. This precipitate was washed and dried in a hot air oven at 120°C for 4 h which showed a Ag:ZnO ratio as 1:2. The spherical and grain shaped morphology of Ag, ZnO particles intercalated on the seaweed polymer giving their average size of the particles in the 20–40 nm range. In addition, the biogenic AgZnONPs exhibited a catalytic photodegradation and decolorization performances against cationic (methylene blue) and anionic (reactive blue 198) dyes under direct sunlight irradiations with first order reaction kinetics. AgZnONPs could degrade both methylene blue and reactive blue 198 up to 85% and 95% with rate constant values of 0.026 and 0.024 min^{-1}, respectively (Rajaboopathi and Thambidurai, 2018).

Another similar marine macroalgae *Padina tetrastromatica* was used to synthesize AuNPs with superior dye degrading potential. The influence of reaction parameters (like the quantity of seaweed extract, temperature, precursor metal ion concentration, reaction time and pH) on the biosynthesis of the nanoparticles was evaluated. The variation in the quantity of seaweed extract (SWE) above 2 mL resulted in the development of purple and eventually to a blue color indicating the rise in particle size. Hence, the optimum quantity of SWE required for the biosynthesis was 2 mL. A rise in temperature from room temperature to 90°C led to an increase in the particle size of AuNPs owing to the agglomeration of particles, which was further confirmed from the HR-TEM images as illustrated in Fig. 25.9. At room temperature, monodispersed particles of almost spherical shape were synthesized. The optimal concentration of chloroauric acid for the preparation of AuNPs using *Padina tetrastromatica* was 1 mM. Another important factor controlling the morphology of phycogenic AuNPs was the reaction pH. More spherical and homogeneous AuNPs were formed at pH 3.2 while altering the pH to 7 or to 10, which resulted in polydispersed AuNPs. The biosynthesis of AuNPs was complete after 24 h. Optimal reaction conditions resulted in the generation of nearly spherical AuNPs having an average particle size of 11.4 nm which exhibited catalytic reduction of hazardous organic dyes, eosin yellow (96%) and Congo red (92%) using sodium borohydride, with pseudo-first order kinetics (Princy and Gopinath, 2018).

AgNPs synthesized using the aqueous extract of brown seaweed, *Sargassum myriocystum*, collected from Keelakarai, Tamil Nadu, India were well dispersed with hexagonal shapes of an average size of 20 ± 2.2 nm. The phycogenic AgNPs not only

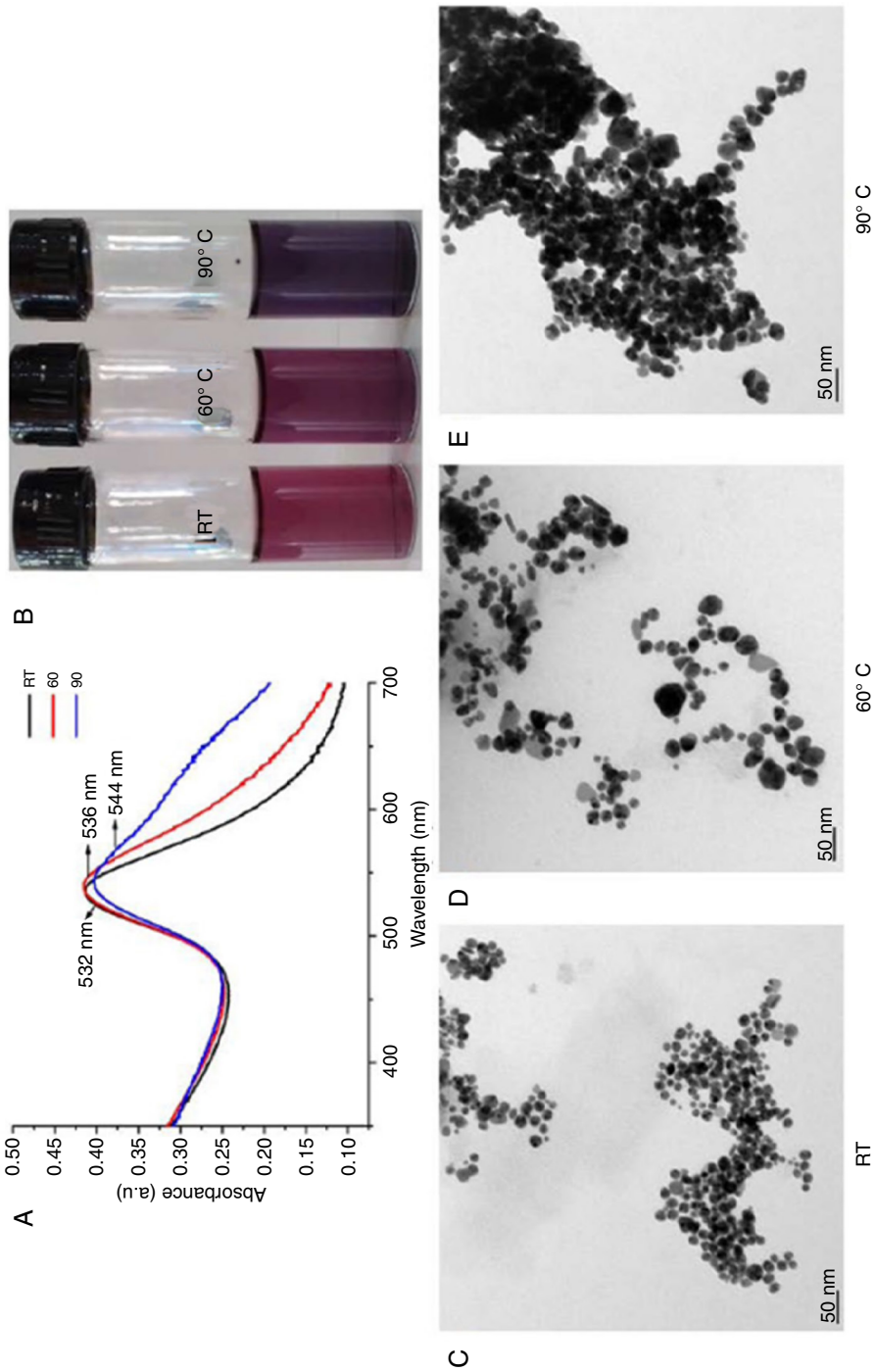

FIG. 25.9 The synthesis of AuNPs by *Padina tetrastromatica*:

(A) The UV–visible absorption spectra of AuNPs formed with 2 mL of SWE at various temperatures, (B) digital images of AuNPs formed with 2 mL of SWE at various temperatures and (C–R) HR-TEM images of AuNPs formed with 2 mL of SWE at various temperatures. Reprinted with permission from Princy, K.F. and Gopinath, A., 2018. Optimization of physicochemical parameters in the biofabrication of gold nanoparticles using marine macroalgae *Padina tetrastromatica* and its catalytic efficacy in the degradation of organic dyes. J. Nanostructure Chem. 8(3):333-342. Copyright 2018 Springer Nature.

exhibited antimicrobial activity against clinical pathogens, *Staphylococcus aureus*, *Proteus vulgaris, Escherichia coli*, *Pseudomonas aeruginosa*, *Staphylococcus epidermidis*, and *Klebsiella pneumoniae* but also showed larvicidal activity against the mosquitos *Aedes aegypti* and *Culex* quinquefasciatus. Moreover, these biogenic AgNPs with antibiofilm and anticancer activity also exhibited potential photocatalytic activity against Methylene blue (MB). The maximum percentage of MB degradation was observed at 98% within 60 min. Decolorization efficiency of the dyes gradually increased with irradiation time (Balaraman et al. 2020).

25.5 Phytogenic nanoparticles

The synthesis of spherical, hexagonal, rod like, cubic and planar nanoparticles using plant extracts seems to be a very attractive alternative to hazardous chemical and physical methods of nanoparticle synthesis. The different phytochemicals (such as reducing sugars, ascorbic acid, citric acid, polyphenols, flavonoids, terpenoids, saponins and alkaloids) present in the plant extracts act as reducing and stabilizing agents in the synthesis of nanoparticles. Various medicinal plants like *Dioscorea bulbifera*, *Gnidia glauca*, *Plumbago zeylanica*, *Gloriosa superba, Platanus orientalis, Barleria prionitis, Litchi chinensis, Dioscorea oppositifolia* and *Adiantum philippense* have been reported to synthesize AuNPs, AgNPs, CuNPs, PtNPs, PdNPs, and even bimetallic nanoparticles (Ghosh et al. 2011; Ghosh et al. 2012a, 2012b; Ghosh et al. 2016a,2016b, 2016c, 2016d; Ghosh et al. 2015b, 2015c, 2015d; Sant et al. 2013; Salunke et al. 2014; Shende et al. 2017; Rokade et al. 2017; Bhagwat et al. 2018; Shende et al. 2018; Shinde et al. 2018; Rokade et al. 2018; Jamdade et al. 2019). This section elaborates on the plant mediated synthesis of nanoparticles for dye degradation.

The leaves of *Alpinia nigra* were collected from Jorhat, Assam, India. Initially, the extract was prepared by suspending 10 g of *A. nigra* leaf powder in 350 mL of distilled water and was added and heated at 50°C for 30 min followed by filtration. Various volumes of this extract (6, 8, 10, and 12 mL) were mixed with a 1mM $HAuCl_4.3H_2O$ solution at 95°C with continuous stirring for 15 min until a purple-red color developed indicating AuNP colloidal solutions designated as G1, G2, G3, and G4, respectively. Higher concentrations of plant extracts facilitated the sufficient reduction and capping for stabilizing the growing nuclei, thereby, preventing aggregation of the phytogenic AuNPs. As illustrated in Fig. 25.10, the average particle sizes for G1, G2, G3, and G4 were 56.40, 48.62, 35.2 and 21.52 nm, respectively. Mostly hexagonal AuNPs were seen in G4 with a few nanotriangles as well. The lattice fringe spacing was 0.21 nm indicating the growth of the nanoparticles in the (111) plane. The AuNPs degraded Rhodamine B to a greater extent (87.64%) compared to Methyl Orange (83.25%) after 120 min with a rate constant of 1.494×10^{-2} min^{-1} and 1.443×10^{-2} min^{-1}, respectively. Fig. 25.10I depicts the main steps involved in the degradation process which are as follows:

Initially, sunlight excites electrons in the gold atoms from a low energy valence band to a high energy conduction band. Sunlight provides the appropriate amount of

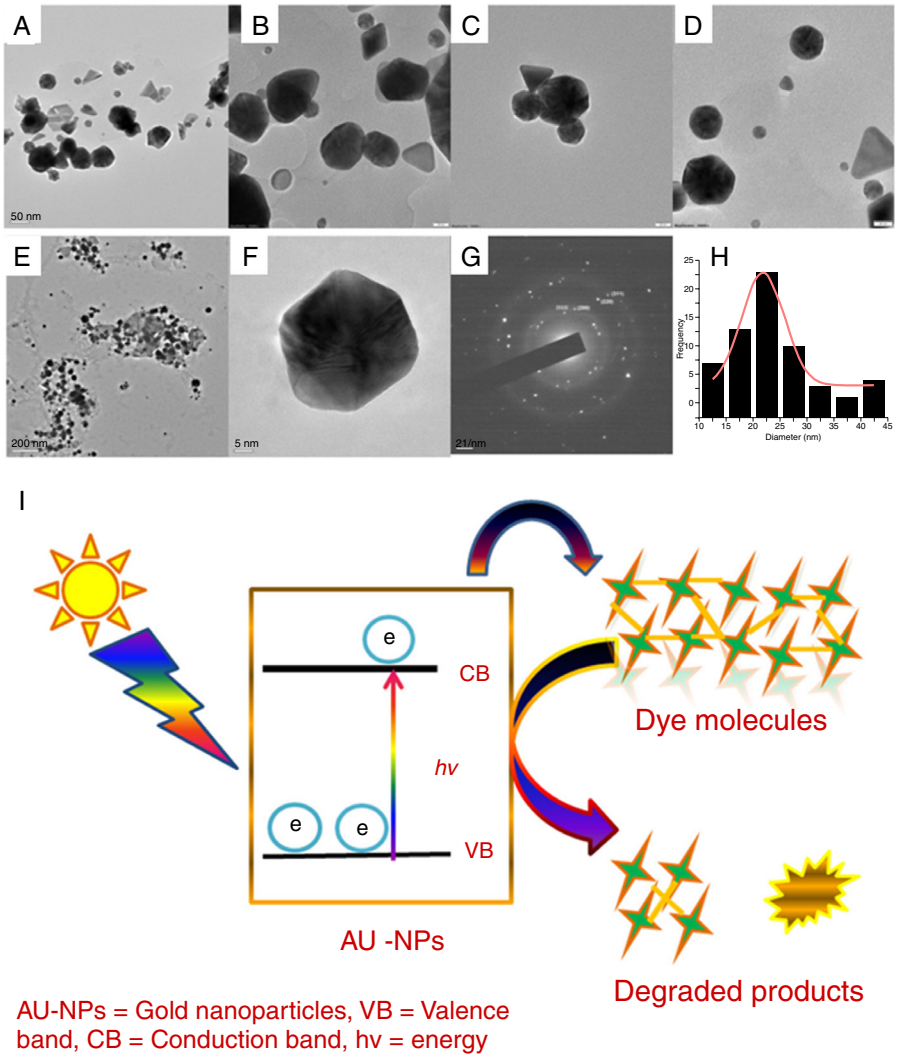

FIG. 25.10 The *Alpinia nigra* leaf extract mediated synthesis of AuNPs with catalytic dye degrading properties.

TEM micrographs of: (A) G1; (B) G2; (C) G3; (D) G4; (E) overall area; (F) HRTEM image; (G) SAED pattern; (H) Particle size distribution histogram of G4; and (I) A mechanistic view of the degradation of dye molecules in the presence of AuNPs. Reprinted with permission from Baruah, D., Goswami, M., Yadav, R.N.S., Yadav, A. Das, A.M., 2018. Biogenic synthesis of gold nanoparticles and their application in photocatalytic degradation of toxic dyes. J. Photochem. Photobiol. B. 186:51-58.Copyright 2018 Elsevier B.V.

energy enabling the electrons present inside the Au atoms to overcome the attraction from the nucleus and jump into the conduction band. Next, the electrons from the valence band on the surface of Au move to the organic dye molecule resulting in their degradation and subsequent mineralization (Baruah et al. 2018).

Vidya et al. (2016) reported the synthesis of ZnONPs by the leaf extract of *Artocarpus heterophyllus* (jackfruit). The porous, sponge-like agglomerated structures were mainly composed of a hexagonal wurtzite structure and the size of the particles was in the range between 15 and 25 nm. In this green synthesis of ZnONPs, zinc nitratehexahydrate was an oxidant and the phytochemicals present in the extract like terpenoids, flavonoids, phenols, steroids, glycosides, carbohydrates, and saponins efficiently stabilized the polycrystalline ZnONPs. Excellent pH dependent photodegradation (80%) efficiency was displayed by the ZnONPs against Rose Bengal dye, a main water-pollutant released by the textile industry. An increase in the degradation rate was observed with an increase of pH from 6 to 8. However, on further increase to 9 and 10, dye degradation decreased. At low pH, the anionic dye remained in their protonated form and semiconductor form and also possessed a positive charge due to adsorption of H^+ ions. An increase in pH might be attributed to the decrease in the repulsion between the dye and semiconductor and hence the photocatalytic degradation increased. However, after certain pH, the semiconductor surface became negatively charged and it again repelled the dye molecule, thereby reducing the photocatalytic degradation. Similarly, the dye degradation rate was found to be highest up to 60 mg of the catalyst with 10 to 30 ppm dye solutions, beyond which, the degradation rate decreased upon increasing either the catalyst or dye concentration.

AgNPs synthesized by the *Colocasia esculenta* plant rhizome powder could effectively facilitate catalytic reduction of organic azo dyes. Initially, the plant rhizomes were dried and pulverized into a fine powder, 1 g of which was dipped into a 0.2M solution of $AgNO_3$ for 7 h in order to saturate the adsorption site. The metal ion loaded powder was collected and dried at room temperature. About 100 mg of this powder was put into 100 mL of a 0.5 M freshly prepared $NaBH_4$ solution resulting in the synthesis of AgNPs after 50 min. The phytogenic AgNPs were spherical with sizes ranging from 57-85 nm (average size being 68 ± 12 nm) and were irregularly distributed on the plant support. Further, the AgNPs showed high efficiency in the catalytic reduction of nitroarenes, such as picric acid/trinitrophenol (TNP), 4-nitroaniline (4-NA), 4-nitrophenol (4-NP) and 2- nitrophenol (2-NP) to the corresponding amines. The AgNPs also notably facilitated the catalytic reduction of organic azo dyes such as Methyl Orange, Congo Red, Methyl Red and Rhodamine B by sodium borohydride ($NaBH_4$). The synthesized AgNPs showed stable catalytic degradation of Methyl Orange dye for 72 h with a 97% dye reduction without any loss in their catalytic activity even after use for five times over 3 days, indicating its promising recyclability and reusability. Also, a 96.9% reduction of Congo Red was completed in 12 min in the presence of AgNPs with an apparent rate constant for pseudo-first order as 2.14×10^{-3} s^{-1}. It took

14 min for 96.29% reduction of Methyl Red in the presence of AgNPs and $NaBH_4$ with a rate constant of 1.12×10^{-3} s^{-1}. Rhodamine B was reduced up to 97.78% by the catalytic AgNPs after just 6 min with a rate constant of 5.68×10^{-3} s^{-1} (Ismail et al. 2018).

Not only can plants but also certain plant metabolites can also synthesize metal nanoparticles with dye degrading properties. Umamaheswari et al. (2018) reported the green synthesis of AuNPs using 5,7-dihydroxy-6-metoxy-3′,4′methylenedioxyisoflavone (Dalspinin) isolated from the roots of *Dalbergia coromandeliana.* The successive extraction of *D. coromandeliana* with petroleum ether, benzene, ethylacetate and ethanol under hot conditions was followed by an ethyl acetate extract to get a dark brown semi-solid mass. This was further subjected to column chromatography over a silica gel column and eluted with benzene: ethyl acetate (6:4 v/v) to isolate dalspinin. The synthesis of AuNPs was initiated by the addition of 1 mL of 1×10^{-3} M ethanolic solution of dalspinin to 5 mL of the freshly prepared aqueous solution of 1.4×10^{-3} M $HAuCl_4.3H_2O$ with constant stirring for 10 min. The color changed from yellow to wine red indicating the synthesis of AuNPs. Dalspinin could act as both a reducing and stabilizing agent in the synthesis process where the spherical AuNPs in a size range of ~10.5 nm were found to be stable for more than 5 months without any aggregation. FTIR analysis indicated the suppression of O-H band at 3408 cm^{-1} in the dalspinin stabilized AuNPs which could be attributed to reduction of Au^{3+} ions coupled with the oxidation of phenolic groups of the isoflavone. An absorption band at 1740 cm^{-1} corresponding to a carbonyl stretching vibration of aldehydic or ketonic groups appeared after completion of AuNPs synthesis. The bioreduced AuNPs showed superior catalytic degradation of Congo Red and Methyl Orange following pseudo-first order kinetics, with a rate constant of 4.5×10^{-3} s^{-1} and 1.7×10^{-3} s^{-1}, respectively.

Guo et al. (2015) reported the synthesis of AuNPs using the *Eucommia ulmoides* bark extract. Various parameters (such as the concentration of reactants, pH of the reaction mixture, temperature and the time of incubation) played a critical role in controlling the synthesis of AuNPs. The ratio of 0.5 mM $HAuCl_4$ against the 2 mL plant extract was chosen as the optimal concentration of reactants while an optimal pH 9.0 and temperature 50°C were found to be most suitable for the complete synthesis of AuNPs within 30 min. The average size of the phytogenic AuNPs was 18.2 nm, while TEM analysis also showed the presence of AuNPs with a smaller diameter (16.4 nm). Biogenic AuNPs followed a pseudo first-order reaction kinetics with a rate constant of 0.390 min^{-1} and 0.500 min^{-1} for the degradation of model azo-dyes, Reactive Yellow 179 and Congo Red, respectively.

Similarly, various metal nanostructures like AuNPs, AgNPs, and CuONPs synthesized by plants such as *Garcinia indica* Choissy, *Mussaenda erythrophylla, Plumeria alba, Ruellia tuberosa, Sterculia acuminata, Viburnum opulus* L., etc. could effectively degrade various hazardous dyes as seen in Table 25.1 (Desai et al. 2018; Varadavenkatesan et al. 2016; Mata et al. 2016; Vasantharaj et al. 2019; Bogireddy et al. 2015; David and Moldovan, 2020).

Table 25.1 Biologically synthesized nanoparticles for dye degradation.

Organism	Mode of synthesis	NPs	Size (nm)	Shape	Dye	% Degradation	Reference
Bacteria							
Bacillus amyloliquefaciens	Extracellular	TiO_2NPs	22.11–97.28	Spherical	Reactive red 31	75.83-99.98	Khan and Fulekar, 2016
Bacillus marisflavi	Extracellular	AuNPs	10-50	Spherical	Congo red	98	Nadaf and Kanase, 2019
					Methylene blue	88	
Erwinia herbicola	Extracellular	SnO_2NPs	10–42	Spherical	Methylene blue	93.3	Srivastava and Mukhopadhyay, 2014
					Erichrome black T	97.8	
					Methyl orange	94	
Escherichia sp. SINT7	Extracellular	CuNPs	22.33 - 39	Spherical	Congo red	97.07	Noman et al. 2020
					Malachite green	90.55	
					Direct blue-1	88.42	
					Reactive black-5	83.61	
Leuconostoc lactis KC117496	Exopolysaccharide mediated	AgNPs	30-200	Spherical	Methyl orange and Congo red	-	Saravanan et al. 2017
Lysinibacillus sp. ZYM-1	Intracellular	SeNMs	3.8 - 200	Spherical, cubical, irregular	Rhodamine B	-	Che et al. 2017

Table 25.1 Biologically synthesized nanoparticles for dye degradation. *Continued*

Organism	Mode of synthesis	NPs	Size (nm)	Shape	Dye	% Degradation	Reference
Fungi							
Aspergillus niger L3	Xylanase mediated	AgNPs	18.11-77.49	Spherical, cylindrical, oval	Malachite green	78.97	Elegbede et al. 2018
					Methylene blue	25.30	
Aspergillus sp. WL-Au	Cell free extract	AuNPs	4-29	Spherical	4-nitrophenol	-	Shen et al. 2017
Cladosporium oxysporum AJP03	Cell free extract	AuNPs	40-60	Quasi-spherical	Rhodamine B	-	Bhargava et al. 2016
Cordyceps militaris	Cell free extract	ZnONPs	10.15	Flower like	Methylene blue	97	Li et al. 2019
Trichoderma longibrachiatum L2	Xylanase mediated	AgNPs	15.21-54.03	Spherical, cylindrical, oval	Malachite green	78.97	Elegbede et al. 2018
					Methylene blue	25.30	
Algae							
Caulerpa racemosa	Aqueous extract	AgNPs	25	Spherical	Methylene blue	-	Edison et al. 2016
Caulerpa serrulata	Aqueous extract	AgNPs	10±2	Spherical	Congo red	-	Aboelfetoh et al. 2017
Chlamydomonas reinhardtii	Cell free extract	CdSNPs	5	Spherical	Methylene blue	90	Rao and Pennathur, 2017
Padina gymnospora	Cell free extract	AgZnONPs	20-40	Spherical and grain shaped	Methylene blue	85	Rajaboopathi and Thambidurai, 2018

Table 25.1 Biologically synthesized nanoparticles for dye degradation. *Continued*

Organism	Mode of synthesis	NPs	Size (nm)	Shape	Dye	% Degradation	Reference
					Reactive blue 198	95	
Padina tetrastromatica	Aqueous extract	AuNPs	11.4	Spherical	Eosin yellow	96	Princy and Gopinath, 2018
					Congo red	92	
Sargassum myriocystum	Aqueous extract	AgNPs	20 ± 2.2	Hexagonal	Methylene blue	98	Balaraman et al. 2020
Plants							
Alpinia nigra	Leaf extract	AuNPs	21.52	Spherical	Methyl orange	83.25	Baruah et al. 2018
					Rhodamine B	87.64	
Artocarpus heterophyllus	Leaf extract	ZnONPs	15-25	Hexagonal	Rose Bengal	80	Vidya et al. 2016
Colocasia esculenta	Rhizome powder	AgNPs	57-85	Spherical	Methyl orange	97	Ismail et al. 2018
					Congo red	96.9	
					Methyl red	96.29	
					Rhodamine B	97.78	
Dalbergia coromandeliana	5,7-dihydroxy-6-metoxy-3′,4′methylenedioxy-isoflavone mediated	AuNPs	10.5	Spherical	Congo red	-	Umamaheswari et al. 2018
					Methyl orange	-	
Eucommia ulmoides	Bark extract	AuNPs	16.4-18.2	Spherical	Reactive yellow 179	-	Guo et al. 2015
					Congo red	-	

Table 25.1 Biologically synthesized nanoparticles for dye degradation. *Continued*

Organism	Mode of synthesis	NPs	Size (nm)	Shape	Dye	% Degradation	Reference
Garcinia indica Choissy	Fruit extract	AuNPs	20-30	Spherical	Methylene violet	89.17	Desai et al. 2018
Mussaenda erythrophylla	Leaf extract	AgNPs	88	Spherical	Methyl orange	-	Varadavenkatesan et al. 2016
Plumeria alba	Flower extract	AuNPs	15.6 ± 3.4 to 28 ± 5.6	Spherical	Methylene blue	-	Mata et al. 2016
					Eosin yellow	-	
					Methyl red	-	
					Congo red	-	
					Ethidium bromide	-	
					4-nitrophenol	-	
Ruellia tuberosa	Leaf extract	CuONPs	20-100	Nanorods	Crystal violet	-	Vasantharaj et al. 2019
Sterculia acuminata	Fruit extract	AuNPs	9.37 - 38.12	Spherical	4-nitrophenol	-	Bogireddy et al. 2015
					Methylene blue	100	
					Methyl orange	100	
					Direct blue 24	100	
Viburnum opulus L.	Fruit extract	AgNPs	16	Spherical	Carmoisine	48	David and Moldovan, 2020
					Tartrazine	26	
					Brilliant blue FCF	97	

25.6 Conclusions and future perspectives

Nanotechnological progress has revolutionized wastewater treatment. Various nanoadsorbents, zeolites, nanoimpregnated membranes are used for the effective removal of contaminants from the industrial effluents. Although physicochemically fabrication process for nanoparticles are largely available, biologically generated nanoparticles have become an attractive alternative. Therefore, bacteria, fungi, algae, and plants are being explored continuously to remove hazardous dye contaminants from waste water. Biological processes are not only safe but rapid and effective. Previously, living or dead microbes and plants were used for bioremediation and phytoremediation, respectively, for dye removal. But these processes face the difficulty of the disposal of a biomass after the biosorption process. Hence, biogenic nanoparticles effectively overcome this problem due to their reusability and recyclability.

The major disadvantage of the biogenic processes is the control over the size and shape of the nanoparticles. Physical and chemical properties of nanoparticles are largely dependent on its size and shape. Hence, there is a critical need to optimize process parameters like reaction time, temperature, pH, agitation, biomass or extract concentration, metal salt or precursor concentration, etc. in order to ensure monodispersed nanoparticles with well defined size and shape. The synthesis with individual active metabolites responsible for reduction and stabilization, isolated from the biological source instead of using the whole extract, can have control over synthesis.

Genetically modified microbes with enhanced production of selective reducing agents and capping agents might help to generate microbial cell factories for nanoparticle synthesis. Similarly, bioreactor base optimized process should be developed to increase the yield of the nanoparticles in order to use it successfully for large-scale water treatment processes. Simultaneously, effective downstream processes must be designed to ensure that the properties, shape and size of the nanoparticles are not altered during recovery due to agglomeration.

Various dye degrading enzymes like azoreductase, laccase, peroxidase and oxidase from bacteria such as *Pseudomonas* sp., *Bacilus subtilis*, *Geobacillus* sp., *Escherichia coli*, *Rhabdobacter* sp., *Enterococcus* sp., *Staphylococcus* sp., *Corneybaterium* sp., *Lactobacillus* sp., *Xenophilus* sp., *Clostridium* sp., *Acinetobacter* sp., *Micrococcus* sp., *Dermacoccus* sp., *Rhizobium* sp., *Proteus* sp., *Morganella* sp., *Aeromonas* sp., *Alcaligenes* sp., *Klebsiellla* sp., *Shewanella* sp., and *Alishewanella* sp. are secreted during the early stationary phase of microbial growth. These enzymes can further be considered for functionalization on the surface of biogenic nanoparticles for designing bio-nano hybrids for water treatment plants.

Thus, biogenic nanoparticle mediated dye degradation may be considered as a powerful strategy to fight against the deadly issue of environmental pollution from toxic textile dyes. It has significant potential to address the challenges of industrial wastewater treatment due to its eco-friendly, inexpensive, and less sludge producing nature.

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CHAPTER

26 Removal of emerging contaminants in water treatment by nanofiltration and reverse osmosis

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26.1 Introduction

Emerging contaminants are organic compounds found in the commercial products used in large quantities in everyday life, such as pharmaceuticals, pesticides, antibiotics and biocides, personal care products (PCPs), surfactants, nanomaterials, etc. Their widespread presence in low concentrations in effluents and mostly in the aquatic environment has recently become an environmental problem, and the public has conveyed human-health concerns regarding the occurrence of these contaminants in water reuse projects. Some of them are extremely persistent. For others, the high degradation rate has been counter balanced by their endless introduction into the aquatic environment. Though the health effects of the consumption of these micropollutants at low concentration levels as of yet have not been fully elucidated, it is agreed that drinking water should be almost free of such compounds. It's therefore crucial to prevent the emerging contaminants from entering the environment, or to decrease significantly their concentrations by sufficient treatment methods. As conventional water treatment processes generally imply to be ineffective in the removal of emerging contaminants, advanced methods such as membrane processes, carbon adsorption, and oxidative treatments should be used for this purpose. The capability of membrane separation processes, specifically reverse osmosis (RO) and nanofiltration (NF), to remove aqurately and economically several substances makes them a accepted choice for removal of the emerging contaminants from water. For almost 30 years, Membrane separation processes have been used in drinking water treatment and in the past decade they have been progressively applied in process water and wastewater treatments, especially where extreme quality standards of a product are required. The effective removal of organic compounds from various waters by NF/RO has been a major challenge for membrane scientists, as confirmed by the frequent studies that have been recently reviewed (Bellona et al., 2004, Hilal et al., 2004). These studies examined the removal of different solutes and parameters that influence

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the removal, and contributed to better understanding of membrane retention mechanisms. The main stream of the studies on the removal of conventional pollutants from several waters by NF/RO were limited to some targeted compounds and they usually covered binary aqueous solutions and synthetic model waters. Wastewaters as a rule contain a huge sort of organic micropollutants in very low, submicrogram per liter concentrations. Hence, in studying the denial efficiency of NF/RO membranes in removing organic micropollutants, experiments should be conducted at environmentally truthful concentrations (Kimura et al., 2003), and using the recently advanced analytical methods efficient of determining many trace compounds present in wastewaters. With such a peculiarity in mind, it seems natural to reconsider the conclusions and general rules that were obtained and established in the plentiful studies on removal of conventional pollutants from waters by RO/NF.

26.2 Emerging contaminants in water

The number of chemical groups constituting ECs is large and continue to grow as new chemicals are recognized to be part of this classification. Richardson and Ternes (Richardson and Ternes, 2011) include In their biannual review of ECs in water, a wide diversity of compounds to the EC group, such as pharmaceuticals, pesticides, antibiotics and biocides, personal care products (PCPs), surfactants, nanomaterials, endocrine disrupting compounds (EDC), human and veterinary drugs, textile dyes, etc. With progression in the chemical industry, the variety of compounds being discharged to the environment which are potentially harmful to humans and the ecosystem over the long-term is expected to grow knowingly over the years. Over the years, researchers have shown an increased interest in investigating ECs, but little agreement exists on the list of substances that should be investigated.

26.2.1 Pharmaceuticals

Important group of ECs are the pharmaceuticals and their presence in drinking water has generated significant concerns regarding the risk of estrogenic and other adverse effects on humans and fauna. The prescribed and nonprescribed drugs for humans and Veterinary use and their metabolites are referred as pharmaceuticals. Human excretion, veterinary usage and disposal of unused products are included as the primary routes of entry into the environment. Veterinary medicines use many antibiotics, which are not merely used for therapy, but are added to the water for promoting animal growth by ending up in drinking water and surface water. The bodies of humans and animals excrete these antibiotics as active substances up-to 30%–90% as per the estimation. Including painkillers, antidiabetics, beta blockers, lipid regulators antibiotics, antidepressants and impotence drugs, approximately 3000 different substances are used as pharmaceutical ingredients. Presence of pharmaceuticals has also increased in surface water, wastewater, ground water, and stormwater runoff in urban areas due to its large scale use.

26.2.2 Pesticides, antibiotics and biocides

The development of bacterial resistance after their release into the environment is a major concern in relation to pesticides, antibiotics, and biocides. These also causes detrimental effects on the biodegradation of plant materials, which disrupt the primary food chain in aquatic ecosystem. The chemicals used for agricultural purpose are referred as pesticides, whereas the chemicals used in urban activities are known as biocides (Margot et al., 2015). Biocides are used for grass management, weed control in bituminous roof ceiling membranes and external facades. Pesticides and biocides are incorporated in surface water and ground water via storm water runoff, during the rain event. Extensive use of pesticide is done in agriculture and forest tree, parks, horticulture public spaces, industrial sides educational facilities, golf courses, etc., and are typically used for industrial vegetation control, grass management and public health (rodent - control areas and mosquito abatement).

26.2.3 Personal care products

These substances applied externally in the human body are known as PCPs, and are the diverse group of common household substances used for health, beauty, and cleaning purpose. PCPs do not undergo any metabolic changes prior to their release into the environment due to their external body applications. Different sub group of PCPs include musk fragrances, sunscreen agents, insect repellents antimicrobial compounds, and preservatives. Nitro and polycyclic musks are the two widely used musk fragrance almost all consumer products have these substances. Urban environment consists of these chemicals widely and include fragrances, insect repellents, sunscreen, and antifungal agents (Pal et al., 2014). They are easily removal into the environment as they are designed for external usages and no metabolic changes occur in their chemical structure. In recent years their presence in urban run off and ground water has also increased significantly.

26.2.4 Surfactants

In wide range of application surfactants are used as chemicals including the production of detergents, paints, pesticides, resins, lubricants, etc. Surfactants can be classified into anionic, cationic, nonionic, and amphoteric. Surfactants on the basis of dissolution in water (Hamza et al., 2016). Anionic surfactants segregate into an amphiphilic anion (exhibiting both lipophilicity and hydrophilicity) and cation, such as lawryl sulfate, dialkyl sulfosuccinate, alkyl benzene sulfonate, and lignosulfonate. Hydrophilic group of nonionic surfactants is nondissociable type as they do not ionize; as such they do not react with magnesium and calcium in water. Ethoxylated aliphatic alcohol, polyoxypropylene glycol, and carboxylic esters are the few examples of nonionic surfactants. Quaternary ammonium salts is the example of cationic surfactants dissociates in water into am amphiphilic cation and anion. Cationic and anionic dissociations are exhibited by the amphoteric (or zwitterionic) surfactants, such as sulfobetaines, betains, and phospholipids. Polymeric surfactants

(or surface active polymer) are recently introduced and are used in the production of food stuffs, paints, cosmetics, and petroleum production additives extensively. The association of one or several macromolecular structure exhibiting hydrophilic and lipophilic characters, either as separated blocks or as gerafts results into polymeric surfactants. As a result of domestic use (house cleaning), industrial uses (detergents, textiles, petrochemicals, and pharmaceuticals industries) and urban uses surfactants find their way into the environment. Around 50% of surfactant production is emitted through WWTPs into surface water is estimated. Before reaching to the environment some of these surfactants biodegrade to nontoxic compounds , concerns have been raised for alkylphenol ethoxylates (APEs) and their degradation products as potential endocrine disrupters. Biotransformation of APCs can be done into alkylphenols. Example 4 nonylphenol and 4 terto ctylphenol. Surfactants retain their foaming properties in natural water in concentration as low as 1 mg/L which is undesirable in drinking water.

26.2.5 Nanomaterials

Functional materials consisting of particles with at least one dimension below 100 nm are the nanomaterials. Due to their possession of unique electronic, mechanical, biological, and thermal properties not found in conventional materials NMs are the core of an emerging technological revolution [9]. Comparatively, the properties of NMs are different from the bulk material. Silver NMs shows different antibacterial activity which does not exist in silver. Sub-groups of NMs are metal based. NMs, fullerenes, carbon nanotubes and organic NMs. Titanium oxide, iron oxide, zinc dioxide, etc. are the examples of metal-based NMs, which are used in the production of sunscreen, cosmetics, surface coating, and some food products. Production of micronized drugs and chemicals (pharma, pigments, and vitamins) as well as polymers dispersion use organic NMs. Issue about risk of the possible release of NMs into the environment and finally impact on human and environmental health have taken the front burners, due to the growing use of NMs. Looking at the above group of ECs, the use of surfactants, PCPs, will not decline; pharmaceuticals will be continuously produced and administered on humans and animals; pesticides will be in continuous use; industries will continue to use chemicals for their daily activities and nanotechnology will maintain its improvement. This will lead the search for a dynamic technology for their removal a very pressing issue.

26.3 Reverse osmosis and nanofiltration

Feed water is forced through a membrane by high pressure exerted on its membrane side and separated into two streams; permeate and retentate (concentrate), is pressure driven membrane processes. The obtained two streams are having widely different solute concentration, the permeate is almost pure water and the retentate have all the suspended particles and mostly dissolved component of feed water. A

goof separation membrane have an asymmetric (anisotropic in vertical cross section) structure with a thin dense selective layer on the membrane surface, which is supported by the much thicker porous layer made from same or different material, as was firstly engineered by Loeb and Sourirajain (Loeb et al., 2021). Cellulose acetate was used to make first successful membranes, afterwards various polymers and their combinations known as composite membranes built from the other cellulosic, aromatic polyamides, polysulfide, polyether sulfone, polyacrylonitrile, polyvinylidenefluoride, and inorganic materials such as ceramics were used. There are four pressure driven membrane processes according to the properties (porosity and electrical charge) of the membrane used; nanofiltration, ultrafiltration, microfiltration, and reverse osmosis. Larger or smaller dissolved particles, ions, and molecules are removed from water in nanofiltration (NF) and reverse osmosis (RO), layer suspended particles are retained on the membrane in microfiltration (MF), and smaller suspended particles and colloids are separated out in ultrafiltration (UF). The use of membrane of various pore sizes is required for adequate operating pressures. So the applied transmembrane in membrane operation also represents the kind of membrane process. Membrane selection and economical arguments in the process are very important. For example, it is sometimes better to use a ore tight reverse osmosis membrane than to use a reliable nanofiltration membrane at slightly less than maximal possible solute denial and at appreciably lower operating pressure to save energy. The basic difference between an NF and a RO membrane is in their denial of ions, as the porosity range of nanofiltration membranes skin (approximately 0.5 - 2 om) does not significantly differ from porosity range of the reverse osmosis membrane skin (approximately 0.2-1 nm). It is regular for NF membrane to reject almost completely and multivalent ions with the hold of univalent ions which is less than 70%n ions hydrate size mostly governs the denial of different ions by a RO membrane which varies less. There is no clear boundary between the denial of nanofiltration and reverse osmosis membrane in case of organic molecules so in this contribution they will be considered together as NF/RO membranes. Plenty of work has been done on the formation of the advanced selective and productive membranes. On solving the solute permeation mechanism through a membrane and a selected application of the membrane process during more than 30 years of reverse osmosis and nanofilteration usage for the water treatment purpose. Now also, there are unsolved problems & uncertainly concerning mostly the retention mechanism of different solutes and their modeling in case of NF/RO membrane. Some researcher's early expectations & efforts to find a membrane that would completely reject solute molecules and ion was apparent. For the production of pure water non process of membrane separation is there. Membrane is a physical barrier, which allows pervasion, with in a driving force, of more or less of each of the feed mixture components, with solutes than water. Hence that permeate will always have traces of the solutes from the feed, i.e; a truly semi permeable membrane does not exist. One of the inventor's (Sourirajan and Matsuura, 1985) of the first asymmetric membrane – S. Sourirajan stated that "The word semi permeable contributes nothing to the scientific understanding of reverse osmosis.

26.3.1 Predictive modeling of reverse osmosis and nanofiltration

Experts have tried early to find theoretical expression and equations that would describe and predict solute denial by the NF/RO membranes as well as parameters affecting the separation process, in the research on the membrane separation process performance. These useful theoretical expressions called as models would be based on solutes to be rejected and on membranes available characteristics. A acceptable agreement of the data calculated by experimentally obtained theoretical equation would be given by a successful model. The description of the NF/RO membrane itself is a basic problem in modeling. The NF/RO separation process; is it a homogenous or it is a porous phase. How can hydrodynamic and charge interaction inside very, narrow pores (voids) can be described? If NF/RO an intermediate between porous and nonporous type barrier as described by Mulder (Fried, 1996). As a result of this ambiguity for the process of solute separation by NF/RO membranes various models are proposed. Means of irreversible thermodynamics was used in earlier attempts to describe mass transport through a membrane. The equations on material transport through a membrane considering membrane system as whole (without specific perimeters) which behaves as a black box was developed by Kedem and Katchalsky (Kedem and Katchalsky, 1963) and Spiegler and Kedem (Spiegler and Kedem, 1966). Hence in this approach the basic physical properties like membrane pore structure, change density and a mechanism of solute transport were not defined. The membrane separation mechanism is find out by both the surface effects and fluid transport through the pores, by the surface force-pore flow mode,l which quantitatively shows the motion that the membrane separation mechanism. Preferentially the membrane's capillary pores is forced through absorbed water on the membrane surface, potential gradient chemically undergoes diffusion by the applied pressure and solute molecules were transported. Earlier, the base idea of dissolution of solute molecules in a barrier membrane and then by their diffusion through it, were model proposed for RO called solution. Recently such models were reviewed and modified, involves intermediate steady – state or unsteady – state organic solute adsorption. To study organic membrane interaction changed models were allowed for the understanding, the model uses hydrodynamic approach and states the transport equations based on the model assumption. Suppose a geometrical model of the membrane and solutes (size, shape, and charge of the membrane pores and of the solute molecule). One such model considered a porous membrane, the transport of rigid solute molecules occurs hindered by steric interaction as bunch of a narrow cylindrical pores due to molecules fiction in the hindered space of the pores. Let be the point charges, in the case of the charged NF membrane and transfer of the charged particles, Nernst - plank equation further transfer along pores is explained. When surface charged density is small and pores are sufficiently narrow, such space charge models and their changes were found applicable for the narrow pore NF membrane. Recently Vander Brugger and Vandecaste (Agenson et al., 2003) proposed a porous membrane model based on Spiegler - Kedem transport equation by NF membranes the flux of uncharged. Organic from pores sixe distribution, retention curves were known. The experimental membrane water flux and diffusion parameter of the membrane was

found by examining. For calculations, the molecular weight values related to the effective solute diameters were used. As an appropriate sixe parameter was needed. The membrane nanofilteration was assessed by Bowen and Wellfoot (Bowen and Welfoot, 2002) critically on previous theoretical descriptions. Latest two parameter model (pore radius and membrane charge) found electrolyte denial and energy hindrance to the ion parting into pores, it involves dielectric exclusion in that form. In ion absorption, the predicted value of effective membrane charge density were knowingly reduced in magnitude and better agreement with physical models, its variation with concentration for divalent salts. Mass transfer of some groups of solutes through certain membranes can be predicted more or less successfully by applying each one of the models but for the NF/RO separation process selection of appropriate modeling approach is difficult task. Denial by the NF/RO membranes and the promising result by the proposed modeling efforts. The knowledge need which is essential for the truly successful prediction model is still limited, regardless of the abundant studies of the organic solutes. Thereupon "To the development of the prophetic model through understanding of the procurators affecting the mass transfer of solute through high pressure membrane is priceless" though statement was made by Bellona et al. in their review (Bellona et al., 2004). With this concern a belief was expressed by the authors that "an assessment of the knowledgebase regarding the procurators affecting the solutes transfer through NF/RO membrane was useful". One of the complex denial mechanism of a solute by NF/RO membrane is a main question that should be answered, which would consider the particular physical properties of the solute and the membrane.

26.4 Solute denial mechanism by the nanofiltration/reverse osmosis membrane

The basic mechanism regulating the denial of various solutes by the NF/RO membrane is discussed in this portion of the paper.

- Size exclusion (sieving, steric effects), &
- Charge (electrical, Danna) exclusion
- Denial regulated by physicochemical intercourse between solvent, membrane and a solvent

There is always an intercourse among these effects in reality, though in many chances one of them lasts. Certain denial mechanism are quite well illustrated; for instance, physical sieving is the major denial mechanism of solutes bigger than the membrane pore size.

In case of inorganic ions as solute the other mechanism of denial like charge exclusion are known to overpower. Still the denial of ionizing organics by the charged NF membranes is not clearly grasped, along with the necessary adsorptive and hydrophobic inter relationship among membrane and solute, operative in uncharged organic denial.

26.4.1 Size exclusion

The basic mechanism controlling the denial of organic solutes by a NF/RO membrane is size exclusion. Pore size is smaller than solutes so cannot allow the solute to permeate through it data on spherical size of the solute molecule and data on the diameter of the cylindrical pores of various membrane would be the knowledge by the assumption for this mechanism both actual complex quantities should be more clearly described because as such simplified assumption in reality do not hold each b of these quantities are representing by several parameters and before their use the explanation of method of their determination together with their significance is necessary. By some other size and morphology parameters like molecular width or molecular length, by the stocks (hydrodynamic or solvated) diameter or by the effective molecular size (which takes into account the shape of the molecule), by its diameter, by its molecular mass the size of a solute molecule can be expressed. For all the solutes, molecular weight is available and its was shown, that with the molecular weight the denial of a number of undissociated organic compounds by the ultra-low pressure RO membranes increases linearly. Vander Brugger et al (Vander Bruggen et al., 1999) asserted that for nanofilteration, the molecular weight is not a suitable size parameter because the geometry of molecules does not represent by it. However if correlations between effective diameter and molecular weight is determined, it might be used (WR et al., 1997). The data on the crystal ionic radia as the size parameter for inorganic ions are available. Ions in aqueous solution are more or less hydrated so for the comparison sake, the crystal ionic radia can be used only approximately, in case of ionic transport through a membrane. The size of hydrated ion should be considered listed in article. The size of tiny organic molecule defining by a quantity more accurately should take into account the molecular shape and its structure. On the basis of stimulated molecular structure by calculation this can be done Van Bruggen et al. (Vander Bruggen et al., 1999) by using an energetic optimization procedure from molecular structure and shape calculated the effective molecular diameter. Later on, for described the retention behavior of an organic compound calculated hydrated diameter might be a letter parameter noticed by him as defined by kiss et al. (Kiso et al., 2001) and used by Agenson et al. (Agenson et al., 2003) by the molecular length and molecular width. The morphology of the solute molecules is described distance between the most distant atoms in the molecule was determined as molecular length, half of the square root of the surface area of the rectangle enclosing the projection of the molecule on a plane perpendicular to the axis of the molecule by this the molecular width was calculated; such as, the most distant atom connecting by the straight line stokes law diameter calculated from the solutes diffusivity (Singh et al., 1998, Khayet and Matsuura, 2003, Bowen and Mohammad, 1998, Yoon and Lueptow, 2005) is often used size parameter. Hydration layer of the molecule shape might include the stokes law diameter assumed sometimes interaction with other molecules (natural organic matter) and changes in the solution chemistry affecting the geometry of a solute molecules are additional factor that influence the size of a molecules (ion). According to the size exclusion mechanism for the meaningful analysis of the solutes denial by a membrane. A membrane pore

size is second quantity which is necessary. The needed quantity is the pore size of the membrane's skin, the asymmetric membrane structure and its determination is not simple. By the models either as narrow cylindrical as bundles of straight pores of the voids between the closed packed sphere of equal diameter, the membranes morphology, skin structure and porosity have been usually described defining the water flux. To through a membrane that is proportional to the applied pressure. Because of skin morphology and structure in reality deviate from their simplified descriptions, hydrodynamic models with the idealized pores could not fully explain experimental data on size exclusion. As material free void space in a dense polymer membrane layer through which fluid transport takes place under a driving force so the pores in the membranes skin should be better envisaged. By the irregular packing of almost randomly kinked stiff-chain polymers, narrow voids or density defects form naturally in solid polymer. Through the membranes skin for the solute and solvent molecules the active voids consequently represent continuous tortuous paths by the geometry along with the tortuous path network and the pore shape, the real size of open, active pores is mostly given. So in the membranes skin, there is always a distribution of pore size. So far in direct experiment could not be measured of the porosity of such specific structure of the vs skin atomic force microscopy (AFM) is often used for characterization method in recent works on surface morphology (i.e roughness) it gives primary information, i.e, not about the size of pores in the skin but tells about the size of pores on the membrane surface (Hilal et al., 2004, Bowen and Doneva, 2000, Hilal et al., 2005). By the solute transport methods (Singh et al., 1998, Khayet and Matsuura, 2003) the porosity of the membranes skin has to be determined indirectly, the minimal size of void constriction present along the voids open to flux this is allow to finding by these methods. Very tiny void dimension of the membranes skin is obtained by this method which is smaller than the surface void sizes. The pore size distribution (PSD) in the skin layer the membrane molecular weight cutoff (MWCO) and the effective membrane pore radius (RP) all skin pore size parameters can be easily described. Matsuura et al. (Singh et al., 1998, Khayet and Matsuura, 2003) by using the transport data of polyethylene glycol and polyethylene oxides of various molecular weights as the standard compounds used for the MWCO determination by determining their pore size and PSD characterized the membranes thin layer porosity. Kosutic and Kunst (Kaštelan-Kunst et al., 1997, Košutić and Kunst, 2002) by the RO & NF membrane based on denial of several disk like markers mostly cyclic ethers determined the membranes PSD. Yoon (Yoon and Lueptow, 2005) using a model of steric interaction of hard spheres in the cylinder pores (Boussu et al., 2021) & estimated the effective pore radia for the membranes. Nghiem et al. (Nghiem et al., 2004) from the retention data of inert organic markers of various molecular masses he determine the various pore size. Steric exclusion and hindered convection and diffusion. Boussou et al. (Boussu et al., 2021) with 6 organic compounds by the MWCO obtained from filtrations experiments characterized the examined membrane porosities and with the log-normal model fitting the retention curve. Kimura et al. (Kimura et al., 2004) emphasized since properties of standard compound used for MWCO determination and those of target compounds might be remarkably different;

however the MWC cannot be used for precise prediction of denial by RO membranes on the retention for the molecules having a molecular weight below the MWCO, does not provide information.

26.4.2 Charge exclusion

Charge exclusion method is use instead of nanofilteration membrane. The solutes which are inorganic ions for that the method was invented and examined. Due to presence of electric current, these methods contains ion in solutes. The ions are present in the form of sulfonic, carboxylic, and ammonium groups which are bonded tightly to the near layer of the NF membrane. When the aqueous solution was placed the opposite charged ions are separated from their functional groups. On the basis of pH, the membrane charge is negative due to the separation of SO_4^- & $COOH^-$ groups from the membrane layer. Zeta potential measurement are used to measure the layer charge of a NF membrane, the pH require for the quantified was pH between 6–8. The pH value was required for the NF membrane was 3–4. The zeta potential values changes with pH value as well as isoelectric point. If the membrane was negatively charged then the membrane layer knows the denial of dissolved ions. The anions are repelled while the cations are attracted with the membrane. The charge exclusion method was based on the electrochemical laws such as, Donnan effect, the Nerst-plank equation & the general principle of conserving electro naturally across a membrane. The electrolyte permits the rate of positive and negative ions transport with the inter diffusion coefficient. The charge exclusion method is simple, so the less inorganic ions results its basic postulate. So multivalent ions are easily separated in the charge exclusion method. Due to the semi permeability of membrane, the ions are attached in tightly condition in nanofilteration membrane, due to its porosity so it is based on size. Two methods completely divided, was a debate for the experimental results.

26.4.3 Physiochemical interaction

By physiochemical properties of the system, the denial of uncharged organic solutes by NF/RO membrane is frequently controlled, in addition to size and charge exclusion mechanism. Among membrane material, water molecule state (general concept of physiochemical interaction) quoted effect example solute adsorption on and in the membrane, to hydrogen bonding between membrane and solutes or too often connected to hydrophobic nonspecific interactions the solute denial by a membrane influence by the solute molecular polarity expressed by its dipole moment and in the aqueous solution the equilibrium between ionized & non ionized species, by physiochemical factor affect the organic denial by the RO/NF membrane also by solute dissociation constant value (pKa). Sourirajan and Matsaur (Sourirajan and Matsuura, 1985) in their fundamental work postulate that at the membrane solution interface by the physiochemical phenomena the membrane separation effect is governed mutual interaction arising from short range force depending on the contribution of polar, Steric and non polar character of the non-ionized membrane material, solvent and

solute involved; this is a preferential sorption of water solution at the interface. Polar or nonpolar or both the nonionized organic molecules polar groups and less-polar groups back bone contain aromatic polyamide chains and water is polar solvent I, different pollutant molecules same membrane material and some solvent if contain by the system the indication of the relative values of mutual interaction by the polarities of the latter means to express quantitatively the polarity of a non-ionized solute molecules are;

- The basicity or acidity value of the solute molecules, and
- For the solute molecule the Taft or the Hammet numbers.

This means that the adsorption properties of the inspected compounds in the membrane were measured by the hydrophobic relations. Validity of the log KO/W value reflecting hydrophobic interactions between membrane and solute, is established by Van Bruggen et al. (Vander Bruggen and Vandecasteele, 2001, Vander Bruggen et al., 2002, Van der Bruggen et al., 2002) and presented that its value links well with adsorption on the membrane for molecules with a molecular weight below the molecular weight cut-off of the membranes, and also adsorption of organic molecules from an aqueous solution on the membrane surface in the pores may result in additional effects such as the membrane flux decline. The further of a given component is adsorbed on the membrane, the larger the membrane's flux decline. Flux decline occurs by a combination of two effects: the molecule should have the suitable size to fill the membrane pores, and the adsorption process is boosted by the hydrophobicity of the component. The membrane flux decline actually points out to the phenomenon of membrane entangling which is partly caused by the adsorption of the organic compounds on the membrane. A good connection was found between the hydrophobicity and the retention: the hydrophobic molecules usually had a minor retention, while hydrophilic molecules exhibited a higher retention. This was credited to an influence of the solute hydrophobicity on the molecule hydration, and via its hydrated, effective size on the solute denial. Hydrophobic compounds have less polar groups and are less solvated. Because of their lesser size, they can effortlessly enter the membrane pores and permeate the membrane. Hydrophilic molecules usually have more OH or O groups, which can form hydrogen bonds with the water molecules. Because of such advanced affinity with the water phase, hydrated hydrophilic molecules are larger permeating in a smaller amount through the membrane structure. Flux decline effect and its relevance at low feed concentrations, at the sub microgram per liter level is investigated by Kimura (Kimura et al., 2003, Kimura et al., 2003). Below such circumstances the adsorption of hydrophobic compounds in the membrane pores could chief to an overestimation of the retention. The adsorption of hydrophobic solutes donates to denial but the adsorption volume of a membrane is finite. Hence, an accurate calculation of the denial of the hydrophobic compounds is possible when the adsorption symmetry of the membrane with the compounds of curiosity is attained. Hydrophobicity of the solute also brings about the development of the permeate concentration, showing a reduction of the solute retention as a purpose of time and because of the solute adsorption on the membrane surface or within

the membrane pores. The denial of hydrophobic compounds at greater concentrations declines until saturation of the membrane was reached and this retention value was called as "steady-state retention". Another physicochemical property, that could influence a denial by the NF membrane is the solute polarity expressed through its dipole moment. The uncharged molecules with the great everlasting dipole moment (above 3 Debye) were revealed to exhibit minor retentions than the molecules of approximately same size but with lower dipole moments. The effect was described by the desirable alignment of polar molecules concerning the charged membrane surface. The polar molecule is by electrostatic magnetism directed towards the charged membrane with the side of the dipole having the opposite charge nearer to the membrane pores. Hence the polar molecule arrives more effortlessly into the membrane, resulting in additional polar molecules permeating the membrane related to non-polar molecules of the same size. It was however specified that such a result should be taken with a reserve because of the effect of a solvent on the solute dipole moment. Viz. dipole moments are usually determined in a polar solvents and their values might be dissimilar in aqueous solutions. In listing numerous effects, which have the effect upon the NF/RO membranes denial operating conditions of the membrane system should also be stated. The feed water recovery impacts the denial of solutes. A reduction of denial was detected for a growth in recovery. The advanced recovery would rise the concentration modification across the membrane and consequently the potential of diffusion. Similarly, the denial of some pesticides was reliant on operational flux and recovery. For a specific pesticide the maximum percent denial arisen at high flux and squat recovery, and the lowermost percent denial occurred at squat flux and high recovery, which specified the basic diffusion-control theory. The diffusion control may control a solute denial if the molecule is in a size range where molecular charge, Vander Waal's forces or other surface connections can affect the contact between the membrane surface and the solute molecule during mass transfer. In the former part the important effects influencing organic solutes exclusion by the NF/RO membranes were registered (see, Fig. 26.1).

26.5 Modern findings

Already discussed in the introduction, the general rules and findings on removal of different solutes and conventional pollutants from water by nano filteration and reverse osmosis were obtained in studies finite to some targeted compound and covered mostly binary aqueous solutions and synthetic model water. according to new studies and investigations the organic micro pollutants retention were conducted at an environmentally relalistic sub micrograms per liter concentrations and on waste water containing a great diversity of compounds the mordern findings and general conclusions might deviate from the previously acquired knowledge. Thus modern results and newly planned studies should display to what extent the earlier knowledge can be applied in form to explain the removal of organic trace pollutants from various waters.

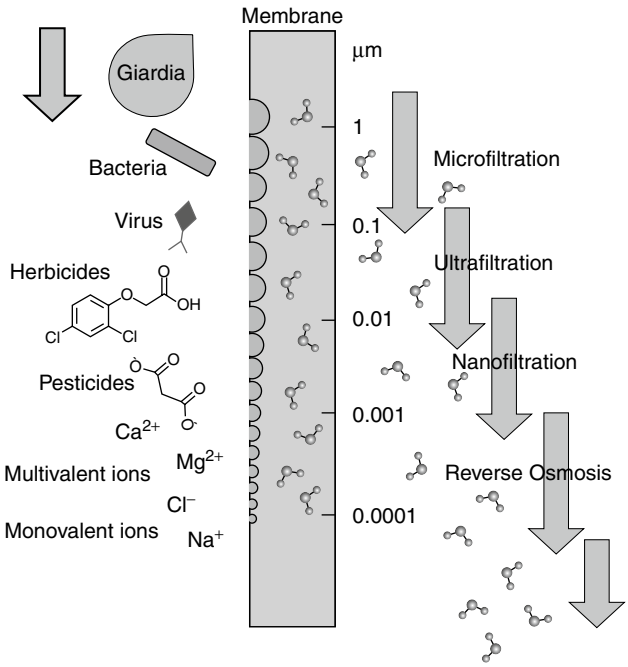

FIG. 26.1 Showing pore size ranges and demonstrative water contaminants removed from every pore size.

To highlight modern findings on the removal of emerging contaminants by the RO/NF, the results in this part are presented in three groups:

1. Removal of Antibiotics
2. The removal of ECs from waste water at low feed concentrations (sub microgram per litre).
3. The Results of the current studies on Organics Removal by NF/RO

26.5.1 Removal of antibiotics

Various new papers noted on the removal of antibiotics, a distinct group of pharmaceutically active compounds, from waters by the NF/RO membranes. The efficiency of the conventional drinking water treatment processes below typical plant circumstances in the removal of seven common antibiotics: carbadox, sulfadimethoxine, sulfamethazine, sulfamerazine, sulfathiazole, sulfachlorpyridazine, and trimethoprim, is calculated by Adams et al. (Adams et al., 2002). Experiments were performed with barbed aqueous solutions prepared from deionized water and water from the Missouri River. The antibiotics were adequately removed by reverse osmosis, sorption on activated carbon, and by oxidation. Again, concentration/deposition with iron salts and alum, surplus of lime/soda ash softening, ultra violet irradiation at

disinfection dosages, and ion exchange were all analogously unsuccessful methods of antibiotic removal. Membrane treatment of the oxytetracycline waste liquor is described by Li et al. (Li et al., 2004). A volume reduction coefficient was 3.5, oxytetracycline in retentate was concentrated more than three times, and oxytetracycline in permeate was decreased from more than1000mg/l to lower than 80mg/l, by using a RO process. A permeate could be then preserved by the biological process, as result of the major reduction in both the organic concentration and antibiotic toxicity. The RO flux capacity did not drop for constant operations, and used membranes could be revive by chemical cleaning. Just because oxytetracycline could not be well cured from the RO retentate by simple crystallization, the further treatment of the RO retentate by ultrafiltration and subsequent crystallization resulted in a recovery percentage of more than 60% and the product purity higher than 80%. Hence, the RO-UF membrane process can be a successful mode for the antibiotic wastewater treatment as well as the antibiotics retrieval from the waste liquor. The removal of antibiotics by NF/RO from two model wastewaters of a manufacturing plant producing pharmaceuticals for veterinary use is explored by kosutic et al. (Košutić et al., 2007). Levamisole, sulfamethazine, sulfaguanidine, trimethoprim, sulfadiazine, enrofloxacin, praziquantel, and oxytetracycline are the used antibiotics. The refusal of the selected RO and the tight NF membranes were tolerably high, enormous in most cases 98%. The loose NF membrane retained the smaller molecules slighter virtually. Reporting the solute denials to the membranes' porosity has shown that size exclusion was the widespread denial mechanism by all membranes. The denial of the low molecular organics by all the tested membranes was lower, ranges between 0.517 to 0.976 for the RO and tight NF membranes, and from 0.247 to 0.506 for the loose NF membrane. They follow the order of the solutes' molecular size, though the distinct physicochemical effects might control the denial of some low molecular organics. Some papers in this field recount on the use of NF/RO membranes in the antibiotics production processes mainly to enhance improvement and pureness of the product all together with a treatment of the process waste waters. These are the papers on separation and purification of benzylpenicillin generated by fermentation (Yakhkind et al., 2021, Tessier et al., 2005).

26.5.2 The removal of emerging contaminants from wastewater at low feed concentrations (sub microgram per liter)

The denial of nominated trace organics and surrogate compounds by NF/RO membranes as a function of their physicochemical properties at primarily very low (100ng/l to100μg/l) micropollutants concentrations in feed water is analyzed by Kimura et al. (Kimura et al., 2003) The experiments showed that charged compounds could be denied to a great extent (i.e., > 90%) disregarding the physicochemical properties of the approved compounds. In contrast, the denial of non-charged compounds was altered mainly by the size of the compounds and was also found that the concentration range of solutes might alter the exclusion ability of a membrane. Examined compounds were picked to cover a certain range of molecular weights and

KO/W. Two membranes made of different materials (polyamide and cellulose acetate) were approved. The analogy of the results showed that the polyamide membrane broadly diplayed superior denials. However, the denial was inadequate, amounting to 57–91%, which could be corresponding to solute molecular weight, approving that the size exclusion leads the retention by the polyamide membrane. In case of the CA membrane, the compounds polarity was better able to define the retention trend of the certified compounds. The results mention that the leading denial mechanism could be distinct depending on the membrane material and the physicochemical properties of the target organic micropollutants. Removal of 52 emerging contaminants from one model water and three surface waters by NF and UF was inspected in the work of Yoon et al. (Yoon et al., 2006). The source waters were spiked with verified compounds at very low concentrations (2–250ng/l). The results showed that all the verified compounds could be divided into two groups: the more polar, less hydrophobic compounds were less reserved than the less polar, and more hydrophobic compounds. While the complete explanations of the retention mechanisms for various compounds could not be given, the authors determined that the retention was administered by hydrophobic adsorption. When the stable-state process is achieved, size exclusion can be leading for solute retention. The retentions of the NF membrane were greater than those of the UF membrane, suggesting that retention was administered by the membranes' pore size. In addition, the retention of solutes seems to be affected by source water chemistry. In extension of the earlier work, the removal of the more polar, less hydrophobic compounds was further investigated (Yoon et al., 2007). Experiments were performed at environmentally relevant solute concentrations ranges between 2 to < 150ng/l. The broad separation trend due to hydrophobic adsorption, was detected. Together size exclusion and hydrophobic adsorption mechanisms were operative at the solutes' retention by the NF membrane, while the UF membrane retained typically hydrophobic solutes owing mainly to the hydrophobic adsorption was again shown in the results. Efficacy of membranes and activated carbons for the removal of emerging contaminants at pilot- and/or full-scale was examined by Snyder et al. (Snyder et al., 2007). Basically varied target compounds at trace concentrations were evaluated. Along with microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO), electro dialysis reversal, membrane bioreactors (MBR), and combinations of membranes in series numerous membrane types and applications were used. Together UF and MF were found to deny very limited targeted compounds, and the MBR system removed some of the micropollutants and it showed better results when followed by the RO. Almost all target compounds were rejected by NF and RO. Extremely effective at removing all target chemicals were granular activated carbon. However, advance curves validated that compounds with greater hydrophilicity breach activated carbon faster than hydrophobic compounds. The discovery confirm that membrane processes and carbon adsorption greatly reduce the concentrations of emerging contaminants; however, numerous compounds are still noticeable in membrane permeate and carbon effluent. The results were approved in the study on the removal of pharmaceuticals and endocrine disruptors from South Korean waters (Kim et al., 2007). Denial of trace organic compounds,

disinfection by-products and chlorinated solvents, by thoroughly characterized RO and NF membranes from aqueous solution at low feed concentrations (100 μg/l) was investigated by Kim et al. (Kim et al., 2005). The denials of compounds of transitional hydrophobicity by the applicant membranes were less than salt denials for these membranes. Such a result proposes that transport of the studied solutes through these membranes is eased by solute–membrane interactions. It was hypothetical that hydrogen bonding plays a role in solute transport through the membranes. The denial of emerging contaminants at very low concentrations by a variety of commercial NF/RO membranes, in order to simulate operational conditions for drinking water and wastewater treatment was examined by Xu et al. (Xu et al., 2005). Also, the effects of various water quality matrices were studied. A variability of organic micropollutants of several physicochemical properties from hydrophilic ionic, hydrophilic nonionic to hydrophobic nonionic were tested. Membranes at lesser feed pressure provides' a product water quality alike to a RO membrane. The presence of effluent organic matter improved the denial of negatively charged compounds. Hydrophobic nonionic compounds were moderately removed by RO membrane, and a tight NF membrane can attain a similar effect. Rise of process recovery did not fundamentally alter the permeate concentration, and the presence of effluent organic matter completely neutralized the impact of hydrodynamic conditions.

26.5.3 The Results of the current studies on organics removal by nanofiltration/reverse osmosis

Nghiem et al. (Nghiem et al., 2004) examined the removal of natural hormones: estradiol, estrone, testosterone, and progesterone by two characterized nanofiltration membranes. The hormones were not separated at the pH of the experiment, so steric exclusion and adsorptive effects conquered in the solute denial. The hormones' molecular size was larger than the usual pore size of both membranes, and their preliminary denial was almost complete and conquered by the adsorption of hormones to the membrane matrix. However, the preliminary high retention declined with time. This was explained by the reached adsorption equilibrium, after which a diffusion of hormones via hydrogen bonding to membranes functional groups takes place, eventually resulting in a lower retention. Bellona and Drewes (Bellona and Drewes, 2005) and Nghiem et al. (Nghiem et al., 2005, Nghiem et al., 2006) has deliberated the contribution of electrostatic interactions to the denial of ionizable trace pollutants. Bellona and Drewes (Bellona and Drewes, 2005) examined the denial of selected organic acids by NF membranes was tested by Bellona and Drewes (Bellona and Drewes, 2005). The refusal of negatively charged acids was significantly altered by the actual surface charge. The refusal, mostly driven by the membrane surface charge, linked well with the degree of ionization of the solutes. The denial of ibuprofen, an organic acid with hydrophobic properties, was also reliant on pH, but at pH values lower the pKa ibuprofen adsorbed and separated through the membrane. At pH above the pKa, adsorption of ibuprofen was minimal and the electrostatic repulsion conquered. The occurrence of calcium in the feed water lowered

the effective membrane surface charge of both studied membranes, however, denial of negatively charged organic solutes declined only for membranes with a MWCO larger than the solute size. The retention of three pharmaceuticals: ibuprofen sulfamethoxazole, and carbamazepine, representing three different drug categories were reported by Nghiem et al. (Nghiem et al., 2005, Nghiem et al., 2006). These small organic molecules vary in their transport through a NF membrane from the behavior of proteins when electrically charged. Retentions of the compounds by two well-characterized NF membranes were investigated in the 1st two papers (Nghiem et al., 2005). The retention of all of them was quite high by a tight NF membrane, i.e., it was conquered by size exclusion, whereas both electrostatic repulsion and steric exclusion administer the retention of ionizable solutes by a loose NF membrane. A decline of solution pH moderated the denial of ibuprofen and especially sulfamethoxazole, which transformed from the negatively charged to neutral species as the solution pH declined. The denial of uncharged pharmaceuticals is altered by their essential physicochemical properties such as their dipole moments. This is obvious in case of cylindrical sulfometoxazole molecule, which in uncharged state permeates the loose membrane due to its high polarity. Retention of the nonionizable molecule, carbamazepine, was free of the solution chemistry. The impact of the ionic strength, solution pH, and existence of divalent cations, on retention of sulfamethoxazole and ibuprofen was solid. Since, the compound alters from a neutral to a negatively charged species when the solution pH increases above its pKa value the retention improved intensely. In contrast, solution ionic strength condensed the efficiency of electrostatic interaction as a major retention mechanism by the loose NF membranes, due to the controlled double layer. The impact of a divalent salt concentration is stronger than that of sodium chloride as the background electrolyte. Size effects and thermodynamics (sorption) are superimposed in RO/NF, which leads to complex behavior that is difficult to interpret in terms of simple concepts, such as the pore size or the molecular weight cut-off was investigated by Ben David, Freger et al. (Ben-David et al., 2006, Ben-David et al., 2006). They offered a new method for direct measurements of a true segregating coefficient of a solute between the aqueous phase and the material of the polyamide active layer that is free of amounts related to possible sorption on supporting structures. Their results on sorption of alcohols, polyols, and some aromatic solutes on the active layers of polyamide RO/NF membranes show that the very use of the actual pore size or MWCO for RO and NF membranes needs much care and should always report the issues of thermodynamic affinity. The fouling propensity in nanofiltration of organics is significant for the membrane transport of water and solutes. Noteworthy influence of the membrane properties were shown by the study of three fully characterized nanofiltration membranes (Boussu et al., 2021). The lowest entangling was witnessed for the most hydrophilic membrane having the largest pore size, the high negative charge in case of filtrating salts and a moderately smooth surface in case of filtrating silica. The conclusion of the feed properties was shown by using aqueous feed solutions containing uncharged organic salts or silica colloids. Colloidal entangling in the occurrence of different NaCl concentrations shown that entangling increased with

increasing ionic strength due to the shielding effect of the membrane and the colloid charge. The effects of membrane entangling on denial of trace organics by NF/RO membranes, using a secondary effluent from a municipal wastewater treatment plant as the feed was described in another paper (Xu et al., 2006). Entangling resulted in more negative zeta potential and changes of hydrophobicity for five tested membranes. The denial of organic micropollutants by CTA, NF, and ULPRO membranes was exclusively influenced, while it was less important in the case of RO membranes. The effect was firm for ionic organic micropollutants, by cause of a more negative surface charge. The hydrophobic non-ionic solutes were also better refused. Nonetheless, the growing surface charge resulted in a higher MWCO of a contaminated membrane due to membrane swelling. This could cause lower denial for hydrophilic non-ionic solutes, especially where NF membranes of a much bigger MWCO were used. The effect of the feed solution (distilled water, tap water, and river water) on the removal of pesticides by NF was examined by Zhang et al. (Zhang et al., 2004). Atrazine or simazine was added to dissimilar water matrices at a concentration of 5mg/l and100 μg/l, and denial of pesticides and the water flux of NF membranes were measured. The denial of pesticides was advanced in river and tap waters than in distilled water, but the water flux was lower. This was chiefly explained by ion adsorption inside the membrane pores, while the presence of natural organic matter (NOM) improved the size exclusion due to formation of NOM-triazine complex. No compelling effect of the pesticides concentration was witnessed. Significant denials of nitrate and organic matter were found, in specific for the membrane with the smallest pores. This proved the supposition that pore narrowing by ion adsorption affected the denials and water fluxes. An experimental porosity characterization of the NF/RO membranes' active layer without resorting to theoretical models was proposed by Košutić et al. (Košutić et al., 2006). Two characteristic parameters were determined from the membrane's flux dependency on pressure: (1) the susceptibility of the active layer structure under pressure and (2) the membrane's pure water permeability. The significance of the characteristic parameters was proved by relating them to the pore size distributions (PSD) and to the effective number of pores in the active membrane layer. The tested RO/NF membranes were classified according to the values of the characteristic parameters, and the classification was demonstrated by the membranes' denial for several, typically organic solutes. The "geometric model" of a solute for a description and better understanding of the denial behavior of elongated molecules by nanofiltration membranes was proposed by Santos et al. (Santos et al., 2006). They signified the solute molecular geometry with a prolate revolution ellipsoid, and the solute characteristics: size, shape, symmetry, and location of functional groups control how the molecule orients during uptake in the membrane and transport through it, and subsequently how the membrane would reject it. The relative contribution of convection, diffusion and charge effects during transport of dissolved organics through NF membranes was examined by Braeken et al. (Braeken et al., 2006). The diffusion was analyzed by the Donnan model and the charge effect was examined by altering the pH of the feed solution, which influenced both the membrane and the compound charge.

Convection was found to be the leading mechanism for transport of organics, and it depended on the compound properties. The retaining of uncharged solutes slightly decreased at high pH, due to the expansion of the membrane pores caused by an increased repulsion between the membrane charged groups. The retaining of charged compounds increased with increasing the pH, owing to an increased repulsion between the charge of compound and membrane. Diffusion through tight membranes became more vital as the molecular weight of the compound raised, because steric hindrance in narrow pores mostly affected convective transport. An attempt was made in the paper of Ali et al. (Ali et al., 2005) to grasp the influence of NF membrane characteristics on the cost of a membrane separation system. This was attained through merging a denial simulation with an economic model for membrane system. Based on the simulation, it was found that the slacker the pore structure of a membrane, the greater the membrane charge capacity needed in order to attain a desired application. Strategies for selection of the most suitable membranes for a specific denial can be developed from the predicted denial. From the budget point of view, the membrane charge density did not have any effect on the budget though increasing the membrane pore radius will lead to a reduction in system separation budget.

26.6 Applications of nanofiltration membranes (Zhao et al., 2005)

Nano filtration membranes are approximately modern advancement, satisfying a void between two deep-rooted technologies: reverse osmosis and ultrafiltration separation processes. The utmost exhilarating characteristics of Nano filtration membranes is their capability to permeate monovalent ions, such as sodium chloride, through the membrane, while refusing divalent and multivalent ions, such as sodium sulfate. This suppleness opens up many possibilities in the growth of specialty process applications across numerous industries. Filtration is chiefly focused on process applications, and so it was a normal fit to advance Nano filtration membranes to enhance to an already diverse product contribution of ultrafiltration and microfiltration membranes. Nano filtration membrane processes are frequently used by a number of industrial processes, including Chemical industry, food, textiles, metal finishing, pulp and paper, pharmaceutical and biotechnology applications, and power generation. The reported applications include mainly:

1. Application in the chemical industry,
2. Detoxification of food industries [dairy, juice processing, sugar industry, soft drinks, beverage products, fish meal, baker's yeast, meat processing and olive processing], Whey partial detoxification
3. Textile dyes purification and brighteners of optical,
4. Removals of metal, nickel, and chrome plating from metal finishing industries and leather industry, 6) Applications in pharmaceutical and biotechnology, and
5) Sanitization spent clean-in-place (CIP) chemicals.

26.7 Advantages and disadvantages

NF is well-known in the removal of calcium and magnesium ions resulting in water softening, and no addition of sodium ions during filtration compared to ion exchange units. NF does not need supplementary chemical treatment to lessen hardness; hence the water softening process is approached efficiently without realizing sodium resin in water which is the case for 50 years. NF does not needs heating or cooling of feed like distillation for example which will shrink the cost of separation successfully. And also, no mechanical electrifying is required which will sustain gentle molecular separation. NF has the vital advantage of handling a high volume of feed in an incessant manner and a steady flow rate of permeate. However, NF has a partial application in the industry because of the pore size of the membrane which is partial to nano-pore size. RO and UF are preferred since they can cover the UF range efficiently without the cost limitation of NF because of extraordinary primary operating and maintenance cost (Mohammad et al., 2007). A function of TDS is to replacement of NF membrane, and are replaced in a shorter time compared to the actual filter lifetime, which increases the NF cost. NF system uses has raised the energy necessities for water treatment 60–150%, low energy systems are vital necessities. As recommended by Sombekke (Sombekke et al., 1997) green energy may behave as an effective way to lessen energy requirement. However, the green energy price is advanced than conventional energy. The only way to lessen energy necessities of NF is to use of leaky NF which will lessen pressure and energy necessities which may affect membrane operation. Therefore, a balance is needed to optimize energy necessities and optimum operation.

26.8 Future perspectives of nanofiltration

RO and UF have been used extensively for different applications but their applications are still inadequate and hard to be prolonged further, NF applications are increasing and substituting other membrane filtration techniques. NF membrane is made up of diverse materials and its preparation is flexible moreover by employing RO membrane polymers such as cellulose acetate and polyamide polymers in addition to other chemically resilient polymers. Recently, NF membranes are also made of ceramic materials to endure great temperature. The flexibility of preparation and the diversity of raw materials for NF preparation will rise and spread its application in diverse processes. With such flexible raw material assortment and broad-mindedness to be revised for diverse applications, NF will be soon the chief and most used membrane filtration technology which needs that research association should focus more on NF development.

26.9 Conclusion

In this paper, the ability of reverse osmosis/nano filtration process to remove accurately the emerging organic contaminants from water was assessed. The valuation of the previously gathered knowledge on the basic rules for the denial of conventional organic pollutants by NF/RO, and on the solute and membrane characteristics have

stated that such knowledge might be mostly applied for the removal of emerging contaminants. This has been recurrently confirmed in the recent studies that deal with the retaining of micro-pollutants at very low, environmentally realistic concentrations, as long as the single, targeted organic micropollutant is examined, and under the supposition that the steady-state adsorption of the compound in a membrane was reached. On the other hand, when abundant constituents were present in wastewaters, the results were limited to the ordinary qualitative facts of higher or lower removal without detailed clarifications on the retention mechanisms and the aspects affecting the membrane's retention. The cogency of the reviewed knowledge and the rudimentary rules of the NF/RO separations in such cases of complex mixtures of solutes could not be confirmed yet.

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CHAPTER

Hybrid bioreactor in combination with ozone-based technologies for industrial wastewater treatment

27

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27.1 Introduction

Water is the most common need of the life on our planet earth and is used to carry out all basic everyday needs and industrial activities. In the past few decades, human beings are facing water crisis due to rapid growth of various industries such as distilleries, fertilizers, textiles, pharmaceuticals, mining, and leather manufacture; urbanization; ever-increasing human population and their rising living standards with higher production of wastewater containing toxic and recalcitrant contaminants. These toxic compounds enter into the aquatic environment in several ways, either from wastewater treatment plants or dumped directly without fulfilling the obligations. Generally, several such water-soluble compounds can easily be transported and dispersed in the water cycle. Due to the low biodegradability index, these contaminants are resistant towards biological treatment and are identified with their low biological oxygen demand (BOD) and high chemical oxygen demand (COD) values. These organic compounds present in wastewater are very toxic, endocrine disruptors and carcinogenic to living beings, hence, can cause serious health problems. It is, therefore, becomes a priority to treat these hazardous pollutants discharged from industries. The biological treatment methods are employed for wastewater treatment if the biodegradability index (BOD_5/COD) is more than 0.4 (Malik et al., 2017).

The biodegradation of a chemical compound refers to as the destruction of the pollutant by the metabolic action of a living species, usually bacteria, fungi, or algae that are abundant in natural water and soil. In this process, the microorganisms with diverse strains utilize enzymes to degrade the industrial contaminants present in wastewater either in off-site (ex-situ) or in onsite (in-situ) mode. The efficiency of biodegradation depends on the genotype and population density of the microorganisms, the accessibility of pollutants to the active sites of the enzymes, and the environmental conditions such as pH, temperature, and nutrients. The advantages

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of biodegradation include high selectivity, cost-effectiveness and good removal efficiency (Vikrant et al., 2018). Biodegradation can be further enhanced either by adding nutrients to stimulate the growth of native microbes (*Biostimulation*) or by adding genetically-modified microbial strains to accelerate the process of microbial metabolism (*Bioaugmentation*). The process of biodegradation requires identification and growth of the effective microbial strains and optimization of the process conditions to yield a high degradation efficiency (Roy et al., 2018). The combination of different types of microbes (such as bacteria and fungi) has also been utilized to further enhance the degradation of certain textile industry pollutants (Sen et al., 2016). Although biodegradation of the industrial contaminants is an economical and eco-friendly process, it is limited by the following factors (Boopathy, 2000):

a) Biodegradation at the large-scale is a very slow process due to its dependence on the metabolic activity of microbes
b) Contaminants must be biodegradable (BOD5/COD ≥ 0.2)
c) Biodegradation is highly specific, and therefore complete mineralization and degradation of a mixture of various pollutants and their recalcitrant metabolites would be difficult to achieve (Vikrant et al., 2018)

The advanced oxidation methods have popularly been known to degrade the industrial wastewater containing hazardous pollutants. Although having high degradation efficiency, the AOPs require controlled operating conditions, high energy requirement that ultimately increases the process cost. During the chemical oxidation, the complete mineralization is costly, since the oxidation metabolites are more and more resistant towards chemical reagents and consume more energy. The biodegradability of the water stream increases when exposed to a pretreatment with any AOPs. Therefore, a potential route is to pretreat the waste stream using these chemical oxidation processes to convert the organic pollutants into more biodegradable forms and their further treatment using low-cost biodegradation.

27.2 Characteristics of industrial wastewater

27.2.1 Pharmaceutical wastewater

In the recent past, pharmaceuticals are a rising source of pollution for the environment. As observed, the effluent released from hospitals has a distinguished number of chemical wastes as antibiotics, disinfectants and other treatment waste in large quantity. Pharmaceutical effluents are biologically active, making their presence in the environment harmful to both humans and aquatic life. The current worldwide difficulties including high growth rate in the population and environmental change have added to the emergence of new diseases and epidemics. During the treatment of patients, hospitals release various pathogenic wastes generated amid different treatment processes like surgeries, laundries, kitchens, wards, and laboratories (Azuma et al., 2016). It has been reported that the concentration of pollutants in pharmaceutical wastewater (PWW) is 4–150 times higher than the domestic wastewater

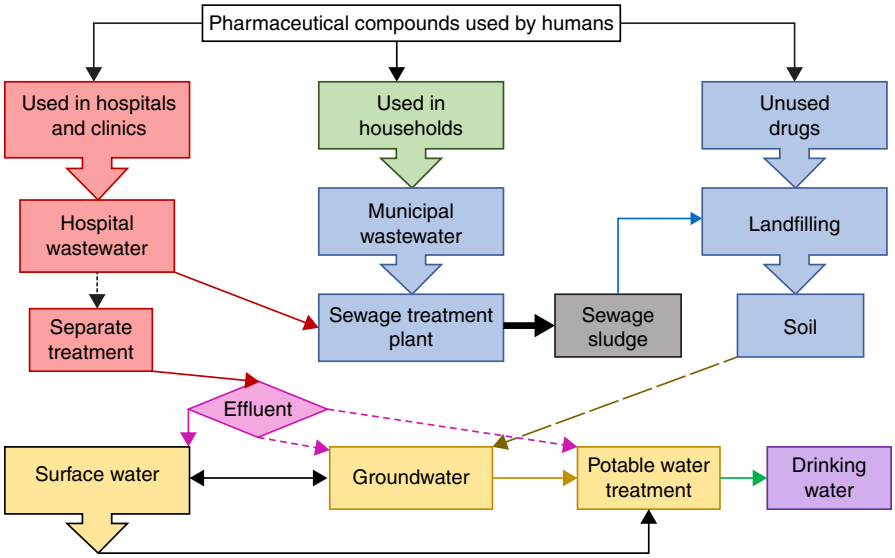

FIG. 27.1 Flow diagram showing the sources by which pharmaceutical can be present in rinking/potable water.

(Verlicchi et al., 2010). Some of the detrimental effects caused due to pharmaceutical pollution include genotoxicity, resistant development in pathogenic bacteria, aquatic toxicity, and endocrine disruption. Moreover, the daily usage of antibiotics has increased so much so that their residues are difficult to detect in the environment. Many new types of bacteria resistant to antibiotics are now a major concern. If this type of trend continues, it will be difficult for every one of us to treat a simple medical problem with the existing antibiotics. Numerous significant parameters like oil, NH_4 content, BOD_5, COD, antibiotic deposits, chlorine, radioactive components, pathogenic microorganisms, and substantial metals are required to access the quality of water released from pharmaceutical industries.

Pharmaceutical compounds are commonly manufactured in batch operations thereby producing wastewater with a wide range of products generated in different processes. A large amount of water is utilized in various operations as the washing of equipment, extraction of products, etc. Pharmaceutical compounds can be present in the drinking water via two sources: drugs and chemical used in hospitals and clinics and common use of pharmaceutical drugs in households (see Fig. 27.1) (Ikehata et al., 2006).

The wastewaters created in various processes in the production of pharmaceuticals and medications contain a wide range of compounds. Further, reuse of water after elimination of contaminants, regardless of whether pharmaceuticals or any industry is required. There are various sections of a pharmaceutical industry that releases plenty of wastewater namely, bulking of drugs, different zones of active

pharmaceutical ingredients (API). In addition to the waste created by humans, the release of pharmaceuticals which are being utilized in agriculture, the industry also contributes to the entrance of pharmaceuticals into water bodies. On the other hand, veterinary pharmaceuticals directly contaminate soil via surface and ground waters and manure.

Organic and inorganic chemicals are used for the synthesis of drugs with specific pharmacological action in the batch process. Multiple chemical reactions with various intermediates and by-products are carried out in reactors. Separation processes such as leaching (solid-liquid extraction), liquid-liquid extraction, filtration and crystallization are used to isolate the products and maintain purity. The products are generally in concentrated form and transferred via pipelines between process vessels and therefore this complex process utilizes a lot of raw water at each step. During the filtration process, water is used for washing of solid cakes and precipitates of organic solvents, leading to an ample release of volatiles into water. These wastewaters from the synthesis and purification stages have high chemical oxygen demand (COD), low biological oxygen demand (BOD), low biodegradability index ($BOD_5/COD < 0.2$), total suspended solids (TSS), and pH ranging from 1–11 (Santos et al., 2013).

27.2.2 Textile wastewater

The textile industry is one of the leading enterprises in releasing loads of polluted waste effluent including dyes, salts and other organic complexes in the soil and water bodies, and hence poses severe risks to the aquatic environment. As per the world dyes consumption report 2017 (Source: IHS Markit), the Asian countries are using ~75% of the total produced synthetic dyes, with India and China as the top two users. It is estimated that more than 10,000 kinds of dyes and pigments are being devoured in the environment with their yearly production of more than 7×10^5 tons (Shah, 2018). The presence of dyes, even at minimum concentrations, diminishes the level of transparency in water and, therefore, decreases the process of photosynthesis and initiates anaerobic conditions eventually in the water bodies. The presence of toxic and nonbiodegradable compounds, such as complex aromatic and polymeric structures in the textile dyes, can be exceedingly poisonous with mutagenic and carcinogenic hazards to the aquatic and terrestrial biota (Ito et al., 2016). It necessitates the removal of dyes from the textile effluents not only for the aesthetic reasons but also for the conservation of lives and ecological parameters.

The textile dyes can be classified based on their sources (as natural and synthetic dyes), and their applications to the substrates (such as acidic, basic, direct, reactive, dispersive, vat, and sulphurous dyes). According to their chemical structures, most of the commonly used dyes belong to the azo class which contains at least one nitrogen to nitrogen double bonds (–N=N–). Azo dyes are one of the most prevalent dyes and contribute to over 70% of the synthetic dyes. The colors of the dye molecules indicate the existence of *chromophores* (conjugated double-bonds) which show absorbance in the visible range. The absorption wavelength can be increased either by increasing the number of conjugations or by introducing a functional group

(known as *auxochrome*, for example, an amino, aldehyde, hydroxyl, carboxylic, or sulfonic group) attached to the chromophore of a dye molecule (Boopathy, 2000). Generally, the discoloration of the textile dyes is accomplished by breaking down the conjugated double bonds present inside the chromophores of a dye molecule. The conventional wastewater treatments are inadequate in degrading the azo dyes because of their recalcitrant nature. Further, the presence of a mixture of various dyes in the textile effluents makes the remediation of a dye-waste even more challenging (Ito et al., 2016).

27.2.3 Municipal wastewater

The municipal waste effluent generally consists of human faeces, nutrients and organic material with a large number of pathogenic microbes. It also incorporates leftovers of personal care products, pharmaceuticals, disinfectants, detergents, and other chemicals used in domestic activities. The portion of suspended solids present in municipal wastewater (around 1%) is dependent on the human activities and habitat (Deng, 2020). Although, these solids are present in very minute quantity, their detrimental effect on the BOD and COD levels is enormous. The components of municipal wastewater can vary greatly from locality to locality, therefore, to understand the local municipal effluent, the study of local demographics is very important (Cruz-Alcalde et al., 2019). The presence of several hazardous pollutants has made it compulsory to treat the municipal wastewater at their sources. The wastewater treatment plants (WWTPs) generally focuses on the major sources of micropollutants emissions and their respective removal depends on their physical and chemical characteristics. The biodegradation process in WWTPs that involves the aerobic degradation of organic contaminants using microorganisms is generally considered as the secondary treatment approach. This is mainly due to the disadvantages of large sludge production, unexpected output with a foul smell and slower treatment time. The delayed reaction time in biological treatment can be attributed to the inhibition of microbes in the sludge due to the formation of toxic metabolites (Zhang et al., 2020). The presence of excess sludge becomes a liability for the industry or treatment facility if an option to reuse it is not available.

27.2.4 Tannery effluents

Tannery effluent is generated during the wet operations employed in the preparation and tanning processes of the leather industry. The tanning process is very complex comprising of various steps like soaking, degreasing, unhairing and liming, deliming, pickling, softening, tanning, neutralizing, retanning, and dyeing. The wastewater from each step is collected separately and mixed in a single wastewater stream containing various substances. The use of various organics and suspended solids makes it dark in colour, highly alkaline and saline in nature. Alkalis, acids, tannins, chromium salts, dyes, solvents, and other compounds used for the transformation of raw skins into finished and commercial products, are not effectively attached by the

Table 27.1 Typical characteristics of tannery wastewater.

Parameters	Concentration (mg/L)
BOD_5	1500-2000
COD	3000-4000
Sulfide	50-100
Suspended solids	2000-3000
pH value	8-11
Total Chromium	60-100

skins and stays in the effluent. The effluent generated has a bad odor with high levels of BOD and COD, which indicates enhanced oxygen consumption. Generally, the waste effluent generated has a high amount of nitrogen, specifically organic nitrogen but rather a very low amount of phosphorus. While COD is considered as a most fundamental parameter to characterize tannery effluent, the total organic carbon (TOC) is more reliable as the presence of high concentrations of sulphides and chlorides can affect the COD analysis (Zhao and Chen, 2019). The wastewater generated from these enterprises has high BOD_5, COD, nitrogen, sulfide, and suspended, with typical ranges as shown in Table 27.1 (Gutterres et al., 2015).

The volume of wastewater generated depends on the production processes, finished products and raw materials used. In the tanneries that also produces salted hides, there is a large amount of sodium chloride present in their effluent as it is also used for skin preservation.

27.3 Selection of an optimal treatment strategy

The selection of a hybrid setup for the treatment of industrial wastewater is a very complex task. To choose from the alternative processes, one needs to know about the environmental standards to be met for the lowest cost and effective treatment. Some of the factors, which must be considered in deciding the application of hybrid wastewater treatment are:

a. Removal of the major pollutants
b. Physical and chemical characteristics of the original wastewater
c. Traditional treatment preferences
d. The capacity of the treatment facility
e. The extent of detoxification for the treated water
f. The overall efficiency of the hybrid wastewater treatment system
g. Comprehensive economic analysis
h. Potential usage of the treated water

Generally, the prospects and effectiveness of conventional treatment systems are very well known. But the information on the efficiency of the hybrid systems for

the destruction of industrial toxic pollutants present in wastewater is very crucial. Therefore, studies based on bench-scale and pilot-scale treatment have been explored recently (Leyva-Díaz et al., 2015; Vincenzo Naddeo, 2013) to generate the information on new hybrid strategies. The application of chemical oxidation as pre or post methods in the treatment line can sometimes be insignificant and changes the properties of original wastewater, although they are theoretically profitable. The following can be the most common reason for this:

a. Inadequacy of selectivity for a preferred attack on the more biologically resistant component of the waste stream
b. Production of less biodegradable stable metabolites
c. Use of excessive catalyst and/or oxidant for chemical oxidation. Some oxidation chemicals, catalysts (metals, metal salts and metal oxides) are toxic to microorganisms

These factors underline the demand for a stepwise research and development methodology to take into account the effect of operating conditions on the pre-treatment section. The information regarding the reaction pathway and kinetics, mechanism, effect of anions and cations in wastewater, the effect of pre-treatment on the biodegradability and toxicity and the application of different hybrid systems must be known for such research studies.

27.4 Hybrid bioreactor combined with ozone-based technology

The industrial wastewater is recalcitrant and therefore just one treatment method is not sufficient to degrade it as per the regulatory guidelines. Since the early 1990s, for the treatment of textile wastewater, ozonation followed by chemical coagulation method has been very popular for obtaining better results (Bu et al., 2019). Combined treatment can help to overcome the disadvantages of a single treatment and provide an effective treatment strategy. Hai et al. (2007) stressed the importance of treating industrial wastewater using combined methods (Hai et al., 2007). The study showed that in the current global scenario, the application of a single treatment for industrial wastewater is not realistic due to the implementation of more and more strict regulations. In the past few years, hybrid materials and processes have gained huge popularity due to the ability to degrade many recalcitrant contaminants.

Many diverse hybrid treatment strategies have been reported in the literature and many significant developments have been done in the application of these treatment methods to prevent the release of various emerging contaminants into the aquatic habitat through effluent discharge. The combinations adopted must have processes that are technically possible and economically practical. Most of the treatment methods constitute a biological system (anaerobic/aerobic/anoxic/microaerophilic) in combination of either a physical treatment (adsorption/coagulation-flocculation/ultrafiltration/nanofiltration/reverse osmosis) or chemical treatment (photo-Fenton/

electrochemical/photocatalysis/ozonation) or both. Biodegradation has played a key role in the effective removal of micropollutants from pharmaceutical wastewater. Various treatment processes such as membrane bioreactor, sequencing batch reactor, upflow anaerobic sludge blanket reactor and activated sludge process have been employed throughout the years to treat different contaminants.

Ozonation is one of the most effective AOPs and has been applied effectively to degrade recalcitrant contaminants in various research studies (Ghuge and Saroha, 2018). Ozone, being a powerful oxidant, reacts quickly with most of the organic compounds including the aromatic rings and the double bonds in azo dyes. The oxidation of organic compounds in the presence ozone takes place via two separate mechanisms (Ozbelge and Erol, 2009):

1. Direct oxidation by molecular ozone (O3)
2. Indirect or advanced oxidation by free radicals (such as •OH, HO2•) produced after the decomposition of ozone.

Direct oxidation has very slow reaction kinetics, and it is selective to primarily unsaturated hydrocarbons (such as alkenes, alkynes) and aromatic compounds having electron-donating groups (-OH, -CHO etcetera). The direct oxidation reaction is favoured in the acidic (low pH) environments, or in the presence of radical scavengers (such as HCO3-, CO3–, acetic acid, tert-butyl alcohol or chlorides) which inhibit the generation of hydroxyl radicals. The indirect oxidation reaction is non-selective and hence it oxidizes all organic compounds. Although the indirect oxidation has a very high reaction rate, this oxidation pathway is limited by the short lives of hydroxyl radicals. The indirect oxidation can be promoted in high pH environments, or in the presence of a radical promoter (such as H2O2) which favors the generation of hydroxyl radicals.

The oxidation of an organic compound during ozonation can be maximized by optimizing various process parameters such as pH, temperature, time, and

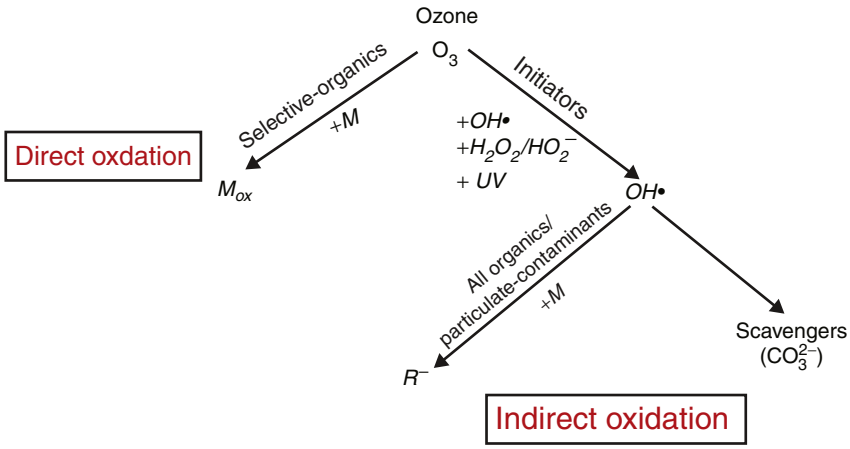

FIG. 27.2 Oxidation pathways in the ozonation process.

concentration of ozone and additives. Ozbelge et al. (Oller et al., 2011; Ozbelge and Erol, 2009), as listed in Table 27.2, have observed that ozone oxidizes the organic carbons gradually at acidic pH via direct oxidation. However, the oxidation reactions become very fast at basic pH and in the presence of radical initiators such as hydrogen peroxide, formic acid and metal ions (Fe^{2+}, Ni^{2+}, Cd^{2+}). Fanchiang et al. (Fanchiang and Tseng, 2009) examined the UV-visible spectrum of the intermediate compounds produced during the ozonation of the Reactive Blue-19 (RB-19) solution to study the oxidation mechanism. They reported complete disappearance of the color and anthraquinone rings of RB-19 after 10 min of the oxidation regardless of initial pH conditions; however, the TOCs were effectively removed only in the alkaline environment. The cause of the increased removal efficiency of TOCs at alkaline pH was attributed to the hydroxyl radical based indirect oxidation of dyes and their byproducts. Somensi et al. (Somensi et al., 2010) have studied the ozonation of dyeing wastewater at different pH conditions in a pilot-scale plant. They also observed a higher color and COD reduction of 67.5% and 25.5% respectively at alkaline pH of 9.1 than the same of 40.6% and 18.7% at acidic pH of 3.0 after 4h of ozone treatment. Different research groups (Khadhraoui et al., 2009; Venkatesh et al., 2017), listed in Table 27.2, have demonstrated that the pH values of various dyeing solutions decrease with increasing the ozonation time. Therefore, the oxidation pathway during ozonation shifts from the *non-selective, indirect oxidation* to the *selective, direct oxidation* despite the initial pH level.

The actual industrial wastewater contains not only various dyes but also different additives (such as inorganic and organic salts, polymers) and several emerging contaminants. Although most chemical treatments of the artificial industrial wastewaters available in the literature do not consider the effect of additives, the presence of additives can alter the efficiency of a degradation process. Pérez et al. investigated the effect of textile additives Na2SO4 and Na2CO3 present in the dyeing wastewater on the ozonation of reactive black 5 (RB5) and Direct Red 28 (DR28) dyes (Pérez et al., 2013). They reported that the presence of additives can slow down the oxidation rate of the ozonation process due to either generation of the *new oxidative* species instead of hydroxyl radicals (as was the case with Na2SO4) or *scavenging nature* of the additive compounds (such as Na2CO3) towards the free radicals. Further, the presence of additives may also enhance the concentrations of organic acids by-products (such as maleic, formic, oxalic, and fumaric acids) formed in the ozonation of dyes. This, in turn, would reduce the pH level of the reaction mixture, favour the direct oxidation pathway, and, therefore, reduce the oxidizing efficiency of the ozonation process.

27.4.1 Membrane bioreactor process in combination with ozone-based technologies

The removal of various contaminants through an membrane bioreactor (MBR) occurs primarily by biodegradation, photodegradation, sorption of contaminants on sludge. A combination of MBR with activated sludge process is observed as the most effective system for the removal of pathogens from hospital wastewater (Tran et al., 2016).

Table 27.2 Summary of the ozonation and integrated ozonation-bioremediation for the degradation of azo dyes.

Type of azo dyes	Type of Process / Objective of study	Results	Shortcomings	References
Acid Red-151 (AR-151)	Ozonation. Effect of initiator (Fe^{2+}) and scavenger (CO_3^{-2}) concentrations on the ozonation. Ozone dosing rate: 13-14 (mg / (L dye solution. min)	Direct oxidation was dominant at acidic pH and low levels of Fe^{2+} and CO_3^{-2} ions (0.8 and 10 mg/L, respectively)		(Ozbelge and Erol, 2009)
Reactive Blue 19	Ozone oxidation and toxicity analysis. Ozone dosing rate: 88.8 (mg / (L dye solution. min)	COD reduction upto 50% and the biodegradability index reached above 0.3	Mineralization of the organic content was not economical	(Fanchiang and Tseng, 2009)
Real textile wastewater	Pilot plant ozonation followed by biological oxidation	Color and COD reduction were 67.5% and 25.5% (at pH of 9.1) and 40.6 and 18.7% (at pH of 3)	Insufficient mineralization	(Somensi et al., 2010)
Reactive Black 5 and Direct Red 28	Ozone based decomposition in the presence of sodium sulphate and sodium carbonate	The presence of additives increases the discoloration of both the dyes		(Pérez et al., 2013)
Reactive Orange 16	Ozonation followed by an aerobic moving bed bioreactor (MBBR) for color and COD removal	Five minutes of ozonation prior to the biological process gave 97% color removal for the initial dye concentration of 100 ppm	Not much effective for TOC removal. Incomplete mineralization	(Castro et al., 2017)
Congo Red	Effect of dyeing additives and toxic by-products on the ozonation process	Lower color removal efficiency in case of a combination of O_3 and H_2O_2 in comparison to the ozonation alone because of the scavenging effect at high H_2O_2 dosage	Provided only a partial reduction of COD and TOC	(Khadhraoui et al., 2009)
Remazol Black B	Ozonation followed by bioremediation for COD and color removal	Color removal efficiencies of more than 96% were obtained by using ozonation as a pre-treatment step	Toxic by-products, hence a posterior process would be required	(de Souza et al., 2010)

Table 27.2 Summary of the ozonation and integrated ozonation-bioremediation for the degradation of azo dyes. *Continued*

Type of azo dyes	Type of Process / Objective of study	Results	Shortcomings	References
Acid Yellow 17, Reactive Black 5	Ozonation. Examine the extent of oxidation and associated color removal	100% color removal, Optimum ozone amount required was 1.8 g/L of dye solution	Incomplete oxidation, biodegradability improved	(Alvares et al., 2001)
Methylene Blue	Ozonation was conducted in a batch bubble column to take advantage of the intensive back-mixing prevailing in such columns. Ozone dosing rate: 24.03 mg/L dye solution. min, dye concentration: 400 mg/L	COD of dye-wastewater was reduced by 64.96% after ozone bubbling treatment under basic pH of 12, 88.43% color reduction was obtained		(Turhan et al., 2012)
Reactive Black 5	Ozonation followed by anaerobic biodegradation using up-flow anaerobic sludge blanket (UASB) reactor	90% COD and 94% color removal with reduced cost		(Venkatesh et al., 2017)
Artificial and real textile wastewater	Anaerobic biodegradation followed be ozonation	Simulated wastewater: Color removal was more than 99%; COD and toxicity got reduced to 85-90% Real wastewater: 70% COD reduction		(Punzi et al., 2015)
Real textile wastewater	Ozonation followed by biological aerated filter: Ozone dosage: 20-30 mg/L. min.	100% color removal using 30 mg/L. min of ozone feed		(Qi et al., 2011)

In the MBR, there is an enhanced growth of nitrogen removing bacteria due to longer retention time. The physical characteristics of the treated water are improved and the process releases high-quality water. Due to high COD removal efficiency, the MBR process provides a stable environment for the microorganisms. It has been noticed in many cases that the antibiotic removal efficiency of both ASP and MBR are equivalent but the MBR works better for the removal of other micropollutants. Although a low-cost process, sometimes, the pollutant removal in MBR becomes a tedious task due to membrane fouling. Generally, the MBR is used in aerobic phase coupled with some chemical and physical treatments such as UV/H_2O_2, ozonation and reverse osmosis (RO). The effectiveness of the process depends upon the sludge retention time and hydraulic retention time. Anaerobic membrane bioreactors have now been used as effective and innovative strategies for industrial wastewater with high reported COD removal efficiency (Svojitka et al., 2017). The membrane used in MBR are generally characterized by their pore length and can be used as submerged or as external modules. The application of MBR treatment alone does not ensure complete removal of micropollutants but needs a polishing step like activated carbon, ozonation photodegradation, etc.

Vo et al. studied a sponge-MBR in combination with the ozonation process for the removal of antibiotics such as ciprofloxacin, norfloxacin, sulfamethoxazole, ofloxacin, erythromycin, trimethoprim, tetracycline from hospital wastewater (Vo et al., 2019). The sponge-MBR used resulted in 45–93% removal of antibiotics with complete elimination of tetracycline. The addition of ozonation as a post-treatment enhanced the overall removal efficiencies for the antibiotics. The mechanisms of ozone oxidation were both direct reaction and via hydroxyl radical. Among the used antibiotics, ciprofloxacin showed the highest affinity towards ozone due to higher electron density at the functional group and in better removal rates. The COD removal (over 90%) for the integrated system was found to be significantly higher than the standalone MBR process.

One of the major drawbacks linked with a membrane bioreactor is the fouling that ultimately increases the maintenance and operations costs. This is because fouling consists of hydroxyl and carboxyl groups attached compounds which shows a higher affinity towards the barrier. The affinity is caused by a higher adhesive force that may lead to the formation of hydrogen bonds. The major contributors towards fouling are soluble microbial products (SMP) and extracellular polymeric substance (EPS) which can be removed by ozonation. Recently, Palani et al. developed a sequential batch MBR in combination with ozonation and microfiltration (Palani et al., 2019). Along with a better TOC removal, a 12% reduction in the energy consumption was also monitored for a three-hour operation due to reduced effect of fouling barrier. Ozonation was able to remove the deposition of sludge over the membrane surface. Another pilot-scale study for the improvement in MBR was conducted by Sathya et al. with the use of UV-based ozonation and photocatalysis for the treatment of real textile wastewater (Sathya et al., 2019). The system used constitutes ozonation followed by an MBR process and finally the photocatalytic reactor for 94% color and 93% organics removal. The pretreatment of real textile wastewater using ozonation enhances

the biodegradability index and the post-treatment of photocatalysis can further result in better color removal.

Therefore, the application of such physio-chemical-biological systems is recommended for higher inorganic and organic loading rates, as it offers lower energy consumption and leads to a zero-liquid discharge (low sludge formation).

27.4.2 Sequencing batch reactor process coupled with ozone-based treatment

Sequencing batch reactor (SBR) process is a refined approach that uses activated sludge for the treatment of organics. This type of process is considered as hybrid arrangement having propensity of continuous stirred tank reactor (CSTR) such as, complete mixing. A single SBR structure consists of different cycles namely, filling the reactor, reaction, sludge settling, drawing the effluent and idle (Patil et al., 2013). Unlike any activated sludge treatment system, the SBR does not have separate tanks for aeration and sludge settling and therefore there is no need for sludge return. This way, the SBR systems require lesser space for the wastewater treatment. SBR is considered as a useful system for hospital wastewater treatment. Anaerobic sequencing batch reactor (An-SBR) is also an attractive treatment for pharmaceutical wastewater but may cause the toxicity to increase for the microbial community. Although with prolonged operation time, the process of homoacetogenesis coupled with methanogenesis supports the stability of microorganisms and mitigates the effect of the high antibiotic.

SBR systems have been used to treat swine wastewater for the removal of macropollutants thereby reducing COD, total nitrogen and phosphorus content. When the veterinary antibiotics laden wastewater is mixed with the swine wastewater stream (both originated from the same poultry breeding industry), it becomes difficult for the biological process to completely degrade the antibiotics such as tetracyclines, sulfonamides, and macrolides. Therefore, it becomes necessary to apply a chemical oxidation process as a post-treatment to prevent the potential threat to the environment. SBR in combination with ozonation has been studied for the progressive removal of antibiotics from the veterinary effluent. For the initial antibiotic concentration of 200 ug/L, the percentage removal was about 85–100% at the ozone concentration of 37.3 mg/L for the SBR effluent. The addition of hydrogen peroxide to the solution could further increase the production of hydroxyl radicals. But these hydroxyl radicals were primarily utilised in the degradation of organic contaminants present in much higher concentration than the antibiotics. A similar combination of SBR-ozonation was used to treat highly polluted industrial wastewater (COD> 12g/L, TOC> 3 g/L and BOD_5> 2 g/L). The SBR alone could only result in around 50% removal of both COD and TOC, therefore a post-treatment using solar photocatalytic ozonation was used for the hazardous waste effluent from cosmetics and petrochemical products manufacture. The use of ozonation in combination with solar energy (Intensity = 550 W/m^2) and titanium oxide-based photocatalysis (0.375 g/L) was able to remove the recalcitrant compounds and reduce toxicity furthermore to make the effluent suitable for discharge in the environment.

The solid waste generated from the urban population has become a menace for the government as they increasingly face the problem of its management. Landfill leachates are generated in millions of tons from various sources like kitchen waste, plastics, papers, pottery, fabric, bricks and stones, glass, discarded domestic appliances, etc. There are some pressure-driven membrane processes like ultrafiltration, nanofiltration, microfiltration and reverse osmosis that generates concentrated leachate (around 13-30% of the incoming stream). This concentrated solution is dark in color with a very high COD, very low BOD_5/COD ratio making it difficult to biodegrade. A combined treatment strategy using electro-ozonation with SBR has been employed for treating this concentrated leachate (Mojiri et al., 2017). The electro-ozonation process was supported with the cathode and anode plates (IrO_2-Ti/RuO_2) were dipped in leachate to be used as the electrical power supply. Ozone consumption was varied in the range of 0.30 to 1.4 kg O_3/kg inlet COD to eliminate 90.4%, 64.8% and 52.9% of colour, COD and Ni, respectively and the contact time required to achieve this was 96.9 min. Further SBR treatment increased the treatment efficiency to 96.1%, 88.2%, and 73.4% removals for color, COD and Ni, respectively.

27.4.3 Upflow anaerobic sludge blanket reactor system in combination with ozonation

Due to the use of varying microbial types, increased biomass content, flexibility, low cost and adaptability to a wide range of pHs and temperatures, the up-flow anaerobic sludge blanket (UASB) reactors are widely applied for industrial wastewater treatment. The higher amount of biomass and retention time allows an enhanced COD removal. Under the high organic loading rate up to 21.02 kg COD/m^3/d (high antibiotics dosage), there is a strive in the growth of sulfate lowering microbes over the methanogens responsible for CH_4 production (Yi et al., 2017). Another variant of anaerobic sludge blanket reactor such as Extended Granular Sludge Blanket (EGSB) has been used in combination with aerobic reactors for the treatment of wastewater generated from oxytetracycline manufacturing (Collins et al., 2006). The mechanisms of acidogenesis and methanogenesis can be separated to prevent the biomass washout by using the sequence of upflow anaerobic stage reactor (UASR) followed by anaerobic baffled reactor (ABR). UASB system was applied for treating hospital wastewater containing avilamycin and tylosin antibiotics and achieved quite an effective result (Yi et al., 2017). At low OLRs, the COD removal efficiency of 75% was achieved which reduced to 45% when the OLR increased up to 3.73 kg COD/m^3/d at hydraulic retention time reduced from 4 to 2 days. The pharmaceutical wastewater not only contains high concentrations of antibiotics but also antibiotics resistant genes (ARGs) and antibiotics resistant bacteria (ARB). These components get proliferated by the use of various biological treatments widely applied to hospital wastewater. Various studies have reported that significant amount of reactive oxygen species are produced during the advanced oxidation processes (AOPs) and when these AOPs are used as post-treatment, they not only degrade the antibiotics present but also destroy the microorganisms (Pal et al., 2015). A bench-scale UASB

reactor was studied with AOPs (UV-irradiation, Fenton, Fenton-UV, ozonation) as post-treatment to monitor the fate and removal of antibiotics, ARB and ARGs (Hou et al., 2019). The use of ozonation (at a commonly used concentration of 50 mg/L and neutral pH) could result in microbial death which is related to damage of their cell surface and the inner molecular components such as ARGs were less affected by ozone oxidant.

The low-cost UASB reactor system has been used in combination with ozonation (pre-treatment) for the degradation of dye effluent containing Reactive Black 5 (Venkatesh et al., 2017). During the ozonation process, a drastic change in the solution pH (10.13 to 3.30) and an increase in conductivity was observed in just 25 min of treatment. Further anaerobic biodegradation using UASB reactor resulted in complete mineralization of the oxalate ions and amines formed in the stream from the ozonation process. The combined process resulted in complete decolorization and 84% of TOC and 90% of COD removal.

27.4.4 Activated sludge process treatment with ozonation

This type of process is generally applied for the treatment of municipal wastewater. The acclimatized sludge is mixed with wastewater stream in an aerated tank for the nutrient digestion and oxidation of organic contaminants in the treatment process. The sludge used is acclimatized at higher pollutant concentration to bear shock loadings that can occur during the treatment. During long retention time, the treatment efficiency of activated sludge process (ASP) is found between 30 to 70% with performance depending upon temperature, dissolved oxygen (DO), pH, microbial community, organic loading and seasonal variations (Castiglioni et al., 2006). Some studies have performed the treatment of pharmaceutics like naproxen, estrogens, bezafibrate, and ibuprofen using aerobic and anaerobic conditions of ASP (Kim et al., 2014). In the ASP systems, the sludge retention time is adjusted to make sure that the decontamination reaches at the desired level before the clarification step where solid/liquid separation takes place. The sludge collected from the clarifier is again sent back to the aeration tank to prevent the working microorganisms.

Waste sludge handling has been a major problem associated with ASP systems because of the low biodegradability of sludge caused by the bio-recalcitrant microorganisms. Recent developments in the activated sludge systems mainly focus on the sludge stabilization, reduction and production of methane gas (Liu et al., 2017). A pre-treatment using ozonolysis was studied for the enhancement of biodegradability and sludge solubilization (Otieno et al., 2019). The work focused on the effect of ozonation on the rupture of extracellular polymeric substance (EPS) of nutrients (phosphates, nitrates, carbohydrates and proteins) and proteinaceous cell wall. After 60 min of ozone treatment (90 mg/min) at a pH of 11, the organics constituents of the sludge could easily be solubilized. Thermogravimetric and infrared spectroscopic analysis showed a reduction in the cellular contents indicating the rupture of bacterial cell wall responsible for the release of humic substances and proteins.

ASP treatment has proved to be an efficient method for slaughterhouse wastewater as it effectively reduces TSS, COD, and BOD for wastewater even at high organic loads. Still, further disinfection is required to reduce the microbial contents of the effluent. Ozone has proved to be one method that can remove the inactive microbes and micropollutants without increasing the toxicity of treated wastewater. A combined ASP- ozonation was used for the treatment of heavily polluted abattoir effluent and also bridged the two processes via a filtration unit (Alfonso-Muniozguren et al., 2018). A 10 min of ozonation results in complete inactivation of total coliforms (bacteria present in the digestive tracts of animals). When ozonation was used as post-treatment with activated sludge system, the average reduction in COD, BOD, TSS and phosphorus content was 93%, 98%, 99%, and 98 % respectively.

27.5 Benefits of hybrid processes in combination with ozonation

Bioreactors in combination with ozone-based technologies have been widely used for the treatment of many types of industrial wastewater. Due to a low biodegradability index and recalcitrant nature of the major contaminants of industrial effluent, hybrid bioreactors and have been studied. Ozonation is one of the efficient AOPs with several advantages like fast reaction and negligible sludge production and is used in a variety of applications ranging from the production of potable water to treating complex wastewater. The combination of these two technologies becomes attractive in the treatment of waste industrial effluent because it can destroy most toxic organic contaminants such as phenolic compounds, organochlorides, ammonium compounds, dye, pharmaceuticals, and various antibiotics. Although, high operational cost is a major drawback associated with ozone oxidation due to the cost of electricity incurred and the installation of ozone generation unit, the high rate of contaminants degradation with greater efficiency by this process overcomes the drawback. We can also apply this AOP with some catalysts like iron, H_2O_2, etc. to increase the hydroxyl generation rate with negligible sludge formation. The high reactivity, easy application, nontoxicity, low solubility in water, and its versatile nature to be used with all types of biodegradation system makes it a promising choice for wastewater treatment in hybrid bioreactors.

27.6 Limitations of hybrid processes with ozone-based technology

Biodegradation systems used as a standalone technology and in combination with other advanced oxidation processes or any physical treatment offers a high degradation efficiency for a variety of complex industrial wastewaters. Since ozone is a very strong oxidant, it becomes very difficult to handle. Also, corrosion, leakage and sometimes excess ozone gas treatment can lead to frequent maintenance operations

for tanks and piping in contact with ozone. Generally, the cost of hybrid bioreactors becomes high because of the use of more auxiliaries with the system. The formation of secondary pollutants in some cases is a big concern for the effective use of this treatment. It was noticed that when ozonation is used as pretreatment, these pollutants can be more hazardous and toxic for the subsequent process than the primary contaminants. This gives rise for identification of the intermediate compounds and selects the optimal treatment process accordingly.

27.7 Conclusion

The reuse of wastewater and its reclamation demands the development of methodologies that are able to secure the natural sources of water and find alternatives for its supply. The treatment of industrial wastewater using biodegradation systems such as UASB, SBR, ASP, and MBR have been critically discussed. The poor mineralization and partial decomposition of contaminants by these methods is a major disadvantage and therefore ozonation appears to be a suitable pre- or post-treatment methods with biodegradation to remove these emerging contaminants and the intermediates. Based on the studied potential hybrid systems with biological degradation as a primary treatment, it can be concluded that UASB reactors with ozonation are the most prospective combination with low cost and high contaminant removal capacity. Though, there is a need for innovation for handing the activated sludge, UASB in combination with ozonation serves as the most optimum and economical treatment method for pharmaceutical and textile wastewater. For the treatment of municipal wastewater, the activated sludge process with ozonation becomes a potential contender among the presented treatment methods.

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CHAPTER

Metal organic frameworks (MOFs) in aiding water purification from emerging and ionic contaminants

28

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28.1 Introduction

28.1.1 Brief overview of emerging contaminants and conventional treatment process

Persistent organic pollutants (POPs) and heavy metals have become a part of intensive monitoring programs with rapid industrialization, due to their toxicity and health hazards. With various emerging technologies, emission of these compounds has been regulated. However, in recent years, emerging contaminants (ECs), such as, endocrine disruptors, pharmaceutical wastes, personal care products, artificial sweeteners, and various household wastes have received attention due to their potential to cause undesirable ecological effects (Petrović et al., 2003). Their ubiquitous presence in the environment, even in very low concentrations, is reported to have a long-term risk on aquatic organisms and human health. ECs are introduced to marine environment by different routes that include landfill leachate, direct discharge of wastewater from municipal, sewage, and surface runoff from urban and agricultural areas. Among the sources mentioned, wastewater treatment plants (WWTPs) continuously discharge these contaminants into the environment at concentrations (ranging from ng/L to μg/L). High water solubility and poor degradability of these contaminants present a potential risk in the drinking water supply (Petrović et al., 2003, Petrovic et al., 2004). Hence the removal of emerging contaminants is essential in the production of safe drinking water. Conventional technologies for wastewater remediation and removal of ECs include physiochemical treatment methods, such as, precipitation, coagulation and flocculation; membrane treatment methods, such as, nanofiltration and reverse osmosis; advanced oxidation process (AOPs) and adsorption. However, the shortcomings of most of these methods are toxic sludge generation, complex dosing, high investment and maintenance costs (Sonune and Ghate, 2004). Treatment methods such as coagulation, flocculation or lime softening shows ineffective removal for endocrine disrupting compounds (EDCs) and pharmaceuticals and

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personal care products (PPCPs). AOPs are found to be effective for the removal of ECs, but these processes can form oxidation intermediates that require further treatment and it might produce by-products with toxic effects. On the other hand, adsorption processes have been found to be superior to other techniques for wastewater treatment in terms of simplicity in design and operation, non-production of toxic substances and zero addition of byproducts (Rossner et al., 2009, Grassi et al., 2012).

28.1.2 Adsorption process in removal of emerging contaminants

Adsorption is a surface phenomenon, which involves accumulation of substances at the interface of two phases, such as, liquid–liquid, gas–liquid, gas–solid, or liquid–solid. Adsorption of solute on solid surface can involve specific interactions, mono- and multilayer adsorption on open surfaces, micropore filling, capillary condensation, and adsorbate clustering (Dong et al., 2016). Adsorption process depends on pore size distribution, point of zero charge (pH_{PZC}), surface functional groups, surface area and experimental conditions such as solution pH, initial concentration of adsorbate, temperature, nature and dose of adsorbent, and nature of coexisting ions in the solution (Chen et al., 2015). Uptake mechanism of ECs takes place by ion exchange, chemical adsorption, specific adsorption, and charged electrostatic effects. For a solid-liquid adsorption process, the adsorbate transfer is usually characterized by either external mass transfer or intraparticle diffusion or both. In most cases, three types of mechanisms take place in the adsorption process by a porous adsorbent: (1) film diffusion, migration of metal ions from solution to the external surface of the adsorbent; (2) particle diffusion, migration of the metal ions into the pores of the adsorbent; and (3) adsorption of the metal ions on the interior surface of the adsorbent (Kuroki et al., 2019). Typically, activated carbons (ACs) have been employed in wastewater treatment and for removal of various ECs from water due to their large surface area and porous nature. Also, AC enjoys superiority over other adsorbents, in terms of its hydrophobic interactions in eliminating most organic compounds (Perrich, 2018). But its use is restricted for following reasons: (i) AC is not recommended for pollutants that are not attracted to carbon and (ii) blocking of pores due to continuous usage lowers removal efficiency of AC. Additionally, regeneration process results in loss of carbon content and the regenerated product may have slightly lower uptake capacity in comparison with the fresh AC (Kuroki et al., 2019, Perrich, 2018, Liu et al., 2010). This has led to the development of novel metal organic frameworks (MOFs) as an alternative adsorbent.

28.1.3 Metal organic frameworks and their advantages

Metal-organic frameworks (MOFs) represent new class of porous materials. They have modular structures, which offer enormous structural diversity and extensive possibilities for creation of materials, with tailored properties. These materials are constructed by joining metal containing units or secondary building units (SBUs) with organic linkers, using strong bonds to create open crystalline frameworks with

permanent porosity. Combination of organic and inorganic structure elements can lead to materials with unique properties (Tranchemontagne et al., 2009). MOFs are characterized by high strength and considerable pore volume. Simultaneously, it is possible to tune its pore size, density and specific surface area, by apprehending proper choice of the initial building units. Distinctive feature of MOFs is large surface area, wide diversity and variability of their structure, in combination with lower topological restrictions on the formation of porous three-dimensional frameworks (Zacher et al., 2011). MOFs can exhibit superior physical and chemical characteristics and have been applied in various adsorption-related areas, such as, hydrogen storage, carbon dioxide adsorption and removal of toxic gases (Furukawa et al., 2013). Due to the promising potential in the areas mentioned above, researchers started to investigate the capability of MOFs to remove contaminants, like, metal ions, toxic dyes, herbicides, oil droplets and humic acid from water. In general, flexible and highly porous structure of MOFs allows guest species to diffuse into their bulk structure. Shape and size of pores lead to selectivity over the guest species that will be adsorbed. Consequently, these characteristics make MOFs an ideal sorbent in solid-phase extraction of heavy metals and other ionic contaminants (Canivet et al., 2014).

28.2 Different synthesis methods for preparation of metal organic frameworks

28.2.1 Solvothermal synthesis

MOFs are commonly crystallized from a solution. The conventional synthesis route is solvothermal or hydrothermal method (Fig. 28.1). The product crystallinity and yield are the key advantages of solvothermal synthesis. In addition, slow crystallization

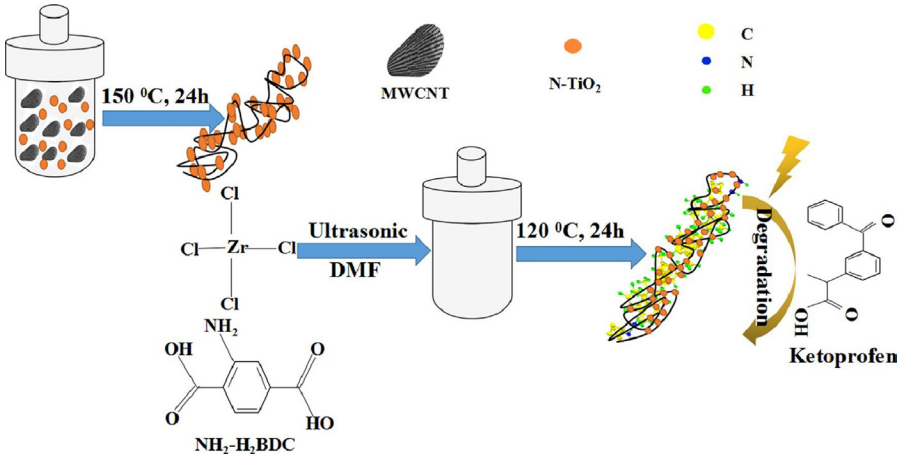

FIG. 28.1 Solvothermal—Hydrothermal approach for MWCNT/N-TiO_2/UiO-66-NH_2 (Sun et al., 2020).

from a solution leads to the formation of regular large crystals with a high internal surface area. The reactions take place in closed vessel under autogenous pressure above the boiling point of the solvent. In addition, slow crystallization from a solution leads to the formation of regular large crystals with higher surface area (Sun et al., 2020).

The nanocomposite of nitrogen-doped titanium dioxide (N-TiO_2) and Multi-walled carbon nanotube (MWCNT) denoted as MWCNT/N-TiO_2 was synthesized using MWCNT dispersed in sodium dodecyl sulphate (SDS) aqueous solution under ultrasonic treatment and then the reaction was kept for 24 h at 150°C in a Teflon-lined stainless autoclave. The mixture was naturally cooled and washed with distilled water for several times, rinsed with ethanol, and then dried. MWCNT/N-TiO_2/UiO-66-NH_2 were prepared by adding zirconium (IV) chloride ($ZrCl_4$), 2-aminoterephthalic acid, MWCNT/N-TiO_2 and benzoic acid dispersed in N,N-dimethyl amide (DMF). The reaction mixture was kept for 24 h at 120°C in a Teflon-lined stainless autoclave. The mixture was naturally cooled down to room temperature and washed with DMF and chloroform and finally dried.

28.2.2 Microwave assisted synthesis

In another synthesis method, i.e., microwave-assisted method (Fig. 28.2), synthesis duration is less, and reaction rate is high. However, it requires specific solvent that can absorb microwave energy and can convert electromagnetic energy into heat (Jaiswal et al., 2018, Choi et al., 2008).

An example of a MOF prepared by this method is shown in this regard. Ferrous chloride ($FeCl_2$•$4H_2O$), ferric chloride ($FeCl_3$•$6H_2O$), sodium acetate and

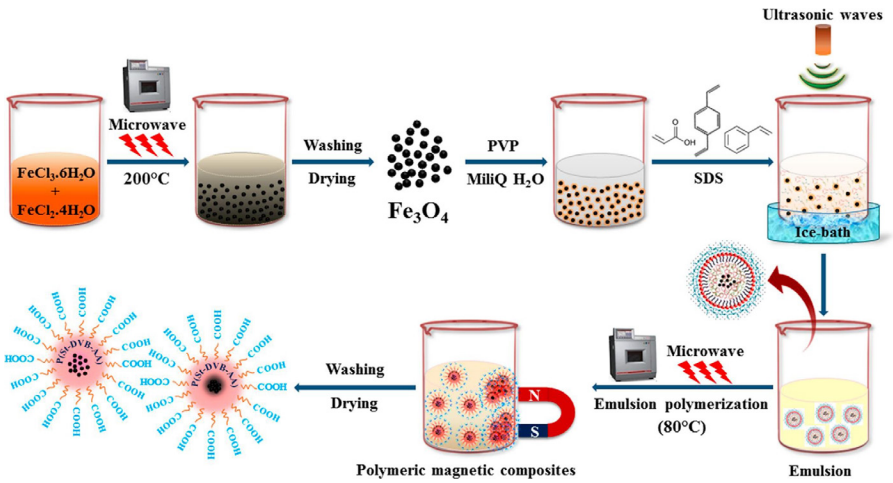

FIG. 28.2 Microwave-assisted synthesis method of Fe_3O_4 nanoparticles and Fe_3O_4/poly(styrene–divinylbenzene-acrylic acid) composites (Jaiswal et al., 2018).

polyethylene glycol were dissolved in ethylene glycol under vigorous stirring and then transferred to microwave polytetrafluoroethylene (PTFE) tubes and subjected to microwave heating for a fixed duration. Polymeric magnetic composites were prepared via emulsion polymerization of organic vinyl monomers in the presence of PVP-stabilized Fe_3O_4 nanoparticles (MNP-3) using microwave irradiation. the MNP-3 synthesized in 10 min microwave irradiation time exhibits highly crystalline nature (average crystallite size 33 nm).

28.2.3 Other synthesis methods

Other synthesis methods, like, electrochemical, mechanochemical, and sonochemical methods, have also been reported (Jaiswal et al., 2018). These methods have certain advantages and disadvantages. In case of electrochemical synthesis, the metal ions are introduced by an electrochemical process, such as deposition of metal cations on cathode. An alternative to this can be the use of protic solvents, but their usage releases hydrogen. Further, prevention of hydrogen dissipation can be remediated by solvents, such as acrylonitrile, acrylates, and maleates. This method produces both powders and films (Martinez Joaristi et al., 2012). Processing technique of solids in which both mechanical and chemical phenomena are coupled on a molecular scale, is mechanochemical synthesis method (Lv et al., 2017). This method allows rapid reactions and high yield without solvent or even in the presence of its small amount. Reactions can be carried out at room temperature under solvent-free conditions, which is especially advantageous, when organic solvents are avoided. Short reaction times, normally in the range of 10-60 minutes, can lead to quantitative yields and generally products containing small particle size are obtained. Moreover, in some cases, metal salts can be replaced by metal oxides as a starting material, which results in the formation of water as sole by-product. In contrast, metal oxides are rarely used in solvent-based reactions due to their low solubility. First few studies, related to mechanochemical synthesis methods, were performed under solvent-free conditions. Use of organic reactants with low melting point and hydrated metal salts, preferentially the ones containing basic anions, were shown to be advantageous. Thus, well-crystalline compounds were obtained using metal acetates or carbonates. As a result, acetic acid is often observed as the by-product that is present in the pores of synthesized MOFs. This synthesis influences the phase formation and assists in the formation of porous and non-porous materials (Chen et al., 2019). Another method for preparation, which is fast, energy-efficient, environmentally friendly, room temperature mediated is sonochemical synthesis technique (Son et al., 2008). Compared to the solvothermal synthesis, which is carried out at higher temperature and longer duration (140°C for 24 hours), milder conditions and faster reactions were reported under this method. However, optimization of solvothermal synthesis to shorten reaction time or reduce reaction temperature was not tested. Size and morphology of the reaction product varied with reaction time. Short reactions led to spherical particles, while reactions for 30 to 90 min resulted in long needles with a diameter of up to 900 nm. This method is time and power sensitive.

28.3 Applications of metal organic frameworks for water treatment

28.3.1 Recent advancements in usage of metal organic frameworks towards water treatment

Table 28.1 summarises the application of MOFs for water treatment containing ionic contaminants. Zr-based MOF-808 [$Zr_6O_4(OH)_4(COOH)_6(BTC)_2$] supported on poly-acrylonitrile (PAN) nanofiber, Fe_3O_4(iron oxide)-ethylenediamine/MIL-101(Fe), 3D cobalt (II) MOF [[$Co_2(TATAB)(OH)(H_2O)_2]\cdot H_2O\cdot 0.6O]_n$ were synthesized for the removal of cadmium, zinc, lead, chromium, aluminium, mercury, and iron from water (Efome et al., 2018, Babazadeh et al., 2015, Abbasi et al., 2015). Fluoride removal was performed using Zr-MOF adsorbent and membrane (He et al., 2016), aluminium fumarate (AlFu) (Karmakar et al., 2016), Zr (zirconium)-fumarate (MOF-801) (Zhu et al., 2018), UiO-66-NH_2 (Lin et al., 2016), lanthanide-based MOFs (Ma et al., 2017) and UiO-66-amine (Massoudinejad et al., 2016). Zn (zinc)-MOF-74 (Tarboush et al., 2018), amino acid assisted hierarchical zeolitic imidazolate framework (ZIF-8) (Wu et al., 2014), ZIF-8 (Li et al., 2014), UiO-66 (Wang et al., 2015), indium MOF (Atallah et al., 2018), MIL-53 (Fe) (Materials of Institut Lavoisier) (Vu et al., 2015), Fe_3O_4@MIL-101 (Folens et al., 2016) were utilized for arsenic adsorption. Hydrothermal or solvothermal method of synthesis is utilized in most of the MOFs. It was observed from the studies that the effect of surface ions played a major role in the adsorption of the fluoride and arsenic. Apart from the effect of surface ions, intraparticle diffusion, electrostatic interaction, $\pi - \pi$ stacking, and hydrogen bonding governed the adsorption process.

28.3.2 MOFs for removal of emerging contaminants and their uptake mechanism

Extraordinary structural and surface properties of MOFs, as discussed before, makes them an attractive alternative adsorbent for the removal of emerging contaminants from aqueous phase. Table 28.2 summarizes the uptake mechanism of MOFs used for the removal of ECs. Host-guest interactions, such as electrostatic, acid-base, pi-complexation, hydrogen bonding, hydrophobicity and coordination with open metal sites, play important roles in adsorption of organic pollutants in MOFs (Cychosz and Matzger, 2010, Wang et al., 2016). Pharmaceutical and personal care products (PPCPs) such as naproxen, clofibric acid, diclofenac, ibuprofen, tetracycline, and ciprofloxacin have been removed using MIL-101(Cr) (Hasan et al., 2012), MIL -100(Fe) (Hasan et al., 2012), ZIF-8/ C_3N_4 (Panneri et al., 2017), ZIF – 8 (Bhadra et al., 2017), PCDM – 1000 (Bhadra et al., 2017), MOF – 5 (Gadipelly et al., 2018), UiO-66(Zr) (Hasan et al., 2016), NH_2-UiO-66(Zr) (Hasan et al., 2016), ED-MIL-101(Cr) & AMSA-MIL-101(Cr) (Hasan et al., 2013). It was observed that the principal adsorption mechanism was linked to electrostatic, $\pi - \pi$, and hydrophobic interactions. Wastewater from the livestock and agricultural sectors are major sources of the environmental accumulation of veterinary drugs, such as p-arsanilic acid (ASA) and

Table 28.1 Applications of MOFs for removal of ionic contaminants.

Adsorbent	Adsorbate	Synthesis route	Surface area (m^2/g)	Maximum uptake capacity (mg/g)	Reference
Zr-based MOF-808 [$Zr_6O_4(OH)_4(COOH)_6(BTC)_2$] supported on polyacrylonitrile (PAN)	Cadmium and zinc	Co-electro spinning	939	225 (cadmium) 287 (zinc)	(Efome et al., 2018)
Fe_3O_4-ethylenediamine / MIL-101(Fe)	Cadmium, zinc, lead and chromium	Solvothermal synthesis	Avg. particle size of 30nm	155 (cadmium) 198 (lead) 164 (zinc) 173 (chromium)	(Babazadeh et al., 2015)
3D cobalt (II) MOF [$[Co_2(TATAB)(OH)(H_2O)_2]\cdot H_2O\cdot 0.6O]_n$	lead, cadmium, aluminium, mercury and iron	Hydrothermal synthesis	Not observed in literature	50% removal efficiency (lead) 60% removal efficiency (cadmium) 80% removal efficiency (aluminium) 60% removal efficiency (mercury) 100% removal efficiency (iron)	(Abbasi et al., 2015)
Zr-MOF adsorbent and membrane	Fluoride	In-situ solvothermal synthesis	740	102	(He et al., 2016)
Aluminium Fumarate (AlFu)	Fluoride	Hydrothermal synthesis	1156	600	(Karmakar et al., 2016)
Zr-fumarate (MOF-801)	Fluoride	Synthesized in a water-based system using formic acid as a reactor modulator	725	40	(Zhu et al., 2018)
UiO-66-NH_2	Fluoride	Hydrothermal	905	59	(Lin et al., 2016)
Lanthanide based MOFs (1)-{$[Ce(L1)_{0.5}(NO_3)(H_2O)_2]\bullet 2DMF$} (2)-$[Eu_3(L2)_2(OH)(DMF)_{0.22}(H_2O)_{5.78}]$ (2)	Fluoride	Hydrothermal	Not observed in literature	104 (1) 57 (2)	(Ma et al., 2017)

Table 28.1 Applications of MOFs for removal of ionic contaminants. *Continued*

Adsorbent	Adsorbate	Synthesis route	Surface area (m^2/g)	Maximum uptake capacity (mg/g)	Reference
UiO-66-amine	Fluoride	Hydrothermal	569	42	(Massoudinejad et al., 2016)
Zn-MOF-74	Arsenic	Room temperature precipitation	690	99	(Tarboush et al., 2018)
Amino acid assisted hierarchical ZIF-8	Arsenic	Room temperature precipitation	587	91	(Wu et al., 2014)
ZIF-8	Arsenic	Room temperature precipitation	1388	77	(Li et al., 2014)
UiO-66	Arsenic	Solvothermal	570	303	(Wang et al., 2015)
Indium MOF	Arsenic	Solvothermal	310	103	(Atallah et al., 2018)
MIL-53 (Fe)	Arsenic	HF free solvothermal method	14	21	(Vu et al., 2015)
Fe_3O_4@MIL-101	Arsenic	Hydrothermal	2270	122 (arsenite) 80 (arsenate)	(Folens et al., 2016)

Table 28.2 MOFs used for removal of ECs and their uptake mechanism.

MOF	Emerging contaminant	Maximum uptake capacity (mg/g)	Uptake mechanism	Reference
MIL-101(Cr) MIL -100(Fe) MIL-101(Cr)	Naproxen; Clofibric acid	132 (MIL-100(Cr) for Naproxen) 115 (MIL-100(Fe) for Naproxen) 312 (MIL-101(Cr) for Clofibric acid)	Electrostatic interaction	(Hasan et al., 2012)
ZIF-8/C_3N_4	Tetracycline	420	Electrostatic and π–π inter-action	(Panneri et al., 2017)
ZIF-8 PCDM-1000	Diclofenac; Ibuprofen	100 (ZIF-8 for Diclofenac) 400 (PCDM-1000 for Diclofenac) 29 (ZIF-8 for Ibuprofen) 320 (PCDM-1000 for Ibuprofen)	Hydrogen bonding, π – π, and Hydrophobic interaction	(Bhadra et al., 2017)
MOF-5	Ciprofloxacin	98	Electrostatic interaction	(Gadipelly et al., 2018)
UiO-66(Zr) NH_2-UiO-66(Zr)	Diclofenac	189 (UiO-66) 106 (NH_2-UiO-66)	Electrostatic interaction	(Hasan et al., 2016)
ED-MIL-101(Cr) AMSA-MIL-101(Cr)	Naproxen; Clofibric acid	154 (ED-MIL-101 for Naproxen) 93 (AMSA-MIL-101 for Naproxen) 347 (ED-MIL-101 for Clofibric acid) 105 (AMSA-MIL-101 for clofibric acid)	Electrostatic interaction	(Hasan et al., 2013)
MIL-100 (Fe)	p-Arsanilic acid; Roxarsone	366 (p-Arsanilic acid) 387 (Roxarsone)	Coordination unsaturated sites	(Jun et al., 2015)
ZIF-8 UiO-66(Zr) NH_2-UiO-66(Zr)	Phthalic acid	654 (ZIF-8) 187 (UiO-66) 224 (NH_2-UiO-66)	Electrostatic & acid-base interactions	(Khan et al., 2015)

Table 28.2 MOFs used for removal of ECs and their uptake mechanism. *Continued*

MOF	Emerging contaminant	Maximum uptake capacity (mg/g)	Uptake mechanism	Reference
ZIF-67	Phenol	378	Electrostatic interactions	(Pan et al., 2016)
NH_2-MIL-53(Al)	p-nitro phenol	298	Hydrogen bonding	(Jia et al., 2017)
ZIF-8	Benzotriazole	298	Hydrophobic & $\pi - \pi$ inter-actions	(Jiang et al., 2013)
HKUST-1	Oil spills	4000	Hydrophobic interactions	(Lin et al., 2014)
MIL-53(Cr)	2,4-Dichlorophenoxy-acetic acid	556	Electrostatic interactions	(Jung et al., 2013)
ZIF-8	Oil spills	6633	Electrostatic & hydro-phobic inter-actions	(Lin et al., 2016)
Cu-BTC@ Cotton	Ethion	182	Coordination linkage & Hydrogen bonding	(Abdelhameed et al., 2016)
MIL-101(Cr)	Xylenol orange	325	Electrostatic interaction	(Chen et al., 2012)
MIL-101(Cr)	Uranine	127	Electrostatic interaction	(Leng et al., 2014)
UiO-67(Zr)	Glyphosate; Glufosinate	537 (Glyphosate) 360 (Glufosinate)	Chemisorption	(Zhu et al., 2015)
UiO-66(Zr)	Methylchlorophenoxy-propionic Acid	370	Electrostatic and π–π inter-action	(Seo et al., 2015)
MOF-235	Methyl orange	477	Electrostatic interaction	(Haque et al., 2011)

roxarsone. These drugs can transform into hazardous inorganic arsenic compounds. Hence, it becomes important to remove such drugs, when they are dumped in aqueous phase without minimum treatment. Adsorption mechanism involved the coordination of p-ASA and roxarsone with coordinative unsaturated sites (CUSs) on the MIL-100(Fe) (Hasan et al., 2013). Industrial effluents consisting of different organic and inorganic chemicals contribute considerably to aquatic pollution. Phthalates are industrial ECs that exhibit endocrine disrupting properties. Removal of phthalic acid (Khan et al., 2015), phenol (Pan et al., 2016), p-nitrophenol (Jia et al., 2017), benzotriazole (Jiang et al., 2013) and oil spills (Lin et al., 2014, Lin et al., 2016) were carried out using ZIF – 8, UiO-66(Zr), NH_2-UiO-66(Zr), ZIF – 67, NH_2-MIL-53(Al), HKUST–1. HKUST-1 (copper-based MOFs) has demonstrated a promising removal capacity (4000 mg/g) of oil droplets from water (Lin et al., 2014). This capacity is approximately six times larger than that of the commercial AC. Similarly, ZIF-8 was also exploited to demulsify the oil and water (Lin et al., 2016). High surface area and positively charged surface of the ZIF-8 effectively removed negatively charged oil droplets from water. Effective removal of oil droplets was influenced by variable parameters such as temperature, pH, and amount of salt or surfactant. Adsorptive removal of 2,4-dichlorophenoxyacetic acid (2,4-D) by MIL-53 (Cr) was studied and it was observed that adsorption was very fast, which was being complete within an hour (Jung et al., 2013). MIL-53 (Cr) showed higher adsorption capacity (556 mg/g) than conventional AC (286 mg/g) and zeolite (256 mg/g) because of its high porosity and electrostatic interactions between the host and guest molecules. Ethion (Abdelhameed et al., 2016), glyphosate, glufosinate, and methylchlorophenoxy-propionic acid (Zhu et al., 2015, Seo et al., 2015) were treated using Cu (copper) – BTC@ Cotton, UiO – 67 (zirconium MOF) and UiO – 66(zirconium MOF). Dyes such as xylenol orange (Chen et al., 2012), uranine (Leng et al., 2014) and methyl orange (Haque et al., 2011) were also treated simultaneously, using MIL – 101(chromium) and MOF – 235.

28.4 Limitations of using metal organic frameworks and alternative strategy

Till date, much of the experimental and theoretical research on MOF applications has focused on adsorption of gases and water contaminants. MOFs have reported high loadings and selectivity for various target contaminants. MOF performance in humid environments can be decisive. As researchers have begun to address water adsorption in MOFs, several features have emerged as being critical contributors to MOF's stability. These features include shielding of coordination sites by functional groups, extent of coordination between the metal and ligand structures and basicity of organic ligand (Burtch et al., 2014, Goesten et al., 2013). Hence, behavior of MOFs in presence of water is important when considering these materials for adsorption applications as the stability of an adsorbent in aqueous environments is a critical property that must be considered.

Following approaches can be utilized to impart water stability –

a. increasing the external crystal surface's hydrophobicity in order to exclude water from entering the pore (Nguyen and Cohen, 2010).
b. increasing crystal surface hydrophobicity via core–shell structures where a more hydrolytically stable, hydrophobic MOF serves as a shell to protect a more moisture-sensitive MOF encapsulated at the core (Li et al., 2013).
c. by turning the organic ligands on the surface of the crystal into an amorphous carbon layer via heating under nitrogen (Yang and Park, 2012).
d. by incorporating surfactants during the solvent drying process (Yoo et al., 2011).
e. introducing hydrophobicity on the internal surface of the structure (Decoste et al., 2012).

Additionally, studies related to MOFs are limited to lab scale usage. In order to use these adsorbents in industrial scale treatment, it is important to have their availability in bulk amount. Following methods can be adopted to scale-up synthesis of MOFs:

a. modulated hydrothermal (MHT) synthesis that can be used to synthesize UiO-66-type MOFs (Hu et al., 2016, Hu et al., 2015).
b. continuous synthesis of MOFs through flow reactors, which is more promising due to its faster heat and mass transfer, thereby leading to higher production throughput (Kim et al., 2013).
c. microfluidic control, confining the reactants or target substrates within micro or nanoliter droplets, is a newly emerging strategy to generate uniform emulsions in order to achieve exquisite control of crystallization with better reaction kinetics and yield (Christopher and Anna, 2007, Baroud et al., 2010).

Apart from water stability and scale-up synthesis, MOFs involve high production costs as large amount of organic solvent and high temperature are used (Kim et al., 2015). To avoid/curb the excess cost, modifications in the synthesis methods can be approached for economic usage of MOFs. Modifications in synthesis technique can be incorporated as:

a. coating MOF particles with hydrophobic polymers as a feasible way to adjust the surface properties of MOF particles (Chun et al., 2014)
b. embedding metal nanoparticles on porous supports, thereby exposing surface atoms (White et al., 2009)
c. introducing extra metal cations into MOFs as an effective way to generate heterogeneity inside MOFs, because different metals have varied coordination modes and affinity toward guest molecules (Brozek and Dincă, 2014)
d. cross linking of functional groups within the MOFs as a utilization tool to tune porosity and functionality of the frameworks (Odian, 2004)
e. ionization process, changing the polarity of MOFs to endow them with new features (Hu et al., 2015)
f. employing two or more ligands with different functional groups to conduct isostructural MOF synthesis, introducing potential asymmetry, heterogeneity and possible synergistic effects into resultant MOFs (Chavan et al., 2014)

28.5 Conclusions

MOFs are special class of adsorbents, accounting for high surface area and coordinating chemistry. They are especially used in gas separation and catalytic process due to their dense structural geometry. Owing to its tunable properties, their coordinating bonds can be replaced by using different metal ion and ligands. They are prepared by different synthesis routes, such as, solvothermal, microwave assisted, electrochemical, sonochemical, and mechanochemical process. However, solvothermal and microwave assisted method are most widely used and reliable methods to synthesize MOFs, having high selectivity. Researchers have also started visualizing their effects in removal of water borne contaminants, especially ionic in nature. They have proved to be beneficial over conventional adsorbents, like, activated carbon and zeolites in this aspect. Due to their aspiring nature in water treatment domain, they are currently being subjected to removal of emerging contaminants, like, pesticides, pharmaceutical compounds, personal care products and endocrine disruptors. These compounds are found in trace quantities in water stream and are more harmful and persistent in nature. MOFs have also proven to have high uptake capacities for such compounds and removal takes place especially by electrostatic interactions. However, MOFs have certain limitations related to its bulk scale synthesis, cost and especially stability in aqueous environments. But these can be overcome by suitably using modifications over existing synthesis methods.

Abbreviations

AC	Activated carbon
AMSA	Aminomethanesulfonic acid
AOPs	Advanced oxidation process
Cu-BTC	Copper benzene-1,3,5-tricarboxylate
DMF	N,N -dimethyl formamide
EC	Emerging contaminants
EDCs	Endocrine disrupting compounds
ED	Ethylenediamine
HKUST	Hong Kong University of Science and Technology
MIL	Materials of Institute Lavoisier
MOF	Metal Organic Framework

pH_{PZC}	Point of zero charge
POP	Persistent organic pollutants
PPCPs	Pharmaceuticals and personal care products
PTFE	Polyfluorotetraethylene
TATAB	4,4′,4″-s-triazin-1,3,5-triyltri-p-aminobenzoate
WWTPs	Wastewater treatment plants
ZIF	Zeolitic imidazolate framework
Zr	Zirconium

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CHAPTER

29

Removal of emerging contaminants from wastewater through bionanotechnology

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29.1 Introduction

Emerging contaminants or contaminants of emerging concerns (COEC) basically includes a diverse range of chemicals and compounds such as pesticides, pharmaceuticals (endocrine-disrupting compounds, analgesics, antibiotics, hormones, and a whole range of other pharmaceutical compounds), nanomaterials (waste nanomaterial during synthesis of nanoparticles and applications), personal care products, disinfection byproducts, plasticizers, and others (Richardson, 2009; Richardson and Ternes, 2014); that are consistently being found in groundwater, surface water, municipal wastewater, drinking water, and other food sources (Bolong et al., 2009; Petrović et al., 2003).

Emerging contaminants are chemicals of synthetic and natural occurring, it may be any microbes that are not generally monitored in the environment but possess serious environmental threat. The hazard lies in the fact that the environmental and human toxicology of most of these ECs have not yet been studied and in the fact that many of these compounds are not or cannot be tested for in municipal water system. Additionally, when these contaminants pass through drinking water treatment systems, by-products are generated whose chemical properties are not yet determined. The presence of chemical contaminants at the lower concentration even in μg^{l-1} level possesses serious threat to the aquatic environment and has become evident with the improvement of analytical techniques (Tran et al., 2018). The availability of advanced techniques like, ICP-MS, NMR, liquid chromatography–mass spectrometry (LC–MS) and LC–MS/MS able to detects polar compounds such as pharmaceuticals, metabolites, and their transformation products that have not previously been amenable to analysis (Dolar et al., 2012); that is the reason these contaminants are referred as emerging contaminants. These contaminants are released from industrial,

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urban, agricultural wastes, and other anthropogenic activities. Most of them are currently undetected due to lack of concerns. Also, most of the chemicals used by consumers ultimately ended up in sewage, "emerging contaminants" is a term that describes nowadays often the pollution of the aquatic environment of that was previously went unnoticed (Grassi et al., 2012). Nowadays, water contamination due to the drugs and pharmaceuticals residues is increasing and very alarming as these contaminants are called as new emerging pollutants (Terzić et al., 2008). The water contamination due to the new emerging contaminants is of great concern due to their endocrine, hormonal and genetic disrupting nature (Poynton and Vulpe, 2009). As few drugs and pharmaceuticals residues are converted into chiral metabolites which are receptor specific and possess serious side effects to human health (da Silva et al., 2019). The present chapter gives detail account of adverse effects of emerging contaminants and discusses the potential removal processes.

29.2 Definition of emerging contaminants

Emerging contaminants (ECs) (Dulio et al., 2018) are a group of natural and synthetic chemicals and their transformation products occurring in aquatic medium which are not monitored at present in the environment but have a high potential to environmental harm and negative effects on human health and environment (Geissen et al., 2015). These contaminants of emerging concern enter the environment every day due to various activities.

The release of ECs has been predicted to be occurring for a long time and through diverse sources with concentrations ranging from μg/L to a few ng/L and sometimes even below, but the discovery, detection, and monitoring of such low concentrations of these persistent compounds was not possible earlier and only until the last decade owing to the development of highly sophisticated detection methods and analytical technologies made it possible to detect the contaminants of questionable emergence (Zhang et al., 2015; Klamerth et al., 2010). Recent advancement in the field of nanotechnology, chemical industry, and pharmaceutical industries will only further add the variety of new complex water pollutants in the coming years (Cassani and Gramatica, 2015).

29.3 Sources of emerging contaminants

People use chemical-based and personal care products every day that includes sunscreens to medicine to health care supplements. These chemicals remain in wastewater for extended period of time and moreover treatment plants are not designed to identify these chemicals at present (Sorensen et al., 2015). Likewise, industrial processes that have their own treatment plants do not remove all these chemicals, either and release such chemicals directly into water (Jones-Lepp et al., 2012). Eventually, they end up in the lakes and rivers and contaminate the aquatic environment. Thus,

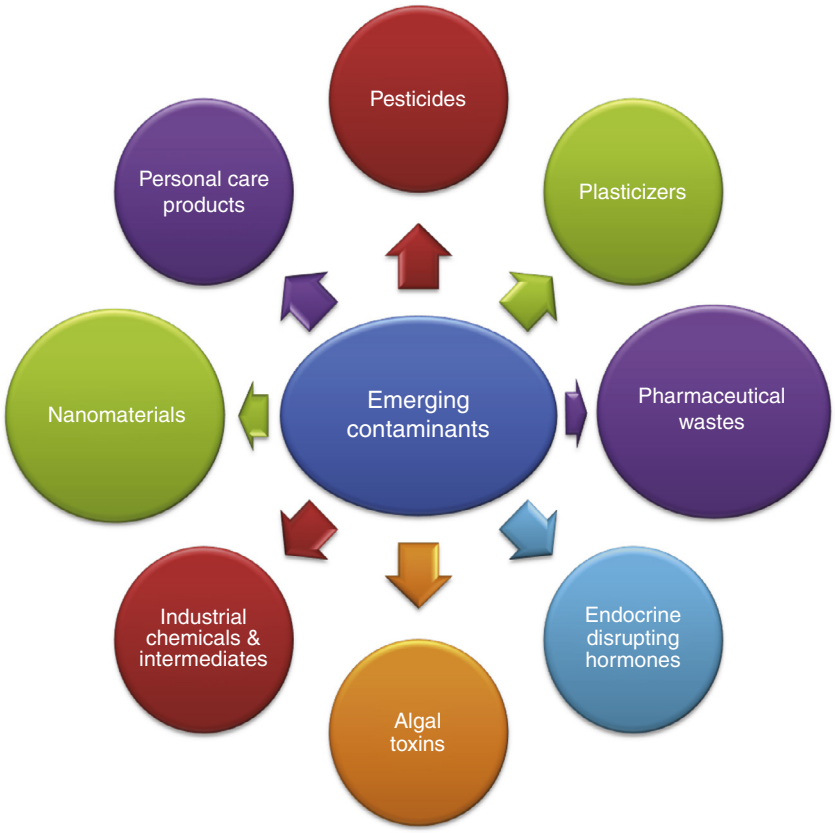

FIG. 29.1 Contaminants of emerging concerns in environment.

in the long term, these compounds are contaminating the environment. They have some serious effects on the environment and humans and their risk is still uncertain (Petrovic et al., 2008). Fig. 29.2 shows the percent of emerging contaminants in the environment.

Pharmaceuticals are a considered as significant class of emerging environmental contaminants (Rivera-Utrilla et al., 2013), as tons of pharmaceuticals wastes are annually produced, consumed, and released in the environment, and their presence in water bodies such as groundwater, surface water, seawater and treated sewage effluents is well-documented worldwide (Birch et al., 2015). It is an issue of great concern, because they negatively affect the growth, reproduction and behavior of non-target organisms and especially aquatic life; many ecotoxicological effects have been reported for pharmaceutical pollutants during past decade. The pharmaceutical residues are also of substantial interest due to their relative stability, such as, it is difficult to undergo biodegradation and incomplete assimilation by animals and humans during their usage; also because of higher stability, these pharmaceutical

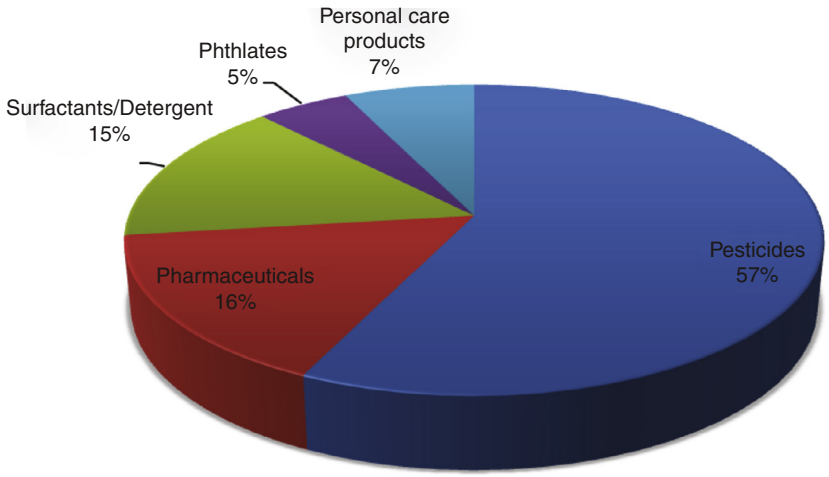

FIG. 29.2 Emerging contaminants in the environment.

contaminants are difficult to metabolize completely and therefore excreted through feces and urine and emerges into wastewater treatment plant and surface water (Terzić et al., 2008). More than 3000 substances were used as pharmaceutical ingredients including painkiller, antibiotics, anti-diabetics, antidepressant, impotence drugs, beta-blockers, X-ray contrast media, contraceptives, and lipids regulators; most of them are excreted out and comparatively hard to eliminate from wastewater due to lack of efficient treatment technology (Sharma et al., 2019). According to research study conducted by Pomati et al. (2006), it was observed that 90% of pharmaceutically active compounds (PhACs) entered the domestic water systems through excretion. Fekadu et al. (2019) have studied recently the emergence of pharmaceuticals wastes in freshwater aquatic ecosystems; it is interesting to note that numerous pharmaceuticals were detected at much high concentration levels exceeding their ecotoxicity endpoint, which needs to be taken for the serious concern. Pharmaceuticals can be successfully removed by nanofiltration (NF) membranes by means of three methods such as adsorption, electrostatic repulsion and sieving (Yangali-Quintanilla et al., 2010). Depending on various compounds the removal efficiencies vary, and is stringently associated to the physicochemical properties of micro-pollutants and membrane properties. NF has been shown to be a propitious option for dispensing with pharmaceuticals, as it can accomplish more than 90% removal efficiency (Yangali-Quintanilla et al., 2011).

Other than pharma wastes, personal care products (PCP) also possess risk. A PCP is any product with healthcare, medical and cosmetic purposes for humans and is referred to as personal care product (PCP) (Jim et al., 2006). Due to their global consumption, low human metabolic capability and improper disposal, along with the inability of wastewater treatment plants to effectively remove them, PCPs makes their way in water bodies at concentrations ranging between ng/L to few μg/L.

Table 29.1 Class and examples of Emerging contaminants.

S.No	Class of EC	Examples
1.	Pharmaceutical Wastes	Antibiotics, analgesics, anticancer drugs, anticonvulsants, mood stabilizers, X-Ray contrasts, diuretics
2.	Pesticides/biocides	Perfluororoctane sulfonates (PFOS) and perfluorocta-noic acid (PFOA). Triclosan, atrazine, organophospho-rous pesticides, thiocarbamates.
3.	Industrial/domestic wastes/Food additives	PAH, Bisphenol A, toluene, chelating agents (EDTA), aromatic sulfonates, sucralose
4.	Personal Care Products (PPCPs)	Cosmetic products, fragrances, sunscreens, insect repellents, disinfactants,
5.	Steroids and endocrine disrupters	Biogenic and synthetic hormones, estradiol, estrones, estriol
6.	Flame retardants and their impurities	Polybromonated diphenyl ethers (PBDEs) and hexabromocyclododecanes (HBCDs), tetrabrmo bisphenol,
7.	Disinfection byproducts	Nitrosamines and disinfection byproducts containing iodine
8.	Illicit drugs	Cocaine & metabolites, amphetamines
9.	Heavy Metals	Mercury, arsenic, copper, chromium, nickel, lead.
10.	Engineered Nanomaterials	Graphene, carbon nanotubes and other metallic nanoparticles

Despite their low concentrations, PCPs may negatively affect human health and the environment; there is the need for improved wastewater treatment of antimicrobials, polycyclic compounds, and UV filters for the prevention of adverse effects on aquatic species (Ramprasad and Philip, 2016).

Antibiotics are also increasingly used in treatment of human and animals, they are less metabolized and discharged through excretion into the wastewater; it is known fact that some antibiotics are partially transformed in wastewater treatment plants and thus are released into water bodies give rise to significant class of emerging water contaminants (Milić et al., 2013; Ebele, et al., 2017).

Table 29.1 presents the class of emerging contaminants with common examples.

29.4 Environmental/health issues and regulations related to emerging contaminants

Due to the absence of relevant data on the impacts, fate and concentration levels of emerging contaminants make it troublesome for governments to control their utilization and also manage the levels that are already persisting in the environment. There are as of now no laws or mandates illustrating the upper limits of concentrations of emerging contaminants in wastewater discharge, drinking water, or the environment (Naidu et al., 2016).

The U.S. Food and Drug Administration (FDA, USA) revealed directions for the evaluation of human drugs. Environmental assessment has reported the expected introduction concentration of pharmaceuticals in the aquatic environment as $\geq 1\ \mu g\ L^{-1}$ (Gogoi et al., 2018). Many disinfection byproducts that are transformation products of ECs after treatment are regulated by the US, European Union and World Health Organization (WHO); But at present in India, there is no such regulation for ECs (Kumar et al., 2019). Contaminants from PhACs, PCPs and EDCs enter water bodies and can exceed and persist beyond acceptable levels. Various Polyaromatic hydrocarbons (PhACs) and EDCs, were enlisted in the Drinking Water Contaminant List as different PhACs, for example, ibuprofen, diclofenac, carbamazepine, erythromycin, naproxen, sulfamethoxazole, gemfibrozil, atenolol, and bezafibrate have been rated prime concern pharmaceuticals to the aquatic environment (Birch et al., 2015). The emergence of ECs in water has high probability of incorporation with the crops irrigated and further contaminates water and possesses risk to human health once consumed.

ECs can have harmful impacts on aquatic and terrestrial life as well as on human communities. Endocrine disrupting chemicals cause a number of reproductive and sexual abnormalities in various organisms and humans. Exposure to such chemicals amid pre/postnatal life can impair the development and signaling of the endocrine system (Bilal et al., 2019); also the effects during development are permanent and irreversible in many cases. Managing ECs in water resources is a critical issue that requires attention especially in sensitive ecosystems and in rapidly developing areas (Pal et al., 2014). Though, the ecological impacts of ECs in natural environment are different from the laboratory tests, as when present in the environment many factors like pH, soil or water type, ionizable compounds, etc. can influence the bioavailability of the ECs (Mohapatra, et al., 2016). It is necessary to comparatively study the degradation pattern of ECs in both the media to get the better understanding.

29.5 Conventional treatment technologies

The present chapter provides an overview of the different classes of emerging contaminants, their impacts, extent of removal by conventional treatment technologies such as activated sludge process, adsorption, flocculation, and known results on emerging innovative technologies.

Several physical, chemical and biological treatment technologies have been established for the removal of the various categories of the ECs. Physical processes such as adsorption by activated carbon and retention by RO/NF membranes found effective for the removal of many pharmaceuticals (Melo-Guimarães et al., 2013). Various biological treatments including conventional activated sludge process, MBR, biologically activated carbon and microalgae based treatment showed promising potential for the degradation of the EDCs, PCPs, beta blockers, pesticides, surfactants and pharmaceuticals (Yan et al., 2010). The conventional and advanced chemical oxidation processes including Ozonation, photo-Fenton processes, and photocatalysis are found as the most effective technologies for a broad range of the ECs such as PCPs,

beta blockers, and pesticides (Lima, 2018). However unlike the advantages, the available treatments has many limitations and challenges which includes high retention time in the biological treatments, final disposal of the sludge containing ECs in physical as well as biological treatments, high operational and maintenance cost associated with the advanced chemical technologies, and poor removal efficiency of many ECs (Rossner et al., 2009). Most of the hybrid systems have applied biological treatment pre and post other technologies for the higher degradation rate.

Conventional wastewater treatment plants exhibit some limitations and their own set of disadvantages with respect to the removal of ECs since ECs were not considered in their initial design. The endocrine disrupting chemicals comprise pharmaceuticals, surfactants, personal care products, various industrial additives and numerous chemicals claimed to be endocrine disrupter; these have become a threat to the ground and surface water systems. Though, advanced oxidation processes using ozone with other oxidation agents such as UV (ultraviolet), hydrogen peroxide, titanium oxide, ZnO, etc., prove efficient, cost effective, and can produce byproducts with unknown toxicity (Secondes et al., 2014). Early results for emerging biological technologies such as membrane bioreactors (MBRs) and granulation biotechnology indicate very promising ECs removal, but membrane fouling proves to be the main drawback of MBRs as it significantly reduces membrane performances which ultimately affect the cost and life (Dolar et al., 2012). On the other hand, the main drawback of granulation technology is the deterioration in granule stability under long-term operation and lack of a successful pilot- or full-scale application. Thus, advance research is required to subside the membrane fouling in MBRs and enhance long-term granule stability in granular systems. The technological revolution offered by nanomaterials (NMs) provides a new potential for the removal of EC through nanoremediation. Effective removal of EC has been reported using nanoadsorbents, nanomembrane filters, and photocatalysts. However, the environmental fate and the toxicological impact of NMs need to be study thoroughly for their potential toxicity and bioaccumulation as they also give rise to new category of contaminants of emerging concerns (Sichel et al., 2011; Zhao et al., 2018). Moreover, various processes such as chemical and biological method and photolysis can transform ECs into intermediate forms that can be more toxic than their parent compound.

Fig. 29.3 provides the overview of various treatment technologies for the removal of emerging contaminants from the wastewater. It shows physical, chemical, and biological method as well as methods of advanced removal techniques.

The current wastewater treatment strategies are not effective for removal of these different classes of emerging contaminants as these have not been monitored due to the lack of proper regulations on emerging contaminants in wastewater. These undesirable compounds are being released, knowingly or unknowingly, into the aquatic environment that affect the whole ecosystem to the greater extent. ECs will be a major challenge for human health and environment as their concentrations are increasing consistently. The contaminants occur in soil, air or water bodies eventually end-up in drinking water systems, and therefore, prevention of release of contaminants and treatment of contaminated water are absolutely needed.

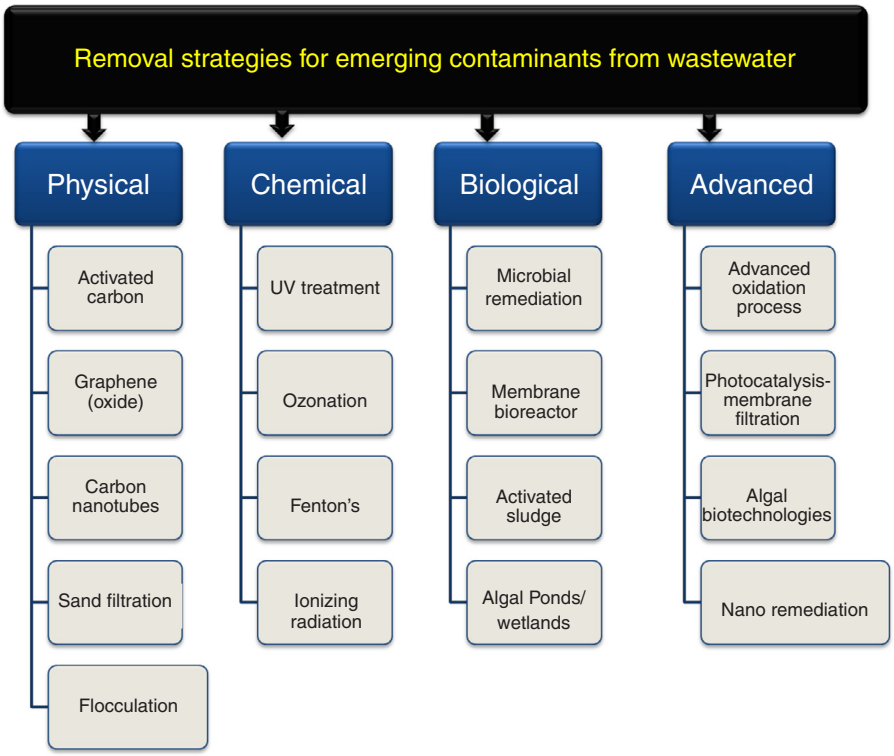

FIG. 29.3 Strategies for removal of emerging contaminants from wastewater.

29.6 Bionanotechnology for the removal of emerging contaminants

The main benefit of bionanotechnological approaches are providing clean, green and sustainable alternative for the removal of ECs. The development of such advanced technologies and its application has enabled mitigation of the environment towards a sustainable development. Nanomaterials are class of natural or engineered small-scale substances that have structural components whose sizes are less than 100 nm (1-100 nm) and at least one dimension (Pico et al., 2017). These include various types of nanoparticles (NPs) that have particles whose structures are nanoscale in at least two dimensions. Nanostructured materials offer unique properties, such as high surface area, high photosensitivity, size effect, quantum confinement effect, catalytic activity and magnetic properties, tunable pore size, and easy recovery, and reusability (Zhao at al., 2018).

These novel features make them suitable for the treatment of ECs in wastewater. So far, a large number of nanomaterials such as carbon nanotubes, carbon based materials, nanocomposites, graphene, nanometal or metal oxides, polymeric sorbents, and

bionanoadsorbents have been studied for the removal of ECs from aqueous solutions, and the results indicate that such nanomaterials show high removal rate (Kokkinos et al., 2020). Nanomaterials that have been reported to be useful in removal of ECs from wastewater are generally grouped into inorganic, carbon based nanotube, composites nanomaterials, polymer-based matrix, ceramic-based matrix, and metal-based matrix (Ghosh et al., 2013).

The majority of conventional techniques such as extraction, adsorption, and chemical oxidation are, in general, effectual for wastewater treatment to the limited extent but are extremely costly. In that manner, advanced nanomaterials prove to be sustainable alternative. Nanomaterials like nanoadsorbents, nanocomposite, and metal nanoparticles with active surface area emerges as the most effective way for the effective removal of wide range of ECs (Dhangar and Kumar, 2020).

At present, water resources have been found to have new such emerging pollutants. Many processes such as chemical transformation, physical separation, and biological treatment have been used to remove contaminants of different origin (Hamza et al., 2016). Nanotechnology offers effective treatment strategy, use and reuse of water and the development of next-generation water supply systems. The excellent properties and effectiveness of nanomaterials make them suitable candidates for the treatment of water and wastewater. The use of nano-based materials which can effectively adsorb and degrade wide range of environmental pollutants such as heavy metal ions, pesticides, dyes, pharmaceuticals, other organic pollutants, etc. and possess interesting antimicrobial properties against various waterborne microbes such as viruses and bacteria (Adeleye et al., 2016). Khan and Pathak (2020) reviewed the trends in nanomaterials applications in environmental remediation and underlined the efficiency of nanomaterials, along with the need to avoid further environmental contamination due to their use.

Several nanoscale materials have found their way to environmental remediation applications such as nanoscale zeolites, metal and metal oxides, titanium dioxide, carbon nanotubes and nanofibers, enzymes, and various noble metals (Dong et al., 2014). The use of activated carbon, nanofiltration and reverse osmosis membranes, oxidation, activated sludge etc. is generally used for the removal of these pollutants. In particular, the nanofiltration membrane removal mechanism is highlighted because of its efficiency in the removal of such micro pollutants. Nanotechnology emerges as the most efficient technology for the removal of emerging contaminants from wastewater. The mail benefit of nanotechnology is that there is no need of secondary treatment. Nanomaterials, such as nanoparticles, nanotubes, and nanostructured membranes are used for the removal of EC from wastewaters (Khin et al., 2012). Nanomaterials possess unique size-dependent properties emerge due to quantum confinement effect; shown great potential for removing these contaminants. Nano particles efficiently remove these pollutants and these are called as new generation nano-adsorbents (Kurniawan et al., 2012). These nanoadsorbents are capable to remove new emerging pollutants even at low concentration i.e. μg/L to nano gm/L under diverse conditions of pH and temperature. The present article describes state-of-the-art of the removal of new emerging pollutants using new generation

nanobiotechnology. Advanced processes based on nanostructured materials such as TiO_2/ZnO or nanofiltration membrane can achieve up to 95% removal of contaminants. The use of bionanotechnology for the removal of EC, utilizes nanomaterials with biomaterials or microbes for the remediation of ECs.

Adsorption is also a promising technique used worldwide for treatment of EC since it is low cost, highly-efficient and has simple operating conditions (Gómez-Pastora et al., 2014). Research has shown that the application of different nanoadsorbents materials such as, activated carbons, nanoadsorbents (carbon nanotubes, graphene, and iron oxide), nanocellulose, composite adsorbents, and other are being used for removal of EC's from water and wastewater (Kyzas et al., 2015). The use of cell extracts (from bacteria, fungi, algae, and plants) as green reagents for the syntheses of nanomaterials has now been recognized as a sustainable, energy efficient, ecofriendly, and cost-effective method for water and wastewater treatment (Chauhan and Talib, 2012). Gautam et al. (2019) studied the synthesis and applications of biogenic nanomaterials in environmental applications. Similarly, Ahmed et al. (2017) reviewed the microbes-based green biogenic nanoparticles (NPs) for water and wastewater treatment.

Different approaches involving the combination of several materials with desirable properties are more effective and efficient as compared with a single nanomaterial (Shah et al., 2015). The stable configuration resulting from adhering nanoparticles is a good alternative to the use of individual nanoparticles. A main factor that needs to be considered is that the properties of the materials being used should not have harmful effects on the environment, hence biodegradable materials are a good choice in this area (Rajiv et al., 2017). The efficient use of biodegradable materials enhances the scope of green nanotechnology, which manages waste in a responsible manner, without creating more waste that has to be dealt with. These novel technologies are now concentrating on particular contaminant-based applications, thereby increasing their efficiency. Cost-effectiveness, nontoxicity, recyclability, biodegradability, and the possibility of reuse through regeneration are some aspects that require consideration when designing nanomaterials (Asiya et al., 2020). The advantages and diverse potential of nanomaterials do not negate the possible adverse effects associated with their use if they are not handled properly.

The approach of bionanotechnology for the removal of environmental contaminants makes a way through the process of biodegradation (Seo and Roh, 2018; Rohela et al., 2019). As we know that, biological processes or bioremediation is a cost-effective technique that uses the metabolic action of microorganisms to degrade hazardous organic/inorganic contaminants. Biodegradation process is able to biotransform the target ECs contaminants through desirable catabolic enzymes to intermediates or end products (Mobasser and Firoozi, 2016). The efficiency of biodegradation varies according to the properties of compound, microorganisms and other environmental factors. The efficiency of biodegradation process varies according the properties of contaminants, microorganism, and other environmental factors such as temperature, light, and climate (Jain et al., 2017). The ECs are diffusely distributed over a widespread area and undergoes transportation by air, runoff erosion,

or leaching until reaching a water body; during transportation process, ECs can be intercepted by the sediments through sorption or degraded and never reach the water bodies (Rohela et al., 2019).

The search for "greener" and sustainable process for the remediation of ECs leads towards the bio-nanotechnology where green synthesized nanoparticles have been used for the degradation of ECs (Fosso-Kankeu, 2019). The processes for synthesizing green nanoparticles which are environmentally friendly, nontoxic are needed to avoid harmful environmental impacts emerge during the synthesis of nanoparticles by chemical methods (Khan, 2020). Several biological resources have been used for the synthesis of nanoparticles, including microorganisms such as, bacteria, fungi, yeasts, algae, and viruses as well as plant extracts. Researchers across the globe investigating different biological treatment processes such as conventional activated sludge, biological nutrient removal, and membrane bioreactors have reported that only easily biodegradable ECs such as caffeine, diclofenac, and trimethoprim can be removed, whereas low biodegradables (e.g., sulpiride, metoprolol, and bezafibrate) may not be eliminated through the process of biodegradation (Bilal et al., 2019). The biogenic (green) nanomaterials have been designed using metal oxides and noble metals of which the nanoscale zero-valent iron (ZVI) has a wider range of applications in removal of ECs.

In a study conducted by El-Gendy and Nassar (2015), they illustrated a comparative batch study for the application of spent waste biomass—yeast *Saccharomyces cerevisiae* by using tea leaves which is one of the major organic wastes in Egypt, as a low-cost bio sorbents for removal of phenol from aqueous solution. Factors affecting the adsorption process such as initial phenol concentration, pH, contact time, and operational temperature were studied. The Kinetic studies showed that biosorption follows the pseudo-second-order reaction; it was observed that increasing pH results in lower phenol loading per unit weight of the biosorbent, while increasing temperature, increases the biosorption efficiency.

In another study Ali et al. (2017) synthesized α-Fe_2O_3 nanoparticles (NPs) using the hot water extract of the mandarin (Citrus reticulum) peel waste. The prepared hematite was characterized by various techniques. The as-prepared α-Fe_2O_3 NPs showed good photocatalytic degradation activity and also showed good capacity for the decontamination of polluted water from anionic and cationic dyes and dicholorophenols under visible light irradiation.

The integration of two or more technologies such as biological and physicochemical methods by sequential application of nanoscale zerovalent iron and bioaugmentation appears to be an innovative way to remove the PCB contamination, which still persists in the environment (Cecchin et al., 2017; Semerád et al., 2020). The integrated approach is found to be one of the most effective remediation technologies for the ECs.

The biogenic (green) nanomaterials have been designed using metal oxides and noble metals of which the nanoscale zero-valent iron (ZVI) has a wider range of applications in removal of ECs. Moreover, variety of nanoparticles have been proposed for the successful remediation in past two decades such as Ag, nZVI, Fe(III)

oxides, Fe(II) oxides, ZnO, TiO_2, and nanocatalysts (Grieger et al., 2015). To assess the suitability of nanoparticles for contaminant remediation, a set of criteria has previously been proposed; highly reactivity, high mobility within porous media, sustained reactivity, low toxicity, and cost effectiveness (Corsi et al., 2018). Not all of the above nanoparticles adhere to these criteria, the nanoparticle which has gained the most attention, nZVI, is well suited due to its high reactivity, cheap cost, and apparent low toxicity. In a study, highly reactive nanoscale biogenic magnetite (BnM), synthesized by the Fe(III)-reducing bacterium Geobacter sulfurreducens, was tested for the potential to remediate an alkaline aqueous Cr(VI) leachate associated with chromite ore processing residue (COPR). The performance of this novel biomaterial was compared to a synthetic alternative, nano-scale zero valent iron (nZVI). Samples of highly contaminated alkaline groundwater and COPR solid waste were obtained from a contaminated and found that Cr(VI) removal from groundwater was inhibited by ~25% (BnM) and ~50% (nZVI) (Watts et al., 2015).

nZVI particles have also been used for the treatment of different organic compounds and pharmaceuticals such as trichloroethylene (TCE), polychlorinated biphenyls (PCB), and ibuprofen. The benefit of using nZVI particles in remediation is due to the electron efficiency. In addition, several studies have suggested that the use of nZVI is very effective in the degradation emerging contaminants, such as trihalomethanes, brominated/chlorinated methane, chlorinated benzenes, and other polychlorinated hydrocarbons in groundwater (Cecchin et al., 2017). Moreover, nZVI has also proven to be effective for the pesticide and dye degradation in an effective way. The efficient removal of polycyclic aromatic hydrocarbons (PAHs) through nZVI adsorbed on soils has also been reported (Boruah et al., 2019).

In biodegradation, microorganisms such as bacteria, fungi and algae degrade the high molecular weight molecules into smaller molecules, or biomineralize them to simpler inorganic molecules such as carbon dioxide and water. Conventionally, during biodegradation, organic compounds are primarily used by microorganisms for their cell growth; but the toxic nature of ECs inhibits biodegradation by resisting the microbial growth (Bilal et al., 2019). Microalgae/fungal-based treatments have reported effective removal of ECs by the mechanism of phytoremediation and biodegradation. These processes showed efficient removal (95–100%) of many ECs such as EDCs and PCPs; but were poor against pesticides removal to some extent. Thus, due to the promising potential of these processes, more comprehensive studies should be conducted and can be coupled with other biological active processes to improve removal of pesticides via biodegradation (Sarathy et al., 2011). Biosorption is the biological treatment process, where sorption and bio-oxidation mechanisms are more dominant due to immobilization of microorganisms over the adsorbents (Yadav et al., 2020; Vijayaraghavan and Yun, 2008). These bionanotechnological approaches promote binding of contaminants on certain biomass/cellular structures. Biosorption can be conducted using either live cultured or harvested rot fungus (microorganisms), however, higher efficiency was reported by live fungus as compared to harvested fungi. Biosorption was found effective for the removal of specific ECs, such as pharmaceuticals (gemi fibrozil, naprox, and ibuprofen) and some ECs (bisphenol

A, triclosan, 4-tert-octylphenol, pentachlorophenol, hence, need to be developed for the removal of wide range of ECs (Mallek et al., 2018).

Melo-Guimarães et al. (2013) conducted a study by integrating the membrane technology (UF), conventional biological treatment (ASP), and flocculation (F), for the cost-effective treatment of various ECs including beta blockers, pesticides, EDCs, and pharmaceuticals. Recently hybrid advanced wastewater treatment system was developed called osmotic membrane bioreactor (OMBR), an integration of the biological treatment, and forward osmosis (FO) was explored in combination with membrane technology (RO) for the removal of ECs (Li et al., 2018). The degradation of pharmaceuticals such as analgesics, antibiotics, PCPs, and many drugs, are widely studied by the hybrid treatments systems.

Photocatalysis is also one such approach for the effective removal of emerging contaminates from the environment. During the photolysis process, the ECs are decomposed through the effect of radiation or light (mostly UV) Photolysis to degrade ECs can be performed in two ways, either by direct photolysis (direct adsorption of photons on ECs) or by indirect photolysis (degradation in the presence of photosensitizes such as hydrogen peroxide) (Khan and Pathak, 2020). Both types of photolysis are effective in the removal of wide range of ECs such as EDCs, pesticides, analgesics and antibiotics; but UV photolysis in the presence of H_2O_2 is more efficient as the direct photolysis shows poor removal of beta blockers (Khan et al., 2018).

Biological oxidation process has many advantages but some of the bio-refractory compounds are not effectively removed; for that advanced oxidation processes (AOPs) can also be useful pre and/or post biological treatments. AOPs, such as photocatalysis, sonolysis, ozonation, electrochemical oxidation, Fenton, and Fenton-like reactions, are based on the production of highly reactive oxygen species, and can be used as pre or post-treatment to a biological process AOPs refer to the processes that assist the elevated generation of hydroxyl radicals. The generation of hydroxyl radicals usually starts with UV radiation and can be attained by various methods, such as photo-catalysis using nanocatalyst (i.e. TiO_2 and ZnO) (Khan and Yadav, 2020).

Other AOPs are Ozone/H_2O_2, UV/Ozone, etc., that enhances hydroxyl radical production. AOPs are very proficient novel strategies for water and wastewater treatment (Korpe et al., 2019). HO- is intense oxidizing agent that oxidizes organic matter, but it is non-specific catalysis. This property is of great significance in wastewater treatment since radicals attack oxidizable organic compounds with rate of $10^6 - 10^9\ M^{-1}\ S^{-1}$. The main drawback of this process is the economic constraint; therefore, nowadays environment friendly, sustainable energy saving techniques using solar energy for oxidation is employed. An investigation using solar heterogeneous photocatalysis with TiO_2, ozonation, and solar photo Fenton was done and it was found that photocatalytic ozonation offers a higher degradation percentage as compared to photocatalytic oxidation (Deng and Zhao, 2015). According to study conducted by Rizzo et al. (2019), they compared the advanced treatment technologies for the remediation of emerging contaminants from wastewater. They commented that advanced oxidation processes especially homogeneous and heterogeneous photocatalysis, have been found most effective for the degradation of emerging contaminants.

29.7 Future outlook

Comparatively less data is available with respect to the adequacy of conventional treatment technologies such as physical, chemical, biological treatment methods, adsorption, membrane filtration, etc. While it seems to be no processes with good efficiency for the removal of every single EC's under regular operational conditions, concluding that advanced treatment techniques should be applied for the effective removal.

With the development of advanced analytical tools; it is now possible to quantify the emerging contaminants from the range of environmental pollutants. Also, different approaches should also be made for the effective detection of new ECs in the complex environment systems and to find their efficient removal strategies. A large number of new emerging contaminants are arising every day that were not reported or detected earlier due to the lack of knowledge. Also, at present the information about the fate of ECs, their persistent transformation products, after the treatment is still lacking, this needs to be sought. Moreover, the ECs behave differently in natural environment and shows different ecotoxicological effects that cannot be predicted by conventional toxicity tests in labs. Therefore, it is required to develop new testing protocols for eco-toxicological analysis and measure different effects by using different organisms with suitable endpoints.

It is suggested that more exhaustive studies be led to fill knowledge gaps in the conduct of ECs under traditional and advanced treatment techniques. Future research ought to incorporate an intense emphasis on the treatment techniques and fate of these emerging contaminants into the environment and their conversion into more toxic or pharmacologically active metabolites during the treatment. Combination of two or three treatment methods should also be applied for removal of ECs that is more efficient in removing, rather than treatment applying single technique or conventional methods. Besides, future research ought to govern and delineate all fundamental treatment plant operational variables since these are crucial for later correlation or analysis.

29.8 Conclusion

In present chapter, we have discussed about the source, impacts and treatment of emerging contaminants. As we know, ECs are chemicals recently discovered in natural streams as a result of anthropogenic and industrial activities. Most of ECs have no regulatory standard as of now and can cause deadly effects in aquatic life as well as human health at environmentally relevant concentrations. As the conventional treatment technologies are not effective for the removal of these vast classes of emerging pollutants that's why advanced water treatments are necessary and need of an hour for the successful remediation of ECs. At standard temperatures and pressures emerging contaminants dissolve quickly without being evaporated, that is why they are commonly found in the water environment. Also, it is equally important to consider direct research on the fate, prevalence, and treatment of such contaminants from wastewaters.

As of now, majority of pharmaceuticals such as antibiotics and their byproducts are discharged directly into the municipal sewage; notwithstanding, there is very limited knowledge about their behavior and biodegradability in water. To predict the sources, fate and behaviors of ECs in the water environment researchers should concentrate on the development of a risk based screening models and framework in future.

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