Advances in Wastewater Research

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Biotechnological Removal of Emerging Pollutants from Wastewater Systems

Springer

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ISSN 3004-9725 ISSN 3004-9733 (electronic)
Advances in Wastewater Research
ISBN 978-981-96-3944-1 ISBN 978-981-96-3945-8 (eBook)
https://doi.org/10.1007/978-981-96-3945-8

This Springer imprint is published by the registered company Springer Nature Singapore Pte Ltd.
The registered company address is: 152 Beach Road, #21-01/04 Gateway East, Singapore 189721, Singapore

We dedicate this book to our parents, family, and teachers for their guidance and motivation

Preface

Emergent pollutants, both inorganic and organic, are known to have detrimental effects on public health and biodiversity. These pollutants, include pharmaceuticals, endocrine disruptors, heavy metals, antibiotics, and personal care products, which are released into surface water, contaminating groundwater, soil, sediments, and seas through anthropogenic sources. Effective removal and degradation of these pollutants are essential for environmental and human well-being. Bioremediation, using microorganisms for detoxification, breakdown, and immobilization, is a promising solution, alongside enzyme biotechnology, which is cost-effective, low-energy, and eco-friendly. However, bioremediation alone may not fully address all pollutants, and a combination of physical, chemical, and nanotechnological treatments is often necessary for sustainable pollutant removal.

This book consists of 18 chapters that explore various aspects of emergent pollutants, their health hazards, and bioremediation mechanisms. It covers the latest policy aspects, and regulation in using wastewater systems. It also includes topics like advancements in bioremediation, how microorganisms can break down pollutants, and the potential for bioremediation to mitigate global pollution. The book serves as a valuable resource for policymakers, researchers, climate change scientists, and students in fields like agriculture, forestry, ecology, and environmental science.

We extend our gratitude to the contributing authors, reviewers, and the Springer Nature team for their support. Special thanks to mentors, teachers, and students for their encouragement, and to colleagues, family, and friends for their unwavering support throughout the preparation of the book.

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Acknowledgments

We would like to express our heartfelt thanks and sincere gratitude to all the authors and reviewers for their invaluable contributions to this book. We greatly appreciate their timely submissions and the insightful revisions they provided. Our thanks also go to the publishing team at Springer Nature for giving us the opportunity to edit this work. We are deeply grateful to our colleagues for their support and encouragement, which gave us the confidence to complete this project. Lastly, we extend our profound appreciation to our family members for their unwavering support and continuous encouragement throughout the entire process.

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Chapter 1
Screening of Emerging Pollutants in Personal Care Products: Propensity of Risk and Preventive Strategy

Soumita Chatterjee, Chaitali Karmakar, and Sutapa Choudhury

Abstract Dermatological exposures to Emerging Pollutant and its pernicious effect on mankind have occupied comprehensive aspect throughout the globe. This study tries to identify the predominant Emerging Pollutants and its potential risks in specific Personal Care Products and also has endeavored to explore consumer awareness and attitudes towards pollutants in Personal Care Products within urban contexts in India. The present study employs multifaceted approach, incorporating a comprehensive literature review along with thick consumer behavior towards their Personal Care Products. Studied participants ($n = 751$) have indicated their regularly consumed Personal Care Products ($n = 153$) and detailed screening of Emerging Pollutants have taken place among all the products. Inclusive analysis has been executed through the interpretative method and inferential statistics for the empirical dataset, and the findings of Emerging Pollutants have been represented with an appraisal of parallel studies. Findings indicate poor consumer awareness about Emerging Pollutants that propel adults towards chronic health problems like endocrine disruption and carcinoma, while children may have sensitive physiology and immune-toxic effect in excessive application.

Keywords PCP · Pollutant · Cosmetics · Effect · Preventive strategy · Consumer behavior · Toxicity

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S. Dey and M. P. Shah (eds.), *Biotechnological Removal of Emerging Pollutants from Wastewater Systems*, Advances in Wastewater Research,
https://doi.org/10.1007/978-981-96-3945-8_1

Abbreviations

BIS	Bureau of Indian Standards
DMDM	Dimethylol-Dimethyl
DNA	Deoxyribonucleic Acid
ECHA	European Chemicals Agency
ED	Effective Dose
EDTA	Ethylenediamine Tetraacetic Acid
EP	Emerging Pollutant
EPA	Environmental Protection Agency
EU	European Union
FDA	Food and Drug Administration
HA	Hyaluronic Acid
LD	Lethal Dose
NTI	Narrow Therapeutic Index
PCP	Personal Care Product
PEG	Polyethylene Glycol
PFAS	Per- and Polyfluoroalkyl Substances
SLES	Sodium Laureth Sulfate
SLS	Sodium Lauryl Sulfate
SPF	Sun Protection Factor
TCS	Triclosan
TI	Therapeutic Index
UK	United Kingdom
US	United States
UV	Ultra Violate
WHO	World Health Organization

1.1 Introduction

Numerous pollutants have contaminated daily care products, presenting a diverse range of both pharmaceutical and personal care products. Personal Care Products (PCPs) are predominantly applied for maintaining regular hygiene levels, beautification, and enhancing the appearance of individuals (Khalid and Abdollahi 2021). In the case of personal hygiene, oral and dental products and bathing essentials are the leading ones. However, cosmetics are the compound products of natural, synthetic, and/or chemical components (Manayi and Saeidnia 2014). These sets of products can be grouped into two like leave on and rinse off. Products like toothpaste, soap, and shampoos usually come into contact for a while on the skin or oral membrane, whereas leave-on substances have occupied prolonged time over the skin, like cream, lotion, lipsticks, and so on (Juliano and Magrini 2017). Every individual has usually applied their PCPs as per their daily requirements and their range may vary in terms of gender, age, season, and ethnic diversity (Wu et al. 2010). Children, especially teenagers, use the highest number of PCPs in their daily life (Wu et al. 2010). Younger girls of less than 10 years were found to use sun spray and sun cream in South Korea than older girls (Oh et al. 2019). In terms of age, older people irrespective of gender used to apply hair dye in an extensive way, whereas younger girls are deeply addicted to hair straightening substances and younger boys intensely prefer hair serum and hair sprays (Biesterbos et al. 2012; Wu et al. 2010; Bernard et al. 2016; Gaston et al. 2019). Eventually, American women can be identified as great consumers of PCPs with approximate usage of 10 products in a day (Loretz et al. 2004, 2006, 2007). The human body can absorb up to 5 kg of life-threatening chemical compounds per annum from PCPs (Rawlings and Hardin 2004; Wang et al. 2019). PCPs are mostly unisexual, though women are the prime sufferers in this context due to their keen passion towards their appearance, beautification, and attractiveness (Khalid and Abdollahi 2021; Kohli et al. 2024).

Millions of studies have already set their benchmarks in terms of water body contamination, EPs as air pollutants, chemical emissions in the environment, and so on. However, dermatological exposures to EP and its pernicious effect on mankind have occupied a comprehensive aspect throughout the globe. Acceptable and embraced findings from international studies have followed up to maintain the research network (depicting in Fig. 1.1) in this study. The present study tries to apprehend the articulation of the context of PCPs with global versus local perspectives.

The speedy progress of the global cosmetics industry indicates around $463.5 billion in revenue will be generated by 2027 (Kohli et al. 2024; Allied Market Research 2016). The total revenue of India has generated from "Beauty and Personal Care Market" is $31.56 billion in 2024; moreover, anticipated market growth will

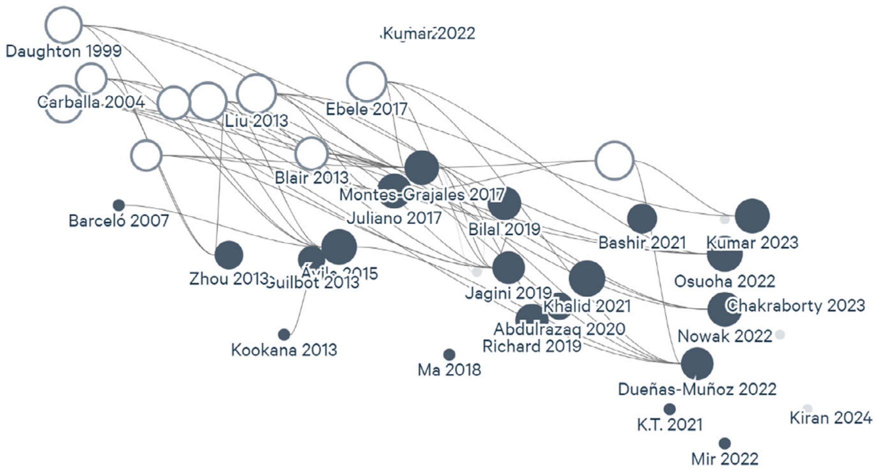

Fig. 1.1 Prepared by author through www.limaps.com

be 2.76% per annum according to CARG 2024–2029 (Statista n.d.). Nevertheless, the USA has set a benchmark with generated revenue of US$ 100 billion in 2024 from beauty and personal care products (Statista n.d.). Accelerated consumption of PCPs actually depicts the wider range of toxic emissions in the human body and environment as well. In the case of the per-day proportional distribution of chemical emissions, the entire load of PCPs in the Hunan Province of Southern China was 506.35 mg/d/1000 individuals, which contributes to the total chemical discharge of 357.56 mg/d/1000 people (Mao et al. 2019). As per the presence of EPs, shampoo and shower gel release per capita siloxanes discharge of 49.25 and 9574 μg/day, respectively (Capela et al. 2016). A vast variety of ingredients in these PCPs sometimes are the potential source of human lethality. Prior studies expressed that the contaminated pollutants typically affect human beings through dermatological exposures by the name of soaps, shampoos, toothpastes, lipsticks, sunscreens, and so on (Lang et al. 2016; Manayi and Saeidnia 2014). Contrastingly, more than 50% of the world populace is absolutely uninformed about the hazards of PCPs. For instance, almost 80% of female college students in South Carolina did not have any knowledge about the toxicity of their regular PCPs, precisely about the toxicity of phthalates, triclosans, and parabens (Hart et al. 2019). Equally, 48.6% of female college students were uncertain about the safety measures of PCP use (Chan et al. 2015). The current study tries to identify the predominant types of EP in specific PCPs and also has endeavored to explore consumer awareness and attitudes towards EP in personal care products within the urban context in India. Additionally, assessing the potential risks associated with EP exposure across different age groups and genders.

1.2 PCPs and Regulations

Currently, there are no proper and uniform regulations of PCPs in national and international markets; rather, the postulated protocols are purely based on geo-spatial markets throughout the globe (Osuoha et al. 2022). Common people have extensively utilized a wider variety of PCPs to maintain their self-care routine without gaining the least knowledge of the notorious effects of existing EPs in their products. Prior studies show that every individual consumes at least two PCPs on a daily basis and above 30% of the dermatologists also prescribed at least one PCPs along with medicines (Pandey et al. 2023; Hart et al. 2019). "Cosmetics" are largely dominating products under the realm of PCPs. According to EU Regulation 1223/2009 (article 2, 1.a), "cosmetic product means any substance or mixture intended to be placed in contact with the external parts of the human body (epidermis, hair system, nails, lips, and external genital organs) or with the teeth and the mucous membranes of the oral cavity with a view exclusively or mainly to cleaning them, perfuming them, changing their appearance, protecting them, keeping them in good condition or correcting body odors." As ingredients and chemical compositions are solely controlled by the regional manufacturers of the cosmetic products, the encashment of lacuna of uniform legislation of PCPs has boldly been expressed through the lens of vague and inappropriate information of proportion and ingredient list (Dodson et al. 2012). As a result, consumers are in deep fallacy regarding exposure of the EPs in self-care products and failed to avoid. Most of the cosmetics contain UV filters, antimicrobials, parabens and many more EPs (Lang et al. 2016).

Above 1500 and 800 chemical components were entirely banned in the manufacture of PCPs in, respectively, Europe and Canada. However, remarkably, only 11 chemical compounds have strict restrictions in the US for the same purpose (Feinstein and Collins 2018). Almost 45% of soaps are still containing antibacterial agents, i.e., triclosan and SLS, in spite of the bulk of legislative restrictions, especially in the US (Perencevich et al. 2001; Weatherly and Gosse 2017). In 2004, globally, 126 substances were documented by the US Environmental Protection Agency (US EPA) for prime contamination out of eight million both natural and synthetic components. Contrastingly, only 3% of materials were properly regulated (Daughton 2004; Hoenicke et al. 2007). Recently, the American Chemical Society (2021) has minutely screened above 180 million substances for PCPs manufacturing purposes (Osuoha et al. 2022; Juliano and Magrini 2017). The majority of the cosmetic products never mentioned "fragrance" as a harmful chemical substance throughout the world (Steinemann 2009).

1.3 Present Scenario of PCPs in India

India is one of the largest markets for cosmetics and daily care products. People use daily care products like soap, hair oil, shampoo, toothpaste, face wash, and hand wash as part of our regular hygiene routines. These products are essential for taking care of our skin, hair, and oral health, and they aren't just used by adults—children use them too. Unfortunately, we trust these products to keep us clean and healthy, but many of them are far from natural ingredients (Sheikh 2023). In fact, most of the products often contain numerous chemical ingredients; many of those ingredients or chemicals are potentially harmful to our health. Many people don't know that some of the chemicals used in the daily care products (Nayak et al. 2023) or cosmetics have been banned in other countries due to their toxic effects, but they are still allowed in India, for example, Lifebuoy Soap (Singh 2021). Hindustan Unilever recalled its Dove and Tresemme aerosol dry shampoos in the US after detecting benzene contamination, a chemical linked to cancer. However, these products are still available for purchase in India on platforms like Nykaa and Amazon (D'Souza 2022). Johnson & Johnson, after losing multimillion-dollar lawsuits over its talc-based baby powder's links to mesothelioma and ovarian cancer, ended sales in the U.S. and Canada in 2020 and announced global discontinuation by 2023. However, the product is still widely used and available in India (Singh et al. 2023).

While the government and laws in India, such as the Drugs and Cosmetics Act of 1940 (The Cosmetics Rule 2020), regulate the requirement to mention the names of chemicals used in products. It is clearly stated in Chapter IV, Section 34(7) of the Cosmetics Rule 2020 by the Government of India that "In all cases, ingredients over 1% must be listed in descending order by weight or volume, followed by those 1% or less, in any order, with the heading INGREDIENTS" (The Cosmetics Rule 2020). However, some manufacturers fail to disclose the actual ingredients used in their products, leading to a lack of transparency. As a result, consumers cannot assess whether the products they use daily are safe or harmful. Without clear labeling or information on what ingredients are used in the products, consumers often rely on marketing claims without fully understanding the potential risks. This highlights the need for stricter labeling regulations and better consumer education, enabling people to make more informed choices for themselves and their families.

1.4 Methodology

1.4.1 Period of Study, Design, and Population

The present study employs a multifaceted approach, incorporating a comprehensive literature review along with thick consumer behavior towards their personal care products. In the case of empirical data, brief interviews were hailed among the common people of Kolkata metropolitan city during the period of May–July 2024, under the frame of convenience sampling. The participants ($n = 751$) were selected in the age group ranging between 18 and 65 years, irrespective of gender and individual's identity, who are inhabitants of Kolkata by birth.

1.4.2 Data Collection and Procedure

To elucidate the empirical dataset, especially a schedule has been prepared, which predominantly emphasized frequency of usage of the products, purchasing patterns, and awareness of EP and its related health risks. Each willing participant has responded to their notable usage of PCPs in their livelihood pattern. Each and every response was labeled from PCPA01 to PCPA751. The studied 751 participants have indicated total 174 types of PCPs. Out of 174 products, 9 are completely hygienic and do not contain any harmful chemical compounds; additionally, 12 products have been marked for their inadequate information of ingredients. Due to these consequences, total 21 cosmetic products have been discarded in the present study. As a final point, information on 153 types of PCPs has been collected from the consumers and 3.9% (06) details of the baby products have also been endorsed by their parents.

Furthermore, detailed screening of EP has taken place among all the products ($n = 153$), as mentioned by the studied participants. Product details have been captured as declared by the ingredient list of the product. Total 153 products have been categorized into skincare (111), hair care (36), and oral care (06). In the case of oral care, six toothpastes of different brands have been included in this study. On the other hand, 111 skincare products describe body lotions, face creams, moisturizers, sunscreens, lipsticks, and lip balms, foundations, under eye creams, soaps, face wash, hand wash, toner, cleanser, shaving creams, shower gel, body oils, and face gel. Furthermore, 36 hair care products represent hair oils, shampoos, conditioners, hair serums, and hair colors.

1.4.3 Data Analysis

Mean and standard deviation were utilized to distribute the continuous variables. Frequency and percentages have indicated the distribution of categorical variables like categories of PCPs (skincare, hair care, and oral care) and numerous factors of consumer behavior like purchase preference, awareness of EPs, health risks and so on. For further quantitative analysis, data have been divided into two groups based on gender. A chi-square test was executed to find the differences between buyers' responses in PCPs and their awareness level of EPs in livelihood patterns. Data was analyzed through IBM SPSS v.23.0 software. A p-value < 0.05 was considered as statistically significant. Inclusive analysis has been executed through the interpretative method in the case of an empirical dataset, and the findings of EPs have been represented with an appraisal of parallel studies.

1.5 Consumer Behavior Towards Contaminated EPs in PCPs

Adverse consumer behavioral pattern and attitude towards contaminated EPs in cosmetic products have been reflected through the lens of both male (315) and female (436) participants in Kolkata with their ages ranging between 18 and 65 years (31.52 $\pm$ 13.37). Numerous perspectives have unfurled (Table 1.1) the acceptance level of EPs under the wrapper of cosmetic products. The present study depicts that younger people (especially those below 30 years) have a higher tendency to use cosmetics than older people (Bilal et al. 2016). Prior studies exhibited that different corners of Indian users (Nayak et al. 2023; Danusha 2022; SaiLakshmi and SureshBabu 2019; Oberoi and Oberoi 2018; Chaudhary and Tyagi 2023; Khan and Khan 2013) have the very least knowledge about the listed ingredients in cosmetics and their related perniciousness effect in daily life. Consumers of Delhi depicted that usually middle-class people demand more cosmetics for greater appearance in their regular routine than other lower- and upper-class people (Oberoi and Oberoi 2018). Every individual has their personal product preferences that are highly determined by gender, age, geo-spatial boundaries, livelihood patterns, and socioeconomic conditions as well. Consumers of Kolkata are demonstrating that 6 different criteria are propelling them towards the purchase of PCPs. Out of all criteria, significant ($p < 0.05$) price sensitivity of the products is dominating (33.95%) over all, whereas few of the studied people (22.23%) are trying to avoid parabens in their PCPs. Oberoi and Oberoi (2018), revealed the deep influence of the advertisement of the product on different age groups and genders. Rural people are more convinced by the TV advertisements than urban individuals (Oberoi and Oberoi 2018). Present findings also corroborate that 12.25% of urban people are simply convinced by the advertisements. The study expressed a significant ($p < 0.05$) variability of purchase preferences among the consumers of Kolkata. 33.15% of people have a great preference for offline shopping due to their skeptical mentality towards online apps and high insecurity of product details; consequently, the outcomes are parallel with (Daroch et al. 2021). However, 8.38% of people (mostly men) indicated online shopping as their purchase preference. Lack of time to visit shop, huge brand variety, and high discounts on product's price are the key reasons for their online purchase; similar reasons have been executed by Singh and Sailo (2013). In terms of the period of usage of the PCPs, 60.18% of participants are using their cosmetics for up to 5 years.

According to their responses, face wash, face creams, sunscreens, shampoos, and conditioners are expressing the longer usage history. A number of people have been extremely habituated to hand wash, body lotion, and winter cream for more than 10 years. According to the respondents, females are mostly (80.73%) experienced and affected by chemicals as they tend to consume more cosmetics than men, which corroborated the study executed by Bilal et al. (2016) in eastern Ethiopia. Some chemical ingredients in the personal care products can cause immediate reactions like allergic reactions such as skin irritation, rashes and even burning sensations (Goossens 2011). Hair and face are one of the most affected parts of the body (Dibaba et al. 2013; Nigam 2009). Lintner (2009) stated that every cosmetic contains at least one malicious chemical component. Larger usage of cosmetic products among women enhances the potential dangers of EPs in livelihood patterns.

On the other hand, consumer awareness regarding the risks associated with EPs in PCPs is remarkably low in South India. More than 50% of women were unaware about the existence of heavy metals and microplastics in their PCPs (Nayak et al. 2023). The present study expressed the parallel findings that only 27.96% of buyers in Kolkata are aware of the presence of EPs in cosmetics. Although significant ($p < 0.05$) differences of opinion towards cognizance of EP have encountered that men are more unacquainted (86.03%) than women (61.92%) about the harmful cosmetic elements. This lack of public awareness depicts inadequate consumer knowledge and its associated health hazards that eventually real-deal with the PCP producers. Regrettably, low trust in regulatory bodies has been revealed through the lens of buyers in Kolkata. A total of 55.12% of participants have reflected core doubts about the efficacy and transparency of cosmetic elements and their proportions as well. Public distrust in regulatory enforcement depicts the insecurity and lack of dependability on cosmetic manufacturers and/or "cosmetic industry" in a broader sense.

Table 1.1 Consumer's perspective towards EP and interpretation

Variables	Scales	Frequencies		Mean ± SD	X^2, df, p
		Male (%)	Female (%)		
Age	Range: 18–65 years			31.52 ± 13.37	11.09, 3, 0.621
Criteria of buying products	1 = pocket friendly	128(40.63%)	127(29.12%)	2.69 ± 1.68	48.43, 5, 0.000*
	2 = free from paraben	62(19.68%)	105(24.08%)		
	3 = media add (promotion)	28(8.88%)	64(14.67%)		
	4 = doctor's recommended	21(6.66%)	84(19.26%)		
	5 = others	34(10.79%)	21(4.81%)		
	6 = all	42(13.33%)	35(8.02%)		
Purchase preferences	1 = online	35(11.11%)	28(6.42%)	2.50 ± 0.647	52.27, 2, 0.000*
	2 = offline	144(45.71%)	105(24.08%)		
	3 = Both	136(43.17%)	305(69.95%)		
Period of usage	1 = less than 1 year	65(20.63%)	85(19.49%)	2.07 ± 0.771	4.40, 3, 0.221
	2 = 1–5 years	178(56.50%)	274(62.84%)		
	3 = 6–10 years	50(15.87%)	49(11.23%)		
	4 = more than 10 years	22(6.98%)	28(6.42%)		
Noticeable health issues	1 = Recognized	250(79.36%)	352(80.73%)	1.80 ± 0.399	1.21, 1, 0.643
	2 = Unrecognized	65(20.64%)	84(19.26%)		
Awareness of EPs	1 = Aware	44 (13.96%)	166(38.07%)	2.09 ± 0.51	39.71, 6, 0.002*
	2 = Unaware	271(86.03%)	270(61.92%)		
Trust in cosmetic regulatory bodies	1 = Trust	126(40.0%)	211(48.39%)	2.11 ± 0.71	57.48, 2, 0.001*
	2 = Distrust	189(60.0%)	225(51.60%)		
Preference of "green products"	1 = Preferred	91(28.89%)	219(50.23%)	2.07 ± 0.47	39.08, 6, 0.004*
	2 = Unpreferred	224(71.11%)	217(49.77%)		

* $P < 0.05$ indicating the significant values

Currently, people set their goal as "sustainable beautification" and avoid consumption of EPs in their daily care routine (Desai 2014). Surat city represents a greater acceptance of "green products" than market-friendly harmful chemicals (Patel and Donga 2018). Kolkata is not an exceptional one. The majority of women participants prefer organic products, whereas a significantly ($p < 0.05$) varied perception towards green products has been reflected. As 71.11% of men do not desire any herbal products due to lack of time management in a regular busy schedule. In a nutshell, a mixed perception has been reflected by these urban consumers, like that very few are aware of the harsh effects of EPs simultaneously; they are highly insecure about online shopping and very much doubtful about the cosmetic regulatory bodies. As a result, their probabilities of suffering due to EPs through their PCPs could not be reduced.

1.6 Exposure on EP in Personal Care Products (PCPs): Predominant Types of EP in Specific Products

Usage pattern and applied quantity of the PCPs can determine the toxicological effects on the human body. Although consumer behaviors reveal that prolonged application and absorption of PCPs (like body lotion, moisturizers, lipsticks, and so on) might accelerate the chances of contamination of EPs (Lang et al. 2016; Hammel et al. 2019), Moreover, selection of brands and list of ingredients also depended on numerous factors such as gender, age, personal requirements or preferences, lifestyle pattern, as well as regional impact (urban or rural area) and socio-economic condition of the buyers (Khalid and Abdollahi 2021). The current study expressed that females comparatively consume a greater amount of PCPs than males, which corresponds with (Khalid and Abdollahi 2021).

Total 153 PCPs, demonstrating 13 different EPs. The common people of Kolkata have mentioned 50.3% of foreign brands and 49.7% of Indian brands as their regular PCPs. 56.9% of cosmetic products are unisexual, whereas 11.1% only for men and 32.0% for women usage. Though adult products are dominating (96.1%) over the products applied for minors (3.9%) only. After screening of PCPs, prevalent types of EPs have been marked out on the basis of the applied area of the products (Table 1.2). For instance, SLS and silicone are the leading EPs in toothpastes. For superficial and short-term usage of toothpastes, silicone does not affect severely. But, as a foaming agent, an overdose of SLS can cause swallowing of gum, even nausea (Liang 2020) and excessive use of silica can cause the disease. Silicosis (lung disease) (Morais et al. 2022; Kostic 2021; Sayyed and Kulkarni 2024). Various PCPs, especially skin and hair care products, comprise several EPs. EDTA, especially Disodium EDTA is mostly found in face cream, moisturizers, after-shaving lotion, and aloe vera gel as a great absorbent and it easily absorbs into skin and also helps other chemicals to absorb into skin. Whereas Tetrasodium EDTA chiefly exists in water-based PCPs like shower gel and shampoo. Disodium EDTA and Tetrasodium EDTA can damage the outer layer of the skin and make the protective layer of the skin fragile. Excessive use of ETDA through PCPs can cause dry skin or eczema. It also can cause itching and skin infections (Krishnan 2022; Tetrasodium EDTA 2016). Similarly, magnesium nitrate is applied for sustaining pH balance for prolonged periods, preventing microbial growth in water-based cosmetics like hand wash, shampoos, and shower gel. Cleanser and toner of the face and shaving cream contain, respectively, SLS and SLES, according to the ingredient lists of the product, which helps to remove dirt and pollution from the skin (Cherney 2019). SLS and SLES pose significant risks to skin, hair, eyes and overall health by removing natural oils from the body, disrupting pH balance, and also allowing other harmful toxins to penetrate the skin more easily and causing hair damage (Liszewski et al. 2022). SLS and SLES can cause dryness, skin irritation, clogged pores, and ache, especially in sensitive skin. SLS and SLS are absorbed in the body and potentially accumulate in organs which leads to long-term health issues (Wang 2024). If SLS is used in low concentration then it doesn't cause any harm, but if it is used in higher concentration, then it is considered a moderately toxic chemical and it has acute or chronic toxicity effects such as carcinogenicity, irritation to skin, eyes, mucous membranes, and problems in the upper respiratory tract and stomach (Dhruv 2023). The majority of hair oil, body oil and serum of both skin and hair represent the presence of paraffin. Paraffin is an inflammable hydrocarbon that can be found in both liquid and solid form. Paraffin can be labeled as paraffin, liquidium paraffinum, mineral oil, petroleum, soft paraffin, or hard paraffin (Sillitoe 2022). Liquid paraffin can cause allergic reactions such as itching, dermatitis, burning sensation, or sometimes temporary vision blindness (Liquid Paraffin 2016). Excessive exposure to mineral oil or liquid paraffin can cause skin cancer (International Agency for Research on Cancer 2012). On the other hand, Triclosan is especially applied as an antibacterial and exfoliating substance in a cosmetic. As a result, facial scrub and scrubbing soap have been identified as specimens for it. Triclosan can affect reproductive health of both males and females and affect liver function by disrupting lipid metabolism, even causing chronic kidney injuries (Chen et al. 2023; Lim and Yoon 2019). Ammonia has especially been applied to sustain color pigmentation and to hold the color on hair and skin. Lipsticks and lip balms and hair color are the specimen products that contain ammonia. Eventually, hair colour has been equally consumed by men and women whereas lipsticks and lip balms are highly prevalent among feminine selves (47). Rigorous exposure and extended consumption of ammonia can bring skin and eye irritation and even respiratory problems in adverse conditions (Padappayil and Borger 2023).

Polyethylene glycols (PEGs) are synthetic petrochemicals commonly found in skincare and hair care products. PEGs are used as thickeners, softeners and solvents and help to enhance the absorption of many other ingredients into the skin and scalp like cream, lotion, aloe vera gel, moisturizer and serum. PEGs themselves are not that harmful if used as skincare or hair care products (PEGs in Cosmetics 2022); due to their penetration enhancement effect, they help to absorb other harmful chemicals into skin or scalps. PEGs contain impurities like ethylene oxide and 1,4-dioxane, which are known as carcinogens and respiratory irritants. Long-term use of ethylene oxide can damage the nervous system, and prolonged exposure to PEG can cause great risk of reproductive toxicity (Ajonuma et al. 2024; Why You Need to Avoid These Five Toxic Beauty Ingredients 2017; PEGs in Cosmetics 2022).

At the present time, sunscreen is the most popular skincare among the tropical people, irrespective of gender and age. Benzophenone-3 is one of the most popular

Table 1.2 Details of EPs in PCPs and its potential risks as mentioned by the consumers of Kolkata, India

Name of the pollutants	Screening of EP in PCP			Applied for	Probable health risks	References
	Hair care (n = 36)	Skincare (n = 111)	Dental care (n = 06)			
1. *Paraben*						
a. Propylparaben	–	27 (24.32%)	–	Preservative, solvent in water based products	Skin irritation, redness, dryness	Berger et al. (2018a, b)
b. Methylparaben	–	30 (27.02%)	–	Preservative element, anti-fungal agent	Decreases sperm count & sperm motility	Jiang et al. (2019), Smarr et al. (2018), Dodson et al. (2012), Kang et al. (2002)
c. Ethylparaben	–	09 (8.10%)	–	Antimicrobial agent, maintain shelf life of the product	Allergy, hormonal imbalance,	Smarr et al. (2018), Dodson et al. (2012)
2. *Sulfate*						
a. Sodium lauryl sulfate (SLS)	07 (19.44%)	12 (10.81%)	06 (100%)	Foaming agent	Skin irritation, increase skin dryness	Fletcher (2022), Liszewski et al. (2022)
b. Sodium laureth sulfate (SLES)	21(58.33%)	12 (10.81%)	–	Mild Cleansing agent to remove oil and dirt	Hair damage, hair loss, occasional eye irritation	Fletcher (2022), Liszewski et al. (2022)
3. Silica (Silicon dioxide)	–	14 (12.61%)	05 (83.33%)	Abrasive particle to exfoliate skin and teeth, oil and sweat absorber component, boost SPF and easy to absorb in skin	Increase skin sensitivity, inhalation risks	Kostic (2021), Sayyed and Kulkarni (2024)

(continued)

Table 1.2 (continued)

Name of the pollutants	Screening of EP in PCP			Applied for	Probable health risks	References
	Hair care (n = 36)	Skincare (n = 111)	Dental care (n = 06)			
4. *Ethylenediaminetetraacetic acid (EDTA)*						
a. Disodium EDTA	12 (33.33%)	53 (47.74%)	–	Stability of emulsions of ingredients, preventing the degradation caused by metal ions	Allergic reactions	Krishnan (2022)
b. Tetrasodium EDTA	06 (16.66%)	15 (13.51%)	–	Prevent discoloration of water based formulation	Mild skin irritation, allergic reactions	*Tetrasodium EDTA* (2016)
5. Magnesium nitrate	01 (2.7%)	02 (1.80%)	–	Maintain the stability and shelf life of product, maintain pH balance, preventing microbial growth in water-based cosmetics	Itching and swelling up skin, prolonged allergic reaction in high concentrations	Bilal and Iqbal (2019)
6. Polyethylene Glycol (PEG)	14 (38.88%)	35 (31.53%)	–	Helps to thicken the substance, maintain stable mixture with other elements	Skin irritation, enhance dryness and in severe exposure its brings carcinoma	Ajonuma et al. (2024), *PEGs in Cosmetics* (2022)
7. Ammonia	01 (2.7%)	01 (0.90%)	–	Especially applied for color pigmentation and to hold the color on hair and skin	Skin and eye irritation even respiratory problem	Padappayil and Borger (2023)
8. Alcohol	01 (2.7%)	03 (2.70%)	–	Alcohol helps preserve the formulation of products, preventing the growth of bacteria and fungi, emulsifier agent to mix oil and water, helps to tighten pores and reduce oil	Dryness in skin, make the skin acne prone	Fletcher (2023)

(continued)

Table 1.2 (continued)

Name of the pollutants	Screening of EP in PCP			Applied for	Probable health risks	References
	Hair care (n = 36)	Skincare (n = 111)	Dental care (n = 06)			
9. Paraffin liquidum	07 (19.44%)	21 (18.91%)	–	Provide smoothing effect and shine, skin hydration	Skin irritation, itching, respiratory troubles	Sillitoe (2022)
10. Benzophenone-3	02 (5.55%)	04 (3.60%)	–	UV filters, active ingredients to prevent sun damage	Hormonal dysfunction, redness in skin, adverse use can change skin pigmentation, delayed in pregnancy	Liao and Kannan (2014), Berger et al. (2019), Huo et al. (2015), Khalid and Abdollahi (2021)
11. Triclosan	–	04 (3.60%)	–	Well preservative, prevent bacterial contamination, absorb odor	Kidney injury & chronic kidney disease	Lim and Yoon (2019)
12. DMDM hydantoin	06 (16.6%)	09 (8.10%)	–	Used as liquid preservatives, prevent any microbial growth in a product	Skin irritation, mild allergy and carcinoma for prolonged usage	Fletcher (2022)
13. Methylpropional	01 (2.7%)	02 (1.80%)	–	Used as water and oil solvent, keep maintaining skin hydration	Eye irritation, burning sensation in skin	Bernauer et al. (2019)

ingredients for sunscreen because it helps to minimize the adverse effect of ultraviolet (UV) radiation on human skin (Maier and Korting 2005). Other than sunscreen, this chemical is also used in shampoos, conditioners, lip balms, talcum powders, anti-aging creams, and other cosmetics to photostabilize these products (Wnuk et al. 2022). Additionally, a number of day creams, foundations, and different makeup products have high concentrations of UV filters (34). UV filters should influence the outer layer of the human skin to protect skin from dangerous UV rays. As Benzophenone-3 has a great absorbent nature, it penetrates through the skin and gets into the stratum corneum by intercellular laminae and then reaches and gets mixed with the blood (Fediuk et al. 2010). It can be carried by proteins in the blood that are attached to serum albumin and can push out drugs, sex, and thyroid hormones, which can affect the body functions of a human being (Wang et al. 2016). Moreover, Benzophenone-3 can obstruct the functions of several tissues and organs of the human body such as skin, endocrine, kidney, brain, reproductive organs, hematological systems and also gestational development (Wnuk et al. 2022). Most of the creams, lotions, and moisturizers contain three different types of parabens as an agent of great preservative and prevent any bacterial and fungal growth. But, it causes extreme lethality irrespective of gender and age. This is linked to concerns about breast cancer and reproductive issues as well as skin irritation (Dodson et al. 2012; Pulcastro and Ziv-Gal 2024). However, DMDM hydontoin is quite a safer pollutant than others in respect to its harmful effects on the human body. This preservative, known as formaldehyde releasers, slowly releases small amounts of formaldehyde over time to prevent microbial growth in water-based products like shampoo, shower gel, body lotion, and so on. Skin irritation, redness, and itching are the key side effects of this after an immediate application of the PCPs (Fletcher 2022). On the other hand, the presence of alcohol is usually noticed in lipsticks, cleansing wipes and after shaving lotion, according to the present dataset. Alcohol helps preserve the formulation of products and is a great emulsifier agent to mix oil and water, helping to tighten pores and reduce oil in skin. The predominant side effect is dryness and increases the sensitivity on skin (Fletcher 2023). Lastly, methylpropional has been applied to retain skin hydration and significantly, it is soluble in both water and oil based compounds like serum, under eye cream and hand wash. This EP can cause eye irritation and respiratory problems in some adverse conditions, though its case reports are very rare (Bernauer et al. 2019).

Some chemical ingredients in the PCSs can cause immediate reactions like allergic reactions such as skin irritation, rashes, burning sensations, and breathing issues, but some have long-term effects that may not show up until years later (Goossens 2011). Certain chemicals, like parabens, cause endocrine disruption and affect the reproductive health of women (Pulcastro and Ziv-Gal 2024).

1.7 Propensity of Risk Factors for EP in Human Life

The primary concern about the deadliness of chemical compounds that exist in PCPs is that these substances were originally produced for positive physiological purposes (Fabbri and Franzellitti 2016). One of the significant issues raised regarding the presence of PCPs in the marine environment is their ability to disrupt the endocrine system, leading to imbalances in homeostasis and undesirable outcomes towards mankind. WHO epitomized the endocrine disrupting chemicals as external substances that disrupt normal functions of the endocrine which causes harmful effects on an organisms' progeny and health (Fig. 1.2). These disruptors encompass a broad spectrum of chemicals that originate from both synthetic and natural sources and are commonly present in consumer products (Haraux et al. 2017).

1.7.1 Symptomatic Versus Asymptomatic

1.7.1.1 Symptomatic Effects

Skin irritation and allergic reactions: Some emerging pollutants such as parabens, paraffin, sodium laureth sulfate, sodium lauryl sulfate, EDTAs, DMDM hydantoin can cause skin irritation and allergic reactions like redness, itching and rashes (Krishnan 2022; Wang 2024; Dhruv 2023; Fletcher 2022). This reaction can be noticed immediately after the use of the products due to containing these pollutants (Soni et al. 2005; Bledzka et al. 2014).

Respiratory issues: DMDM hydantoin, which releases formaldehyde (Fletcher 2022) and PEGs can cause respiratory problems to those individuals who are already suffering from asthma (Anusree et al. 2020; PEGs in Cosmetics 2022). Inhalation of such chemicals can cause symptoms like coughing, wheezing, and even shortness of breath.

Endocrine disruption: Paraben and Benzophenone-3 can mimic hormones and can cause endocrine disruption, leading to symptoms like an irregular menstrual cycle in women and also decreased sperm counts in men (Soni et. al. 2005; Bledzka et al. 2014; Wnuk et al. 2022). These disruptions can reflect fatigue, mood swings, weight loss, or weight gain.

1.7.1.2 Asymptomatic Effects

Cumulative Toxicity: Long-term use of emerging pollutants in personal care products can lead to cumulative toxicity to the human body. Prolonged exposure to Triclosan can develop anti-biotic resistance bacteria in the body (Khalid and Abdollahi 2021).

Carcinogenicity: Pollutants in PCPs like Methyleparaben, Mropylparaben, DMDM Hydanoin, sulfates (both sodium lauryl sulfate and sodium laureth sulfate)

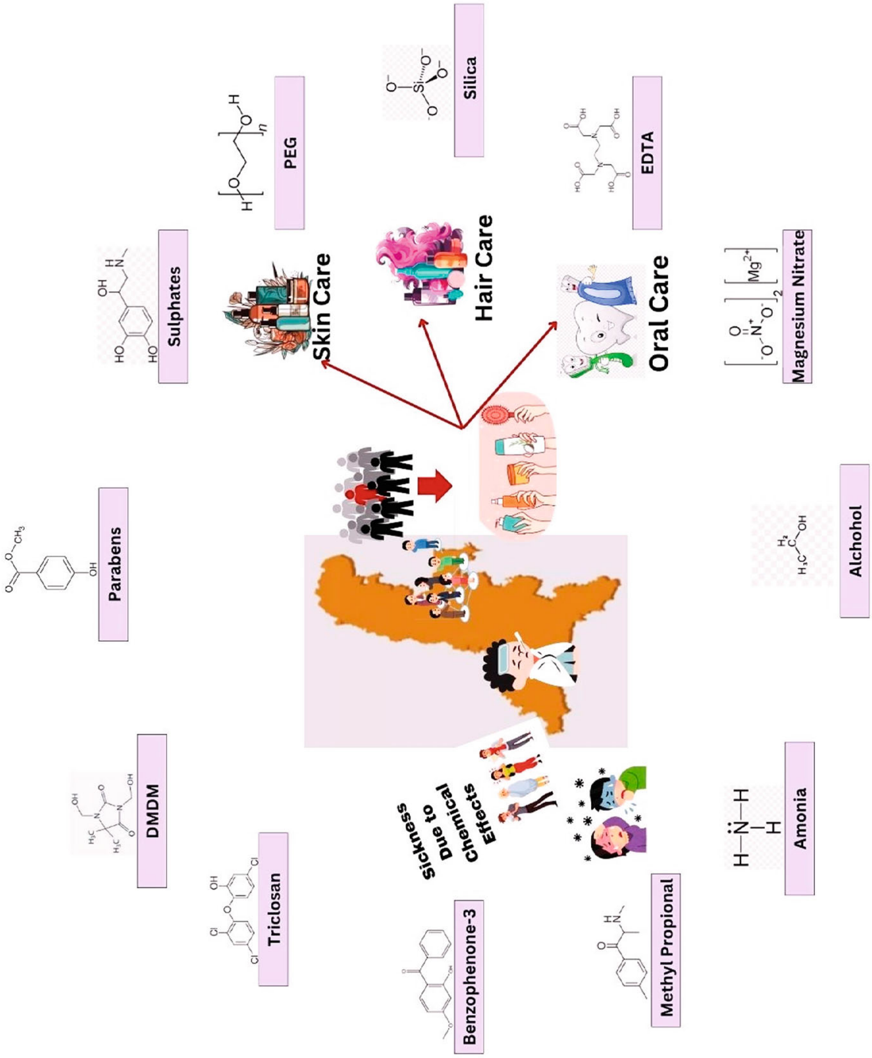

Fig. 1.2 Contamination of EPs in PCPs among the common people of Kolkata, India prepared by authors

and PEGs are identified as potential carcinogens (Fletcher 2022; PEGs in Cosmetics 2022). Initially, the carcinogenic effect of these chemicals is not exposed immediately, but these can cause chances in the cellular lever slowly and potentially leading to cancer after years (Khalid and Abdollahi 2021).

Reproductive and developmental issues: Long-term exposure to Parabens and Benzophenone-3 can impact the reproductive health of both men and women. These are linked to developmental delays and congenital disabilities. These are primarily asymptomatic and do not appear immediately after use (Wnuk et al. 2022).

1.7.2 Short-Term Versus Long-Term

1.7.2.1 Short-Term Effects

Short-term effects of emerging pollutants on humans occur immediately after using the products that contain EPs. These effects are acute in nature and can be cured shortly after treatment. Parabens, paraffin, sulfates, EDTAs, and DMDM Hydantoin are great absorbent and they easily absorb into skin and also help other harmful chemicals and pollutants to absorb into skin which cause skin irritation such as redness, itching and dermatitis. (Krishnan 2022; Wang 2024; Dhruv 2023; Fletcher 2022). Disodium EDTA and Tetrasodium EDTA can damage the outer layer of the skin and make the protective layer of the skin fragile. Excessive use of ETDA through PCPs can be cause of dry skin or eczema (Krishnan 2022; Tetrasodium EDTA 2016). Other than dermatitis, people also encounter respiratory issues such as cold and flu, sneezing, coughing, wheezing and sometimes shortness of breath due to the exposure of PEGs and DMDM Hydantoin (Fletcher 2022; Anusree et al. 2020; PEGs in Cosmetics 2022). Sodium laureth sulfate and sodium lauryl sulfate are generally found in soap, shampoo and face wash and cause eye irritation and also redness and burning sensations on the eyes (Cherney 2019; Wang 2024). Triclosan can be found in oral care products such as toothpaste and mouthwash can cause gastrointestinal distress including abdominal pain and nausea (Khalid and Abdollahi 2021).

1.7.2.2 Long-Term Effects

Long-term effects of EPs can lead to chronic health conditions that cause irreversible damage and develop slowly over time due to their cumulative impacts. Endocrine disruption, hormonal imbalance, endocrine disruption, reproductive issues, developmental problems, diabetes, obesity, kidney disease, neurological disorders, cancers, etc. are examples of the long-term effects caused by various EPs used in personal care products (Khalid and Abdollahi 2021). Long-term exposure to Triclosan develops antibiotic-resistant bacteria in the human body, reduces metabolism, and also develops cognitive deficits and neurodevelopmental disorders (Khalid and Abdollahi

2021). Pollutants found in personal care products, such as methylparaben, propylparaben, DMDM Hydantoin, sulfates and PEGs can lead to cancer (Khalid and Abdollahi 2021; Fletcher 2022; PEGs in Cosmetics 2022). Ammonia, which is generally found in hair dyes; long exposures to this can cause bronchopneumonia, lung fibrosis, asthma and even permanent eye damage (Padappayil and Borger 2023).

1.7.3 Male Versus Female

1.7.3.1 Male

Men's health mostly affected in terms of hormonal disruption and reproductive health. Though psychological and behavioral changes can also be measurable in terms of hyperactivity, aggressive nature and anxiety (Radke et al. 2018). According to the current study, Paraben and Triclosan bring lethality to life. Apart from these two pollutants, rest chemicals can cause skin problems and prolonged allergies in some extent. Numerous studies revealed that TCS can activate estrogen receptors, increasing estrogen release and disrupting endocrine homeostasis. Long term usage and overdose of Triclosan can decline testosterone secretion levels, which may contribute to reduced spermatogenesis and negatively affect sperm quality and infertility in some extent (Hipwell et al. 2018).

1.7.3.2 Female

They mimic estrogens, the primary female sex hormone. They may also interfere with male reproductive functions. Various studies indicate that methylparaben applied on the skin reacts with other chemicals, leading to increased skin aging and DNA damage (Darbre 2004). A study mentioned that, women have greater concentration capability to absorb parabens than men (Jurewicz 2017). Moreover, excessive consumption of parabens can accelerate the chances of breast tumours and breast cancer as well. Prior studies have reflected a strong association between obesity and parabens; also, neurological function can be disrupted over time (Kolatorova et al. 2018; Jiang et al. 2019; Roje et al. 2019). Long term consumption of contaminated chemicals like phthalates and parabens has been notoriously connected with endometriosis, polycystic ovarian disorder and other reproductive disorders.

1.7.4 Minor Versus Adult

1.7.4.1 Minor

The term "minor" depicts a broad range of age groups. This range starts from the neonatal phase (1 year after birth) up to puberty and adolescence. Infant skin does not properly develop like adults; rather, their skin is extremely sensitive and occupied with a low tolerance level in respect of harsh chemical exposure (Cortez-Pereira et al. 2010; Evans and Rutter 1986). Toddler's epidermis is very susceptible to any kind of dryness, even affected by seasonal fluctuation. In this consequences, the neonates required moisturizers, body lotion, body oil and cream to maintain their healthy skin (Avila et al. 2015; Simpson et al. 2010). In this study, the parents of infants have mentioned only two brands, i.e., Johnson & Johnson (USA) and Himalaya (India), as a form of PCPs for their offspring. According to Cortez-Pereira et al. (2010), baby shampoo, soap, baby lotion from Johnson & Johnson contain some EPs that do not match the infant skin tolerability. The presence of SLS and PEG is common in baby shampoo and soap, which causes skin irritation, unwanted dryness, itching and in adverse conditions, erythema can also be noticed (Cortez-Pereira et al. 2010; Avila et al. 2015).

As per physiological consequences, children's skin is thinner and more absorbent than adults due to a lack of their adipose tissue and underdeveloped epidermis and subcutaneous fat layer, which can lead to a fast and higher absorption frequency of harmful chemicals 35 (Gaston et al. 2019). Neonates have a wider range of surface area in respect to body weight ratio, which leads to an to an extensive application area of PCPs, i.e., baby oil, lotion, moisturizers and so on. Paraffin (body oil), disodium EDTA and DMDM in lotion and cream and PEG (body wash and shampoo) are predominant EPs in the products of Himalaya. At the initial stage of application of body oil (paraffin liquidium), it helps to reduce external dryness but, in some long-run cases skin sensitivity level has increased and redness has raised (Sillitoe 2022). In that condition, an immediate medication can cure the skin problem (Sillitoe 2022). However, SLS (foaming agent) and PEG (remove dirt on skin and scalp) can cause a temporary irritation (PEGs in Cosmetics 2022; Liang 2020). On the other hand, disodium EDTA and DMDM are chiefly used as agents of fast absorbents, especially in oil and water-based products. For extended use and excessive application, it can indicate an "immunotoxic effect." Thus, in toddler's phase, the bodyimmune system is in a developing stage; these EPs make the skin more sensitive, potentially increasing susceptibility to infections and allergies.

1.7.4.2 Adult

Adult people may express some cumulative health effect under exposure to EPs. PEG shows some evidence of genotoxicity and can cause irritation and systemic toxicity if used on broken skin (Bridges 2002; Khan and Alam 2019). In the case of adult people, some behavioral changes can be identified, like cognitive decline and rapid mood swings due to consumption of multiple EPs in the long term (Gabriel et al. 2021). In a nutshell, apart from minors, adult people eventually suffer by all of the means.

1.8 Preventive Strategies of EP and Therapeutic Index

Numerous emerging pollutants, such as parabens, paraffin, sulfates, triclosan, benzophenone-3, DMDM hydantoin, ammonia, PEGs, alcohol, magnesium nitrate, and EDTA are commonly found in personal care products (skincare, hair care, oral care) used by both adults and children. These substances can lead to short-term and long-term health issues (Bilal and Iqbal 2019). However, certain preventive measures can be taken to minimize adverse effects and reduce exposure to these harmful pollutants.

The U.S. Environmental Protection Agency (EPA), the European Chemicals Agency (ECHA) and the Bureau of Indian Standards (BIS) are some governments and regulatory bodies that set standards for the permissible levels of pollutants in PCPs. Certain harmful chemicals have been banned or restricted in various jurisdictions. The European Union has prohibited the use of specific chemicals in cosmetics under the Cosmetics Regulation, EC No 1223/2009 (European Commission 2009). Likewise, the U.S. FDA has restricted the use of certain harmful chemicals in cosmetics (FDA 2020). Regular monitoring of the ingredients of daily care and cosmetic products can help ensure to maintain the safety standards regulated by the different regulatory bodies.

The companies must eliminate or reduce the EPs from their products to lower the health risk of the consumers. The manufacturer can use safer alternatives to the harmful chemicals. Use of green chemistry can reduce the toxic impacts of chemicals. Green chemistry, which is also known as sustainable chemistry, is a new thing that encourages the design and development of chemicals using methods that usually help to minimize the use of toxic chemicals (Heindel and Zoeller 2015). The main goal of green chemistry is redesigning products and the process of product manufacturing to reduce the serious health impact of people and also the impact on the environment (Lewandowski 2014).

1.8.1 Preventive Measures in Livelihood Patterns

To reduce the exposure and effects of emerging pollutants, which are usually found in PCPs, some preventive measures can be taken.

1.8.1.1 Use of Natural and Chemical-Free Products

People should choose natural, herbal and chemical-free products, especially pollutant-free products, which can help to reduce the risk of exposure to the harmful chemicals (Johnson et al. 2022).

1.8.1.2 Avoid Products that Contain Toxic Chemicals.

People should avoid the products that have an artificial fragrance, an allergic reaction, or any long term hormonal imbalance (Tips for Safer Cosmetics and Body Care-Toxic-Free Future 2023). Long lasting and waterproof labeled products can be dangerous for health as this kind of product is more likely to contain Per- and Polyfluoroalkyl Substances (PFAS) which may cause many health issues such as weakened immunity, high cholesterol, and even cancer. Most of the companies even did not disclose this chemical's name in the ingredient list (Selby 2024).

1.8.1.3 Consumer Awareness

People must read the ingredient details of the products carefully before buying them. If any harmful chemical is found in the ingredient list, irrespective of the parentage of the chemical, people should immediately discard that product and should stop buying those products (Akhand et al. 2023). Products that are labeled as "organic", "natural", or "pure" don't mean that those products are really safer. All these could be a marketing strategy. People must choose those products or companies that have certification of selling non-toxic products (Sissons 2019).

1.8.1.4 Replace Older Products

Every product has its self-life, and over time every product can lose effectiveness and even grow bacteria due to contamination, which can lead to serious health issues. To avoid these situations, read the instructions of preservation, including storage instructions, expiry dates and so on (Akhand et al. 2023).

1.8.2 Therapeutic Index

Therapeutic Index (TI) helps to assess the safety and efficacy of chemicals. The existence of drug or chemical components in blood or plasma concentration reflects the therapeutic effect as well as the degree of toxicity of the chemicals (Katzung et al. 2012). TI can be measured as the lethal dose (LD) of a drug for 50% of the population allocated through the lens of effective dose (ED) for 50% of the population, i.e., TI

= LD50/ED50 (Tamargo et al. 2015). The therapeutic index of any PCPs is actually expressed as the ratio of the Toxic Dose (TD50) to the Effective Dose (ED50). A higher therapeutic index indicates a greater margin of safety between effective and toxic doses. The ratio between 10 and 50 describes "the safe profile of drug or chemical." contrastingly, the ration less than 10 and especially nearer to 1 indicates a Narrow Therapeutic Index (NTI). NTI demonstrates the overdosing of malicious chemicals or drugs and reduces the chances of curability (Tamargo et al. 2015; Tucker 2016).

In a nutshell, the therapeutic index of EPs helps to determine the safe percentage of chemicals in the personal care products. For instance, Benzophenon-3 or Oxybenzone are the predominant EPs to control UV filters in sunscreen, which provide the Sun Protection Factor range (SPF 15–100). Above SPF-20 is denoted as a drug, whereas the product containing below SPF-4 is labeled as cosmetics (O'Donoghue 1991). In that respect, a higher range of SPF will determine the NTI (Hexsel et al. 2008), but morosely say that sunscreens containing a higher range of SPF are always widely accepted by the common people (Pandey et al. 2023).

On the contrary, cosmetic products have also been applied for therapeutic purposes in a particular dermatological condition. Hyaluronic Acid (HA) is one of the key components in skincare products that provides great elasticity in skin. Most anti-aging creams and moisturizers contain sufficient amounts of HA. Dermatologists talk about how regular consumption of above 120 gm of HA can provide permanent relief from dry skin (Di Cerbo et al. 2015; Sato et al. 2002; Al-Halaseh et al. 2022).

1.9 Conclusion

The comprehensive research conducted on Emerging Pollutants (EPs) in personal care products highlights the significant variations in consumer awareness, regulatory strategies, and health impacts of humans throughout diverse geographical locations and socio-demographic groups. Reduced EP levels and enhanced product safety have resulted from strict laws and increased consumer awareness in nations such as the United States and the European Union. On the other hand, the regulatory systems in India are still in the developing stage, and poor consumer knowledge combined with lax enforcement leads to higher levels of EPs in personal care products. This scenario puts vulnerable people in particular danger. Adults may develop chronic health problems as a result of long-term EP exposure, while children may have behavioral and developmental issues due to their increased exposure and sensitive physiology. Implementation of strict regulatory procedures, repurposing items to remove or minimize the EPs, and improving knowledge of the consumers through better ingredient labeling on products and also awareness campaigns are examples of preventive methods that are essential in limiting these dangers. Additionally, by discovering and using the EPs therapeutic index, chemical toxicity can be prevented and appropriate concentration limits can be maintained. Furthermore, future efforts must be focused on strengthening the international legislation, improving the safety of the products and educating the consumers to guarantee safer personal care products for everyone and also reduce the health concerns associated with EPs.

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Chapter 2
Detection of Emerging Pollutants in Wastewater: Current Challenges and Innovative Solutions

Sneha Dutta, Sanjula Sarkar, Pranabesh Sarkar, and Bhavya Srivastava

Abstract Emerging pollutants encompass a range of chemicals and compounds newly recognized as environmentally hazardous, raising significant threats for both ecosystem and human health and well-being. The "emerging" reflects the growing apprehension surrounding pollutants, many of which lack regulation at national or international levels, heightening the risks. These compounds are often biologically active and have the potential for persistence and bioaccumulation, making them particularly concerning for environmental condition and human health. The main topic of this chapter is the environmental and health ramifications of emerging pollutants, with specific emphasis on methods used for analysis like traditional methods (chromatography, spectroscopy) alongside improved, sophisticated detection techniques (mass spectrometry, biosensors, or nanotechnology-based methods). Case studies are employed to determine the causal events and potential solutions to make successful strategies through technology. In this chapter, the authors delve into the various aspects of emerging pollutants as well as challenges (such as regulatory gaps, technological limitations, and resource constraints) and future perspectives (viz., developments in analytical techniques, remediation technologies, and regulatory frameworks). It helps to contribute to ongoing efforts to protect human health and environment simultaneously from the threats posed by these hazardous substances.

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S. Dey and M. P. Shah (eds.), *Biotechnological Removal of Emerging Pollutants from Wastewater Systems*, Advances in Wastewater Research,
https://doi.org/10.1007/978-981-96-3945-8_2

Keywords Emerging pollutants · Ecosystems · Hazardous substances · Bioaccumulation · Conventional techniques · Advanced detection methods · Biosensors

2.1 Introduction

Emerging pollutants (EPs) are a diverse group of chemical and biological agents that pose growing environmental and health concerns (Raouf et al. 2019). Traditional sewage treatment plants fail to effectively eliminate these substances owing to their diverse chemical structures resulting in many EPs remain unregulated (Geissen et al. 2015). Thus, emerging pollutants may be essentially described as substances that are not legally controlled yet, but have the potential to damage people, animals, and plants. EPs were found in the aquatic environment during the beginning of the 1800s, coinciding with the advancements in science and technology (Patel et al. 2020). Historically, the focus of pollution control efforts was on persistent organic pollutants (POPs) and heavy metals when they are included in extensive monitoring programs due to their non-polar hazardous nature (Marathe et al. 2021). Emerging Pollutants are classified into Organic and Non-organic, encompasses an enormous range of substances including pesticides, pharmaceuticals, personal care products, food additives, surfactants, flame retardants. Plasticizers, various industrial additives, medications for humans, animals and personal hygiene items, surfactants, and their by-products of various other chemicals commonly used in everyday life. EPs can have three kinds of targets: (i) recently discovered compounds, molecules; (ii) pollutants that were already known but had not yet been discovered to have environmental concerns or to be of interest; and (iii) newly discovered information about the environmental risks associated with these pollutants that casts doubt on the knowledge of some legacy pollutants (Sauvé and Desrosiers 2014). EPs also include rare earth elements (REEs), commonly referred to as the lanthanide group compounds (GCs). Similar to most EPs, these are: (1) not currently regulated and not routinely monitored in humans and the environment; (2) micropollutants that can be detected with very low detection limits analytical equipment; and (3) poorly understood mechanisms of their toxic impact to both humans and environment (or, ecosystem). EPs enter the ecosystem via various sources, like domestic use, agricultural runoff, industrial processes, and improper disposal of medications (Luo et al. 2014). Point sources are bathing, flushing unwanted medications, domestic usage, and excretion in the urine and feces of humans and animals. Non-point sources are stormwater runoff, terrestrial runoff from roads, cities, highways, and agricultural land fall under this category (Patel et al. 2020). Emerging pollutants infiltrate the environment in metropolitan areas through other pathways that include septic tank effluents, agriculture runoff, animal waste dumping, and sewage overflows. Additionally, these pollutants get into the environment via cleaning supplies, personal care items and leftover medications.

High rate of transformation and persistence of EPs have an adverse effect. The persistence and bioaccumulation of EPs within individual and ecosystem can be a significant threat to ecosystems and human body. Birth deformities, prostate cancer, the feminization or masculinization of women, long-term toxicological consequences, thyroid and other malignancies, and a surge in bacteria that are immune to antibiotics only some hazardous impacts of these pollutants (Patel et al. 2020). It is able to disrupt oceanic life, alter reproductive and behavioral patterns in wildlife, and contribute to the emergence of microbes resistant to antibiotics (Dolejska 2020). Detection along with analysis of EPs in wastewater have evolved significantly with time. Traditional methods of analysis like liquid and gas chromatography (LC and GC) are replaced by advanced techniques such as electrospray mass spectrometry (ESMS), tandem mass spectrometry, high-performance liquid chromatography (HPLC), and high-resolution chromatographic methods (LC-HRMS), coupled chromatographic and mass spectrometric techniques, ultra-high-performance liquid chromatography (UHPLC-MS/MS), etc. These modern techniques offer higher sensitivity, selectivity, and specificity to detect EPs at minute-level concentrations with enhanced analytical power (Luo et al. 2014).

The possible threats of EPs in the humans and the environment have gained a lot of public and scientific attention recently. Despite recent advancements in detection technologies, the elimination of EPs from sewage water remains challenging due to use of conventional treatment methods like coagulation–flocculation, activated carbon filtration, ozonation, and membrane processes. That are often failed to eliminate these pollutants completely (Morin-Crini et al. 2022). Advanced oxidation processes and bioreactors are also utilized to enhance removal efficiency (Salimi et al. 2017). However, the rules and controls along with regular observation of these substances are falling behind, primarily due to the lack of comprehensive quantitative testing methods. The pollution load is often measured in relation to ammonia, pH, turbidity, chemical and biochemical oxygen demands (BOD and COD), etc. (Kanu and Achi 2011; Surbhi et al. 2020). During the 1960s, a new environmental subfield of toxicology, ***Ecotoxicology*** that was first introduced and was defined as the subfield of toxicology which deals with the harmful consequences brought on by both synthetic and organic pollutants.

2.2 Classification of Emerging Pollutants

EPs are categorized into two main types: organic and non-organic. Examples of these pollutants include pesticides, medicines, synthetic organic dyes, polycyclic aromatic hydrocarbons (PAHs), heavy metal ions, plasticizers, per-fluorinated chemicals, flame retardants, and surfactants (Fig. 2.1). These substances, originating from human activities such as household use, healthcare facilities, agriculture, and industrial processes, pose significant threat to animals as well as people because of their widespread presence in the environment and unique physical and chemical properties (Rout et al. 2021).

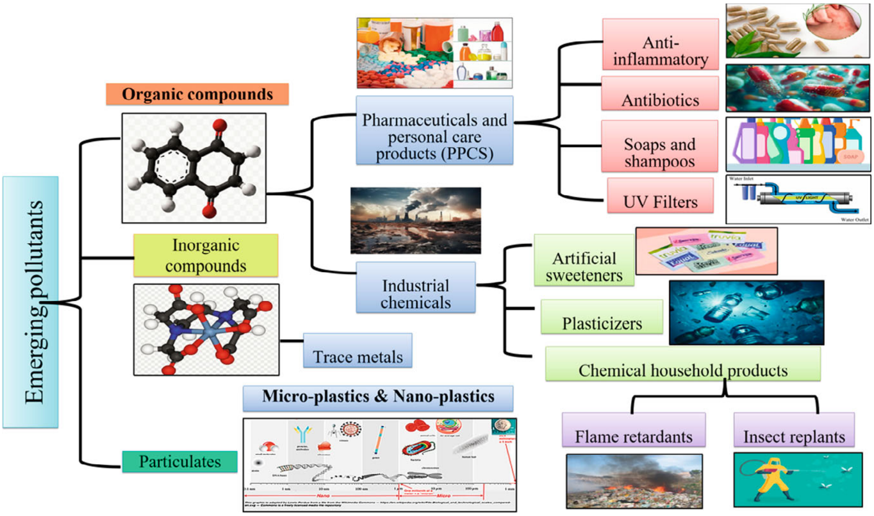

Fig. 2.1 Classification of emerging pollutants

Their detection is challenging because they come from various sources of generation and exhibit a range of diverse activities. Even in small amounts, these pollutants can cause endocrine disruption, persistent toxicity, and increased resistance to pathogens (Calderon et al. 2021).

2.2.1 Pesticides

In agriculture, pesticides are a group of chemicals that act as organic pollutants used to control harmful insects, weeds, microbes, and other plants. These chemicals pose significant risks through groundwater contamination and bioaccumulation in plants, animals, and sediments. Commonly used pesticides are phorate, chlorpyrifos, atrazine, methyl parathion, bentazon, diazinon, cyanazine, simazine, phosphamidon, terbuthylazine, alachlor, and dimethoate. Among these, dichlorodiphenyltrichloroethane (DDT) and hexachlorocyclohexane are extensively used as herbicides, fungicides, and insecticides, accounting for about 67% of pesticide usage (Poonia et al. 2021).

2.2.2 Pharmaceutical Industry

Pharmaceuticals are among the most prevalent organic pollutants discovered at low concentration in water resources all over the world (Chinnaiyan et al. 2018). They are utilized extensively in veterinary and human health care for prevention, treatment, diagnosis, and even nutrition. Various pharmaceutical products can negatively impact humans, poultry, livestock, fish, and other aquatic life. This includes hormone-containing drugs, antibiotics, and pollutants found in surface and groundwater. Common pharmaceuticals are detected in wastewater include beta blockers, pain relievers, salicylic acid, fluoxetine, antacids, clofibric acid, steroids, antidepressants, ciprofloxacin, nitroglycerin, tranquilizers, lipid-lowering medications, hormones, and stimulants. These substances contribute to widespread environmental contamination and pose risks to health and ecosystems (Richardson and Kimura 2017). Pesticides and pharmaceuticals are identified as significant threats to water systems due to their toxic nature and bioactive by-products. Among these, antibiotics are particularly worrisome as their release in ecosystem can participate in the proliferation of bacteria that are immune to antibiotics.

Illegal drugs are considered as emerging pollutants as they are discovered in various ecosystems. These substances and their by-products enter the environment through intentional or unintentional disposal from clandestine drug labs or via human excretion after use (Castiglioni and Zuccato 2010).

2.2.3 Industrial Waste

Mining activities have significantly increased the introduction of harmful chemicals in the ecosystem. These include selenium (Se), aluminum (Al), cadmium (Cd), arsenic (As), copper (Cu), iron (Fe), lead (Pb), nickel (Ni), and zinc (Zn). Se contamination via mining operations is a newly recognized pollutant that enters water, soil, and plants posing a serious threat to both people and nature because of its bioaccumulate properties.

2.2.4 Personal Care Products (PCPs)

PCPs are chemically derived products which are used for health, beauty, and cleaning purposes, and various medications such as clofibrate paracetamol and nonsteroidal anti-inflammatory drugs (e.g., naproxen, ibuprofen, and diclofenac) and their metabolites (Brausch and Rand 2011). Insect repellents and antimicrobial preservatives (methyl, propyl, butyl, ethyl, isobutyl, isopropyl, and benzyl parabens) are also prevalent in medicines, cosmetics, and some food products. Polycyclic musk is used in cosmetics, lotions, hair care, and cleaning products (Juliano and Magrini 2017).

2.2.5 Surfactants

Surfactants are man-made compounds that are present in personal hygiene products, paints, emulsifiers, detergents, and insecticides. They are harmful to aquatic life and are categorized into three groups: zwitterionic, anionic, and cationic surfactants. Commonly used surfactants include alkyl phenol ethoxylates, lignin sulfonates, fatty alcohol ethoxylates, and linear alkyl benzene sulfonates. Nonyl-phenol ethoxylates and octylphenol, as well as solvents like toluene, benzene, and xylene, are highly toxic at trace-level concentrations (Mandaric et al. 2016).

2.2.6 Food Additives

These substances include artificial sweeteners, preservatives, colorants, and flavor enhancers. Artificial sweeteners like acesulfame, saccharin, and sucralose are widely utilized in food, medicine, and sanitary goods. Sweeteners often find their way into household wastewater through human excretion that are challenging to remove. Similarly, preservatives (benzoates and nitrates) were used to prevent spoilage and can contribute to wastewater contamination. Food dyes and flavor enhancers like monosodium glutamate (MSG) can end up in wastewater systems (Tollefsen et al. 2012).

2.2.7 Flame Retardants (FRs)

Phosphorus-containing flame retardants known as organophosphate ester flame retardants (OPEFRs) and halogenated flame retardants like polybrominated diphenyl ethers (PBDEs) are used to lessen the combustibility of various consumer and industrial products. OPEFRs are used in electronics, furniture, fabrics, and building materials, as well as plasticizers in floor coatings and polishes. When wastewater treatment facilities release OPEFRs into surface waters can lead to toxicity in the marine environment. PBDEs are primarily used as additives in carpets, computer components, polyurethane foam, electrical cables, etc. (Venier et al. 2014).

2.2.8 Microplastics

Microplastics represent a significant global concern today, classified as another category of pollutants. These are minute fragments of plastic somewhat smaller than 5 mm, pose a persistent challenge for environmental cleanup. Microplastics have been detected in diverse environments including soil, oceans, and even in food and beverages, presenting numerous threats to both humans and nature. Microplastics originate primarily from the sources such as textiles, clothing, tire wear, urban dust, plastic wastes, marine coatings, and road markings. The most found polymers include polypropylene (PP), polyethylene (PE), polyamide (PA), polyvinyl chloride (PVC), and polyethylene terephthalate (PET). Microplastics have a tendency to build up in water bodies and can enter the food chain, potentially imposing hazards to marine organisms and ecosystems. There is a risk of potential transfer of microplastics entering the body via ingestion of compromised seafood and *water* (Stapleton and Hai 2023).

2.2.9 Nanoplatics

They are polymer-based particles that are degraded from microplastic and possess particles that range in size from 1 to 100 nm. They are difficult to define as they lack uniform material or composition (Shen et al. 2019).

2.3 Sources and Pathways of Emerging Pollutants into Wastewater Systems

These emerging pollutants came from different sources like domestic wastewater, hospital, industrial effluents, etc. (Stefanakis and Becker 2016). The substance's characteristics and exposure levels are determined by the kind of source (Table 2.1). The transport and transformation of EPs are significantly influenced by chemical properties such *as* polarity, volatility, and water solubility as well as environmental factors including, organic matter content, temperature precipitation, altitude, and latitude (Stefanakis and Becker 2016).

There are mainly two types of sources:

1. Point Sources: It comprises of bathing, flushing unwanted medications, domestic usage, and excretion in the urine and feces of people along with wildlife. Primary sources are processed wastewater, released from wastewater treatment facilities into rural and urban areas (Luo et al. 2014).
2. Non-point Sources: It comprises stormwater, terrestrial discharge from roads, cities, highways, and agricultural land that fall under this category. Numerous EPs, including hormones, veterinary medications, natural poisons, and the breakdown products of manmade chemicals employed in agriculture (Luo et al. 2014).

Table 2.1 Sources for different categories of emerging pollutants

Category	Subclasses	Major sources	
		Distinct	Non-exclusive
Pharmaceuticals	NSAIDs, lipid regulators, anticonvulsants, antibiotics, β-blockers, and stimulants	Domestic wastewater (excretion) Hospital effluents Runoff from CAFOs[a] and aquaculture	Sources that are not exclusive to individual categories include industrial wastewater (product manufacturing discharges) Landfill leachate (improper disposal of used, defective or expired items)
Personal care products	Fragrances, disinfectants, UV filters, and insect repellents	Domestic wastewater (bathing, shaving, spraying, swimming, etc.)	
Steroid hormones	Estrogens	Domestic wastewater (excretion) Runoff from CAFOs and aquaculture	
Surfactants	Non-ionic surfactants	Domestic wastewater (bathing, laundry, dishwashing, etc.) Industrial wastewater (industrial cleaning discharges)	
Industrial chemicals	Plasticizers, fire retardants	Domestic wastewater (by leaching out of the material)	
Pesticides	Insecticides, herbicides and fungicides	Domestic wastewater (improper cleaning, runoff from gardens, lawns and roadways, etc.) Agricultural runoff	

2.4 Effects of Emerging Pollutants

The negative impacts EPs on existing organisms, can cause detrimental consequences on people and animals, including acute, chronic poisoning, and endocrine disruptions (Stefanakis and Becker 2016).

2.4.1 Impact on Environment

Ecological Effects: Pollutants have the potential to change an ecosystem's structure and composition, which might have an impact on biodiversity and ecosystem

(Salimi et al 2017). EPs such as nitrogen oxides and sulfur tend to alter soil pH affecting the nutrient content resulting in stunted plant growth.

Toxicity: Toxicity of EPs can alter the behavior, reproduction, and population dynamics in aquatic animals (Morin-Crini et al. 2022). For example, lead exposure in fishes induces oxidative stress causing synaptic damage and neurotransmitter malfunction.

Persistence: Pollutants can linger in nature for extended periods, continuing to be dangerous to ecosystems. Persistence Organic Pollutants (POPs) remained in ecosystem for decades and take even centuries to decompose as a result of their long half-life that leads toxicity and metabolic disorder to both human and wildlife.

Bioaccumulation: EPs tend to accumulate in the human tissues/bones due to the active exposure for prolonged period of time, having detrimental consequences on people and nature (Puri et al. 2023).

2.4.2 *Impact on Humans*

Different classes of emerging pollutants have various negative side effects on the human which are as follows (Stefanakis and Becker 2016) (Fig. 2.2):

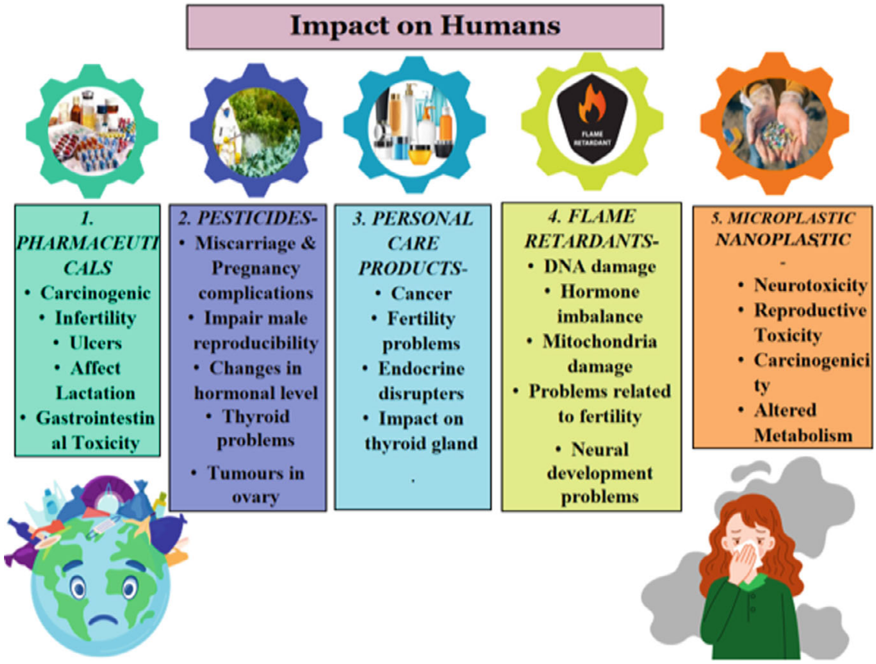

Fig. 2.2 Impact of EPs on humans

1. PHARMACEUTICALS

Pharmaceuticals have a detrimental effect on the human body. They are carcinogenic and cause fertility problems in both males and females. It induces gastrointestinal toxicity leading to ulcers. It affects lactation in pregnant women.

2. PESTICIDES

It can lead to miscarriage and other complications in pregnant women. It can impair male reproducibility. They induce changes in hormonal levels. It causes abnormalities in the thyroid and tumors in the ovary (Poonia et al. 2021).

3. PERSONAL CARE PRODUCTS

They are carcinogenic and cause fertility problems. It interferes with the hormonal system either by mimicking or disrupting the actions of natural hormones. They have detrimental effect on the thyroid gland (Juliano and Magrini 2017).

4. FLAME RETARDANTS

It damages the body at a cellular level (DNA and mitochondria). It causes hormonal and reproductive problems. It negatively affects the development of the nervous system (Venier et al. 2014).

5. MICROPLASTICS and NANOPLASTICS

They are extremely harmful to both nervous and reproductive systems. They can induce alterations in the metabolism and are carcinogenic (Shen et al. 2019).

2.5 Methods of Analysis of Emerging Pollutants (Eps)

Conventional and modern techniques are applied for the analysis of EPs. Conventional methods of analysis are spectroscopy, liquid chromatography (LC), gas chromatography (GC). Conventional methods are replaced by advanced methods. The non-volatile, polar, and thermolabile EPs are examined by applying LC, while the nonpolar, thermostable, and volatile EPs—such as flame retardants, filters, and certain pesticides—*are* effectively ascertained with the help of GC using these methodologies.

LC and GC are analytical techniques used for separation and works on the principle of differential partition. For sample preparation, Solid Phase Extraction (SPE) is used which particularly retains target compounds on solid sorbent thus extracting, purifying, and concentrating analytes from complex matrices (wastewater). Spectroscopic techniques such as Ultra-Violet–Visible (UV–Vis) spectroscopy calculates the sample's absorption of light in the UV–Vis region, while Infrared (IR) spectroscopy measures the absorption and emission of infrared radiation of a sample. UV–Vis and IR can provide complementary information to chromatographic methods, especially for compound identification.

Current Challenges in Detection of EPs

Analytical

- Diverse nature and sources of Eps,
- Presence of EPs in complex matrices,
- Tedious sample preparation,
- Lack of standardized methods,
- Analytical instrumental limitations.

Technical

- Time and cost consuming,
- Resource intensive,
- Inconsistent or lacking regulatory framework for different regions,
- Limited funding and resources for research and monitoring programs,
- Lack of detection methods for transforming EPs and their by-products.

To overcome these challenges, advanced methods of analysis are utilized for better detection and management of EPs.

2.6 Advanced Methods for the Analysis of the Eps

Advanced Detection Methods

Advanced techniques like LC-MS/MS, UHPLC, HRMS, ICP-MS, and FTNIR are used as cutting-edge detection methods for tracking and regulating the existence of EPs in wastewater (Ismail and Mokhtar 2020; Zhao et al. 2014). These hyphenated techniques offer detection at trace levels with high accuracy and reliability (Table 2.2).

2.6.1 Liquid Chromatography

Liquid chromatography (LC) is a method wherein the constituents of the mixtures are separated on their relative affinity towards stationary and mobile phase (Kayillo 2005). The advance and hyphenated technique can be used to detect EPs are mentioned below:

1. ***LC-MS/MS***: Tandem mass spectrometry (MS/MS) is a very powerful technique in which two mass analyses are performed in sequence with a fragmentation step in between, using a combination of mass analyzers (Kayillo 2005). Combining two or more mass analyzers of the same kind in sequence is one method of using MS/MS. Mass spectrometry analysis is done by filtering, and then introducing ions into a collision cell where fragmentation of ions takes place and after that the second mass analysis starts (Neil et al. 2021). MS/MS is combined with LC

Table 2.2 Advanced techniques for detecting various kinds of emerging pollutants

Analytical techniques used for detection		Target EPs
Liquid chromatography	LC-MS/MS	• Pesticides • Pharmaceutical product • PCPs • Industrial products
	LC-QTOF/MS	• Endocrine active compounds • Pesticides • Pharmaceuticals
	LC-TOFMS	• Pharmaceuticals • Drug of abuse • Pesticides • Nitrosamines • Flame retardants • Plasticizers Perfluorinated compounds
	LC-Orbitrap-MS	Pharmaceuticals
	UHPLC-MS/MS	• PCPs • Pharmaceuticals • Illicit drugs
	UHPLC-Q-exactive Orbitrap MS	• Pesticides • Drug residues
	UHPLC-HRMS	• Pharmaceutical • Herbicides • Stimulant • Illicit drugs • Preservative agent
	UHPLC-Q-Orbitrap-MS	• Pharmaceutical • Personal care products
	UHPLC-Q-orbitrap	• Antibiotics
	LC-MS	• Drug of abuse • Pharmaceuticals
	UHPLC-QqLIT-MS/MS	• Pharmaceuticals • Transformation products • Pesticides
	LC-HRMS/MS	• Artificial sweeteners • Flame retardants • Pesticides • Fungicide • Herbicide • Veterinary drugs • Insecticides • Industrial chemicals • Plasticizers • Pharmaceuticals
	UHPLC-QTOFMS	• Pharmaceuticals

(continued)

Table 2.2 (continued)

Analytical techniques used for detection		Target EPs
Gas chromatography	GCxGC-TOFMS	• Pesticides • Organohalogens
	GC-MS with derivatization	• Parabens • Hormones • Anti-inflammatory drugs • Triclosan • Bisphenol A
	GC-MS/MS	• Polycyclic and Nitro-aromatic musk • Brominated, Chlorinated flame retardants • Methyl triclosan • Chlorobenzenes • Organochlorine pesticides • Polychlorinated biphenyls
Metal analysis	SP-ICP-MS	Metal pollutants (Hg, Zn, Au, Sb, V, Fe, Cr, Ni, Pb, Se, Tl, Co, Cd, Mn, Li, etc.)
	GC-ICP-MS	Flame retardants
	HPLC-ICP-MS	Mercury
	ICP-MS	• Trace metals • Colloidal trace metals • Heavy metals • Organic pollutants
	ICP-OES	Heavy metals
	HPLC	• Heavy metals • Organic pollutants
Spectroscopic method	FT-NIR	• Pharmaceuticals

which helps to isolate compound of interest from matrix component and remove interferences like isobaric compounds. This technique offers high precision in the detection through selectivity, sensitivity, and specificity (Thomas et al. 2022).

2. ***LC-QTOF/MS***: This technique offers improved sensitivity and selectivity for simultaneous identification and measurement of complicated mixtures or unidentified substances (Zhao et al. 2014). Ion selection and fragmentation are provided by the quadrupole, while high resolution and mass accuracy are provided by the time-of-flight analyzer for accurate compound identification (Guale et al. 2013).
3. ***LC-TOF/MS***: Time-of-flight mass spectrometry (TOFMS) is combined with LC for separation, detection and measurement of EPs in intricate mixtures or unknown substances. This method can quickly examine pollutants through several ionization modes without rigorous sample preparation (Guale et al. 2013). It is an effective analytical method that combines Orbitrap mass spectrometry

for higher resolution and mass accuracy analysis of complex materials with LC for the separations (Li et al. 2009; Neil et al. 2021; Shuken 2023).

4. ***UHPLC-MS/MS***: In this technique, ultra-high-performance liquid chromatography (UHPLC) is coupled with MS to get accurate analytical findings with better resolution, quicker analysis times, and higher sensitivity. The conjunction of UHPLC-MS/MS improves the recognition and quantification of analytes in intricate matrices by the ionization of separated components and subsequent (m/z) ratio analysis (Thorstensen et al. 2022).
5. ***UHPLC-Q Exactive Orbitrap MS/MS***: This method is useful for detection and identification of targeted and non-targeted residue analysis of pesticides, plant growth regulators, and plant metabolites. This system combines UHPLC with a high-resolution MS (Orbitrap) and utilizes smaller particles in the chromatography column due to its high-pressure operation (Neil et al. 2021). It may be used for the examination of intricate mixtures in the pharmaceutical, biological, and environmental industries (Li et al. 2022).
6. ***UHPLC-HRMS***: UHPLC-HRMS combines the benefits of HRMS with UHPLC (Ma et al. 2022). The concept behind UHPLC-HRMS is separation of sample components by using UHPLC, and their detection and identification by using HRMS on the basis of their (m/z) ratio (Perez de Souza et al. 2021; Núñez et al. 2020).
7. ***UHPLC-QqLIT-MS/MS***: This analytical method pairs the benefits of hybrid linear ion trap mass with three quadrupole spectrometers (QqLIT-MS/MS) with UHPLC (Ma et al. 2022). Three quadrupoles and a linear ion trap make up the QqLIT-MS/MS apparatus (Perez de Souza et al. 2021). To choose the relevant precursor ions, the first and third quadrupoles (Q1 & Q3) functions as a mass filter, and the second quadrupole (Q2) acts as a collision cell, which breaks apart the chosen precursor ions by applying Collision-Induced Dissociation (CID). This method is employed in the analysis of pharmaceuticals, pesticides, and transformation products (Rathod et al. 2019).
8. ***LC-HRMS/MS***: This analytical method integrates the elemental composition determination, high mass precision measurement, and separation capability of LC with MS sample components are examined by LC-HRMS/MS with remarkable sensitivity and precision (Shuken 2023). Since LC-HRMS/MS can give precise chemical structural information with quantification can be applied in metabolomics, environmental monitoring, medicines, and clinical research (Pitt 2009).
9. ***UHPLC-QTOFMS***: This analytical method integrates QTOF MS for accurate mass measurement and structure identification with UHPLC's high-resolution separation capabilities. QTOFMS provides high mass accuracy and resolution for accurate identification and quantification of these compounds and UHPLC enables quick and effective separation of compounds (Thorstensen et al. 2022).

2.6.2 Gas Chromatography

In GC a gaseous or vaporized sample is introduced into a long column in order to separate the constituents present in the sample. By monitoring the retention time, each component that is flushed successively from the column to the detector can be recognized.

1. **GCxGC-TOFMS**: This technique improves separation and offers higher peak capacity by combining two GC columns with distinct stationary phase. To further separate the compounds based on polarity differences, the effluent from the main column is then re-injected onto a secondary column with a different stationary phase, usually a more polar phase (Pierce et al. 2006). Small amounts of the primary column effluent are captured, focused, and reinjected into the secondary column at regular intervals, usually every few seconds, by a modulator device that is positioned between the two columns (Lovestead and Urness 2019).
2. ***GC-MS/MS***: This method uses GC to separate the constituents of the sample, and two phases of MS (MS/MS) are used to identify and detect the separated molecules. In the first phase (MS1), the ionized molecules are separated based on their (m/z) ratio. Selected precursor ions from MS1 are subsequently separated and fragmented by CID and create product ions in second step (MS2), which undergo analysis yielding comprehensive structural details about the parent molecule that facilitate its identification (Lovestead and Urness 2019). This method can detect target analytes with minimum interference from co-eluting chemicals, present in complicated sample media. Applications of GC-MS/MS are common in areas including food safety, forensics, environmental analysis, and pharmaceutical research.

2.6.3 Inductively Coupled Plasma Mass Spectroscopy (ICP-MS)

1. ***ICP-MS***: Ionizing chemical species in a sample and classifying ions based on their (m/z) ratio is the basic idea behind Inductively Coupled Plasma Mass Spectrometry (ICP-MS*)*. Ionization of sample is done by applying *inductively coupled plasma* and it is subsequently sorted in the MS (Wilschefski and Baxter 2019). ICP-MS is ideal for analyzing EPs, food adulterants also polymers (Clases and Gonzalez de Vega 2022). In this method, a sample of liquid is introduced into the core by dispersing it into an Ar or He gas stream. After being heated, the sample is vaporized and ionized. A small number of ions travel through another slit in high vacuum after the ions are transported via a core into an area of reduced pressure. For detection, usually quadrupole mass analyzer is used (Mozhayeva and Engelhard 2020). At the detector, the transmitted ions are gathered where the m/z ratios match the element's natural isotope. Since the quantity of the element in the sample determines how many ions are found for each isotope, the approach

is quantitative. ICP-MS has extremely low concentrations of metal and certain non-metal detection capabilities (Khan et al. 2022).

2. ***SP-ICP-MS***: Single-particle ICP-MS works by detecting individual nanoparticles by introducing them one at a time into diluted solutions (Wilschefski and Baxter 2019). This approach has extreme efficiency of detection based on nanoparticle's size, distribution, particle number, and concentrations in suspensions (Clases and Gonzalez de Vega 2022).
3. ***GC-ICP-MS***: This technique works on this principle where the sample is first split apart by GC and then transferred to the ICP-MS system where an ICP ionizes the sample components, while MS subsequently separates and detects the components of the ionized sample (Clases and Gonzalez de Vega 2022). This method is very useful for analyzing substances at the trace level, identifying unidentified compounds, and deciphering the structures of complicated molecules (Mozhayeva and Engelhard 2020).
4. ***HPLC-ICP-MS***: In this method HPLC is coupled with ICP-MS, to detect separated compounds. It is very helpful for identifying unknown chemicals, analyzing substances at the trace level, and deciphering the structures of complicated molecules (Mozhayeva and Engelhard 2020).
5. ***ICP-OES***: ICP-Optical Emission Spectrometry (ICP-OES) utilizes inductively coupled plasma to excite the atoms in a sample and cause them to emit electromagnetic radiation. The radiation is analyzed to ascertain the elemental content in the sample (Mozhayeva and Engelhard 2020). As the sample dries up, melts, and vaporizes due to the high temperatures of the plasma, a light is released specific for each element to generate its own spectrum, (Khan et al. 2022; Wilschefski and Baxter 2019).

2.7 Removal Technologies for Emerging Pollutants in Wastewater

Various removal technologies (Table 2.3) have been developed and employed to mitigate EPs (Thuy et al. 2008; Luo et al. 2014).

2.7.1 Coagulation–Flocculation

The techniques involve the addition of chemicals to aggregate and remove EPs (Matamoros and Salvadó 2013). A study found that the musk (such as galaxolide and tonalide) in hospital wastewater significantly decreased (by around 80%) utilizing this process (Suarez et al. 2009; Alexander et al. 2012). Alum and ferric salts, some

Table 2.3 Removal technologies for EPs and their removal efficiency

Technology	Removal efficiency	Cost	Scalability	Environmental impact	Complexity
Coagulation–flocculation	Medium	Low-medium	High	Moderate	Low
Activated carbon adsorption	High	Medium-high	Medium	Low-moderate	Medium
Advanced oxidation processes	High	High	Medium	Moderate	High
Membrane processes	High	High	High	Low to moderate	High
Membrane bioreactor	Medium-high	Low-medium	High	Low	Medium

polymers (added later by me) can be used as common coagulants. Several parameters, such as temperature, pH, alkalinity, mixing conditions, quantities of destabilizing anions and divalent cations (such as *bicarbonate, chloride, and* sulfate), can influence the efficacy of coagulation–flocculation processes (Thuy et al. 2008).

2.7.2 Activated Carbon Adsorption

Pollutants are removed from water by adsorption onto solid materials like activated carbon. This method has superior efficacy to eliminate EPs when compared to the coagulation–flocculation procedure, and has significant promise for treating secondary effluent (Kovalova et al. 2013). There are two types of activated carbon: powdered activated carbon (PAC) and granular activated carbon (GAC) are commonly used in adsorption processes. Surface adsorbent properties like surface area, pore volume and pore size, surface morphology, and mineral matter concentration, while adsorbate properties like molecular dimensions, specific functional groups, KOW (octanol–water partition coefficient), and pKa (acid dissociation coefficient) can influence the efficiency of this method (Luo et al. 2014).

2.7.3 Advanced Oxidation Processes

Advanced oxidation processes (AOPs) are effective methods for eliminating EPs by using particularly reactive hydroxyl radicals (−OH) to oxidize as well as degrade organic pollutants. For the removal of EPs, AOPs are coupled with molecularly imprinted polymers (MIP) as selective adsorbents and combined with bioelectrochemical systems (BES-AOP) (Hernández-Leal et al. 2011). Ozonation, photocatalysis, and Fenton and photo-Fenton reactions are used in AOPs to obtain specific results (Thuy et al. 2008).

2.7.4 Membrane Processes

EPs can also be eliminated from wastewater by interacting with organic matter and adhering to membrane polymers. Membrane processes consist of three main steps: charge repulsion, adsorption onto the membrane, and size exclusion (Schäfer et al. 2011). Various factors like the features of the membrane, operating environment, and characteristics of EPs can influence these removal methods (Jermann et al. 2009). Since membrane pore diameters are far bigger than the molecular sizes of EPs, they are not effectively removed by UF (ultrafiltration) and MF (microfiltration) instead methods like *reverse osmosis (RO*) and nanofiltration (NF) having considerably "tighter" structures than UF and MF are used (Steinle-Darling et al. 2010). Although RO could eliminate micropollutants entirely, it is not a perfect barrier and other treatment methods should be considered to accomplish total removal (Sahar et al. 2011).

2.7.5 Membrane Bioreactor

Membrane filtering and biological treatment of activated sludge are combined in this method (Ngo et al. 2012). This method has the capacity to hold onto sludge that has several chemicals attached to it resulting in the effective removal of a broad range of newly developing EPs (Chen et al. 2008). Activated sludge is an aerobic process which involves a mixed microbial community used for degradation of pollutants. The chemicals are introduced by the membrane surface, help to accelerate the microbial breakdown of EPs. An increase in the retention times of sludge present in bioreactors is recorded as per the onset of degradation (Kovalova et al. 2013). Various factors like pH, temperature, concentration, conductivity, sludge age, composition of wastewater, and anoxic and anaerobic compartments, influence the removal ability of bioreactors (Radjenović et al. 2009).

This method is found useful in the successful removal of the pharmaceutical drugs and alkaloids like naproxen, ibuprofen, acetaminophen, hydrochlorothiazide, and paroxetine (Chen et al. 2008). Hydraulic retention, sludge retention, and temperature are the factors which can affect the proper management of EPs (Hu and Stuckey 2006). Huge concentration of nitrifying bacteria in the biomass are proven beneficial to successfully degrade the developing EPs too (Roh et al. 2009).

2.7.6 Growth Treatment Process

This process is a feasible alternative for activated sludge procedures to entail the attached growth on mobile or stationary carriers suspended in the reactor (Guo et al. 2012). The inert media surfaces like plastic, rock, or gravel are utilized to support microorganisms' growth in a biofilm. This contrasts with suspended growth processes where the microorganisms are free-floating in the liquid, e.g., trickling filters and moving bed biofilter reactor (MBBR). The overall growth treatment process has a potential for decreasing the levels of EPs in wastewater (Serrano et al. 2011).

2.7.7 Phytoremediation

Phytoremediation is an efficient environmentally friendly technique for the removal of EPs. It is utilized in place of conventional tertiary treatment techniques (cost-effective) to remove EPs from wastewater (Ghosh and Manchanda 2019). Metal-accumulating plants like *Tagetes patula*, *Bassica scoparia*, and *Portulaca grandiflora* can effectively remove *heavy metals like cadmium, mercury, zinc, chromium, and lead*. The plants absorb heavy metals from water through roots and move them to different locations (Table 2.3). As a result, by preventing their migration (back to water), plants immobilize heavy metals which later get precipitated at the root zone (Bhat and Bhat 2016).

Advantages

Advanced analytical methods significantly improve the detection of emerging pollutants compared to conventional methods in several ways (Guale et al. 2013):

Higher Sensitivity: Advanced analytical techniques particularly modern techniques Orbitrap technology's high-resolution accurate-mass (HRAM) MS can offer greater sensitivity with low detection limits (down to nanogram level) detection of EPs (Shuken 2023).

Improved Selectivity: Select Reaction Monitoring (SRM) techniques offer specific detection of EPs and targeted chemicals. MS/MS provide greater selectivity in measurement of EPs in intricate environmental matrices like sewage water and sludge.

Enhanced Identification Capabilities: The structure of unknown compounds may be precisely identified by advanced techniques which include HRAM and Orbitrap technologies, significantly reducing foreign entities resulting in more reliable and reproducible identification (Perez de Souza et al. 2021).

Increased Analytical Power: The spectrum of analytes that may be identified can be increased by using more advanced and hyphenated techniques (chromatography, laser ablation, or single cell analysis) to accomplish, better quantification, speciation, and material characterization (Ma et al. 2022).

Better Handling of Complex Matrices: Modern techniques are better suited to deal with complicated environmental matrices, such as soil, air, and wastewater, which frequently include a variety of pollutants and interferences. The advanced techniques offer to extract, detect, and quantify a variety of EPs and their products (formed by transformation) with high resolution (Núñez et al. 2020).

Improved Detection of Unknowns: The structural elucidation capabilities of advanced MS techniques allow for the tentative identification of unknown EPs. Advanced approaches are made to identify and quantify chemicals by assessing their molecular composition and properties instead of only their chemical properties, they are more successful at detecting undiscovered developing pollutants (Pitt 2009).

Automation and High-Throughput Analysis: The development of automated, high-throughput analytical techniques have significantly enhanced the screening and monitoring of EPs in environmental samples, overcoming challenges and limitations of conventional analytical approaches.

2.8 Analytical Applications

GANGA ACTION PLAN {GAP}: It was the first major initiative launched by the Indian government (Ministry of Environment and Forests) in 1985 to clean up the Ganga. GAP aimed to avoid hazardous and industry chemical debris and to intercept, redirect, and treat household sewage in order to improve Ganga's water quality from reaching the river (Rai 2013). It was implemented in two phases: GAP-I from 1985 to 2000 spanning over 25 towns in West Bengal, Bihar, and Uttar Pradesh; GAP-II from 1993 to 2000 covering 7 states (UP, Bihar, WB, Uttarakhand, Jharkhand, Haryana, Delhi) and tributaries like the Yamuna and Gomti (Tare et al. 2003; Rai 2013). The factors like poor operational skills, lack of maintenance of assets, and inadequate sewage treatment capacity of the STPs are the responsible factors are the limitations of the GAP, leading to a more comprehensive Namami Gange program 2014 to overcome the limitations (Balkrishna et al. 2024). This program focuses on riverfront development, biodiversity conservation, solid waste management, wastewater treatment, and afforestation. The significant objective of the program was the construction of wastewater treatment facilities in towns and cities alongside the bank of the Ganga ghats that treated domestic wastewater on site with the help of STPs techniques like AOPs, membrane bioreactor to remove EPs (Srinivas et al. 2020).

YAMUNA ACTION PLAN {YAP}: The Yamuna River is considered as one of the most polluted rivers in India. Due to the presence of EPs sourcing from household sewage, industrial effluents, and agricultural runoff (Naithani and Pande 2015). The primary objective of the YAP was to improve water quality and content of river Yamuna. It starts with the treatment of domestic sewage and a complete regulation on industrial effluent flow. Constructing sewage treatment plants, reducing the open defecation, and preventing the burnt and unburnt human remains are the key factors for the cleanness of river Yamuna (Nallathiga 2008). The scientific techniques such as phytoremediation have been used to remove heavy metals, coagulation–flocculation in drain zones to reduce phosphate content, a play significant role to make Yamuna River free from contaminations. The regular monitoring of physical and chemical properties like pH, DO, BOD, total and fecal coliforms are done by analytical techniques like LC-MS/MS, HPLC, LC-TOF MS, LC-QTOF MS, HRMS, GC-MS/MS, and FT-IR.

2.9 Forensic Applications

Deliberate contamination of water supply as an act of bioterrorism is a critical threat to a country's infrastructure, potentially targeting water sources and distribution networks to cause severe disruption. Deliberate contamination results acute and chronic poisoning, which can have severe implications for public health, medicine, and the economy. Mass poisoning incidents involve numerous individuals experiencing similar symptoms due to exposure to toxic substances. This can occur through various means, as

- *Food poisoning*: Involves botulism toxin, mycotoxins, and heavy metals.
- *Water poisoning*: Includes arsenic and nitrates.
- *Air pollution*: Involves carbon monoxide, hydrogen sulfide, and chemical fumes.
- *Occupational exposure and illicit drug use*: Also contribute to mass poisoning.
- *Biological agents:* bacterial, viral, and fungal pathogens, can cause waterborne diseases like anthrax, cholera, and hepatitis
- *Chemical weapons*: The most common chemicals include nerve agents, Lewisite, and sulfur mustard. After World War II, significant amounts of chemical weapons were disposed of in the ocean, impacting a continuous risk to environment and human health as they can persist on the ocean floor for years.
- *Radiological pollutants:* It comes from industrial waste or natural sources, pose a cancer risk. Groundwater contamination with radioactive elements is more problematic than surface water contamination.

Forensic analysis in these cases is crucial for pinpointing the cause, source, and responsible parties. This complex process necessitates a multidisciplinary approach to accurately identify the cause, mitigate the impact, and bring perpetrators to justice.

Key steps in the forensic investigations (Fig. 2.3). This comprehensive approach ensures thorough investigation and response to mass poisoning incidents.

2.10 Future Perspectives

Advanced detection technologies can be used to achieve more sensitive and selective detection of EPs such as Next Generation Sequencing for microbial DNA analysis. Nanotechnologies and biosensors can be utilized for detection and management while Machine Learning algorithm can be used for data analysis. Portable field devices can be proven beneficial for on-site detection and real-time monitoring. Strict regulation

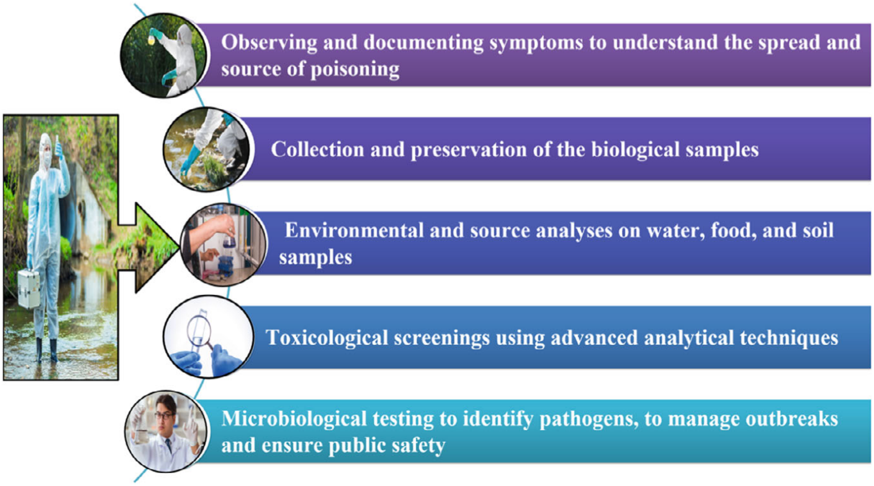

Fig. 2.3 Key steps in the forensic investigations

and policies must be introduced to cover a broader spectrum of EPs incorporating advanced scientific tools. Standardized guidelines and protocols should be drafted for better monitoring and controlling of EPs in wastewater. To effectively identify and quantify EPs in water and wastewater samples, new and sophisticated approaches must be developed via ongoing research and innovation in removal of EPs (Sui et al. 2015).

2.11 Conclusions

The existence of emerging pollutants (EPs) in water and wastewater, and by-products of their transformation poses significant challenges since they have complex chemical structure and low concentrations makes them almost undetectable. The persistent and bioaccumulation of EPs cause potential risks to ecosystem as well as human health causing severe health hazards like birth deformities, cancer, etc. Due to their transforming nature, identification and detection of EPs have not been successfully done with conventional methods. EPs infiltrate the ecosystem through different routes like domestic wastewater, commercial/industrial effluents, and runoffs from terrestrial and agricultural land. That necessitates the active removal and management of EPs through advanced detection technologies in complex matrices. Advanced analytical techniques like UHPLC-HRMS, LC-MS/MS, LC-TOF/MS, LC-QTOF/MS, LC-TOF/MS, GC-MS/MS, ICP-MS, and ICP-OES have significant impact on detecting and analyzing emerging pollutants (EPs). Advanced oxidation processes and bioreactors have enhanced removal efficiency, but the lack of comprehensive testing methods has hindered their widespread adoption. HRMS and LC-MS/MS are crucial tools for analyzing EPs in water and wastewater. To combat the threat posed by EPs, it is crucial to enhance detection technologies, develop effective removal methods, and establish comprehensive regulatory frameworks to monitor and control these pollutants in the environment.

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Chapter 3
Fundamental Distinction of Surface Water Potential Zones and Identification of Suitable Monitoring Locations in the Mahanadi Watershed, Odisha, Using Level Based Weight Assessment (LBWA), Geographical Information System (GIS), and Decision Tree (DT) Techniques

Abhijeet Das

Abstract The Mahanadi River, Odisha, India, possesses strong links to the locals both traditionally and economically. It offers enough arable plains and hills for farming, as well as suitable areas for communal hunting and fishing. Because of the abundant natural resources it offers, it is significant not only for the residents of particular areas but also for the state of Odisha. However, increased organic matter content downstream of watersheds highlighted the seriousness of non-point source (NPS) pollution. So, the assessment of the pertinent physicochemical parameters of 19 locations of surface water quality from the river basin is taken into account, for a period of 8 years (2015–2023). The standard guideline values were compared to the physicochemical results as advised by the World Health Organization (WHO) regarding water consumption and public health, to have a general overview of surface water quality in this recent scenario. The results further indicated that the majority of the parameter values fall below the highest amounts that are allowed to be consumed in accordance with the WHO guidelines except TKN and TC, during summer season. Using geographical information system (GIS)—Inverted Distance Weighting (IDW) methods with ArcGIS 10.8 application software, spatial distribution maps have been created. To identify and allocate the sources of pollution and analyse the spatiotemporal variation, the dataset was exposed to a widely accepted coherent approach employing Level Based Weight Assessment (LBWA/L) Water Quality Index (WQI) and Multi-Criteria Decision-Making (MCDM) analysis, coupled with Machine

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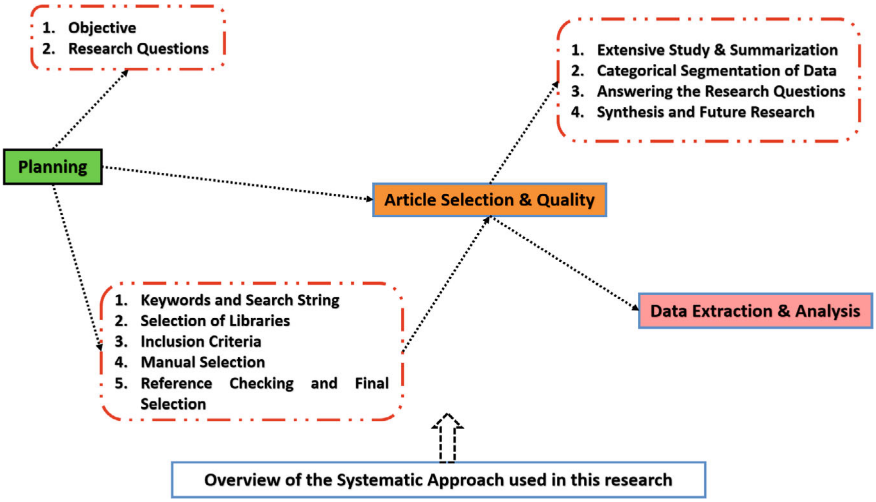
S. Dey and M. P. Shah (eds.), *Biotechnological Removal of Emerging Pollutants from Wastewater Systems*, Advances in Wastewater Research,
https://doi.org/10.1007/978-981-96-3945-8_3

Learning (ML) techniques, namely Decision Tree (DT) Algorithm. It is observed that samples mostly contained the anions $Cl^- > SO_4^{2-} > NO_3^- > F^-$, while the primary cations were $Fe^{2+} > B^+$. For each and every sampling site, L-WQI was established to be 23–412, respectively. It is found that most of the test sites were located in excellent to unsuitable category, as determined by this approach. The results revealed that 36.84% samples are excellent for drinking, 10.53% good, 31.58% poor, 15.79% very poor, and 5.26% unacceptable and, thus, unsuitable for consumption. Further, at sites X-(2), (5), (6), (7), (8), (9), (10), (11), (12), (13), and (19), water quality is mostly impacted by agriculture and industrial inputs. In addition, sample sites situated in the upstream and downstream regions see declining water quality indicators as a result of hydroelectric dams, evolving land use patterns, growing populations, and deforestation along riverbanks and catchment areas. The present study points out from the spatial distribution maps that EC, Cl^-, SO_4^{2-}, NO_3^-, TKN, and TC played a major part in influencing the river's WQI, showing that during the monsoon season, both insignificant human actions and natural causes have an effect on surface water chemistry. However, to find a better alternative in estimating the level of ranking of pollution, a mathematical technique DT has been adopted. This will offer helpful information to prioritise and preserve the water quality of drinkable sources and lessen the negative effects that consuming subpar surface water resources have on human health. It is also adaptable, impartial, simple to compute, and time-saving. Moreover, the results showed that the score and its rank at X-(9) (0.95), signified as mostly polluted site, in comparison to other locations. The cause may include human activities, prolonged wastewater use, excessive surface water extraction, and modifications to land use patterns. Ultimately, both LBWA and DT are permitted to identify elemental correlations, and their probable origin was man-made as opposed to nature. These findings are crucial to comprehending the study area's surface water sustainability for drinking. Hence, the present study will serve as the foundational database for all upcoming work in the area. The recommended mitigation measures include debris removal, silt extraction, river bank stabilization, modern hydraulic structures, improved waste management, systematic removal of water hyacinth and decomposed materials, and spoil bank design in spilling zones to restore the river's natural flow.

Graphical Abstract



Keywords Mahanadi River · LBWA · DT · Population · Deforestation · Water extraction · Sustainability

3.1 Introduction

Water is among the most vital components of life on Earth, and life itself depends on it, in its purest form (Ikram et al. 2022). The sources of fresh water are severely constrained by the current population growth and human inventions, which have a significant negative influence on the degradation of water. Approximately 2.5% of water worldwide is accessible as fresh water from every water resource on the planet. However, historical evidences demonstrate how anthropogenic pressure has changed the quality and amount of water, which has caused numerous human settlements to disappear (Dimple et al. 2022). The quantity of water that is available to people is found in underground water, rivers, lakes, and reservoirs. The adjacent landscapes that regulate water and chemical exchange between nearby land and stream systems and serve as an interface between the aquatic and terrestrial ecosystems are known as riparian zones. Thus, changes in the topography can have an adverse effect on the energy and material exchanges between aquatic and terrestrial organisms, which can worsen the quality of the water. Approximately, 58 billion cubic metres of surface water are extracted each year. Consequently, the quality of the surface water has declined, while the water table has grown in a lot of regions with irrigation. Furthermore, the quality of surface and ground water, as well as the consequences for human health, has been negatively impacted globally by increased urbanisation, building, agricultural practises, industrial uses, and natural processes (Rajput et al. 2023). Numerous studies have shown that the two biggest threats to water security today are water exploitation and water theft. Likewise, riparian zones create a distinct ecosystem and serve as a barrier between streams and uplands and are essential to the watershed's well-being. Additionally, stress on hydrologic and hydrogeologic systems could result from the annual and seasonal variations in climate that lead to a decline in water quality. Afterwards, seasonal variations in surface water quality were ascribed to surface–surface water interaction driven by the monsoon. Hence, for humans to survive on Earth, there must be an ideal amount and acceptable quality of water, yet maintaining an acceptable quality of water is difficult in the field of water resource management (Vishwakarma et al. 2022; Das 2022). Surface water is becoming as a prerequisite for food production and human civilisation. Thus, particularly in arid or semi-arid regions, it serves as the primary source of fresh water for food, energy, and ecosystem support and is frequently the only reliable supply of such resources (Cooley et al. 2021). As a result, the dissolved elements in water are always present in different amounts due to both natural (rainfall, weathering, and the breakdown of rocks and soil) and human activity processes (residential and commercial) (Gao et al. 2021). An essential component of managing this valuable resource is estimating the effects of seasonal flooding on surface water quality and level as a result of heavy precipitation. Therefore, understanding the seasonal variations in surface water quality is crucial. Hence, degradation of quality poses a problem to sustainable development in addition to scarcity of resources (He et al. 2021). Numerous techniques and elements have been developed for the evaluation of water quality and contamination. Moreover, the multiple anthropogenic activities and natural processes contribute significantly that promote worsening of the purity of surface water. It is crucial to evaluate the surface water quality in addition to its other resources in order to guarantee the safe and sustainable use of these resources. In today's culture, developing a novel technique for determining pollution load is considered a wide topic. Hence, different techniques and mathematical instruments are employed and determined which one was most suitable for evaluating water contaminants. So, to guarantee its wellbeing, a rigorous and watchful approach to monitoring and assessment is required (Singha et al. 2021). The most effective way to examine water behaviour is to calculate the index score, for purposes in industry, agriculture, and cities. Therefore, Water Quality Index (WQI) may be assessed by applying a simple mathematical method that distils a large number of water characteristics into a single figure that illustrates the combined effect of all water quality indicators (Masoud et al. 2022). Sustainable water supplies under changing climatic conditions and local environmental strain require an understanding of the geographical and temporal change in surface water quality. Numerous strategies were familiarised with to enhance comprehension of the state of water quality: Water quality modelling, statistical techniques, neural network-based techniques, fuzzy logic, artificial intelligence, and conventional methods for determining WQIs, either alone or in combination. To keep an eye on the quality of the water, traditional approaches have been discovered to be untrustworthy as a result of sampling flaws. Twenty-two water quality characteristics from 24 water well samples were used for the quality assessment. The YSR district's Obulavaripalli Mandal's WQI demonstrates that 40% of samples are suitable for drinking, and 30% of testing samples are not safe for drinking. The overall assessment indicated that the water quality is unfit for human consumption based on the analysis of ten water parameters, typically taken from twenty surface water samples. From September 2014 to January 2016, four seasons and 96 places along major rivers were sampled. Our results are valuable for managing water quality and might be applied in the Taihu Basin of Lake Tai for quick and inexpensive water quality testing. Further, according to the WQI for Loktak Lake, it demonstrates how the wetland is under stress due to growing human activity. The WQI for the examination of water potential for five sample locations was generated using eleven factors. Considering its significance, every attribute received a relative weight between 1.46 and 4.09. Hence, WQI-based maps are simple to comprehend and help raise public awareness of water pollution. They also support the enforcement of laws requiring the proper management of wastes released from various sources and placing limitations on the extraction of surface water, all of which can contribute to the development of efficient management strategies that safeguard water from contamination (Elsayed et al. 2021). To consistently offer clean drinking water, its quality needs to be watched after and protected. Prior to assessing whether water is suitable for a given function, it is important to comprehend the chemical makeup of surface water. Environmentalists create the indexes for the water quality analysis using these datasets. By compressing the dataset and displaying the water quality measurements clearly, this kind of indexing makes use of mathematical techniques. To deal with the possible issues with surface water quality, a geographic information system (GIS) and trend detection techniques would be beneficial in analysing the long-term changes in water quality. It is computed starting from the point at which surface water is suitable for human consumption. By combining the measurements of water quality characteristics, it functions as a single number that expresses the quality of the water. Also, it expresses the data in a logical and simplified manner by condensing the majority of the information from several water quality parameters into a single value (Behnam et al. 2022). The fact that this quantitative evaluation approach needs in-depth familiarity with the distribution of variable weights in order to compute the score—implying that the true conclusion is ambiguous—is one of its biggest shortcomings (Uddin et al. 2021). However, an evaluation of the water bodies' quality could provide us a general idea of how they are doing and whether they pose a risk to different usages (Behnam et al. 2022). Model analysis has had a noteworthy impact on the evaluation of water quality. To evaluate, lessening the subjectivity of the WQI technique has been the focus of various research studies and has proven to be an effective and important tool for precise weighing systems, by adapting Level Based Weight Assessment weights (LBWA/L) to remarkable indicators of water quality and, finally, determining the WQI score (Marghade 2020; Alam et al. 2021; Li et al. 2020). This approach is an improvement over traditional WQIs, which are based on the expert survey method, the analytic hierarchy process (AHP), and the Delphi method, which assign weights to parameters based on expert opinion and subjective judgement. The parameters used here are frequently equal or weighted based on how important they are thought to be to the overall quality of the water. Such viewpoints frequently result in the important loss of information regarding the region's or area's water quality (Tigrine et al. 2021).

Moreover, these techniques are frequently tiresome and time-consuming exercises. Furthermore, excessively weighted characteristics may have an impact on the index's sensitivity, so weighing the parameters based on the amount of water utilised for irrigation, drinking, and residential use is essential (Kabiri et al. 2021a). Therefore, for an integrated water resource management programme to be implemented successfully, it is essential to comprehend the quantity, quality, and recovery of surface water resources. By properly allocating weights, issues like eclipsing and ambiguity can be resolved (Gong et al. 2021). In order to get rid of the subjectivity involved in the weight assignment process and overcome the erroneous weighting of factors in previous techniques, an approach like Level Based Weight Assessment (LBWA/L) measures the degree of ambiguity or chance present in the datasets (Skourtos et al. 2021). Numerous scientific and engineering fields, including anatomy, heredity, pharmacology, physics, particle physics, computational methods, entropy, communications engineering design, and road construction, have effectively used it (Rezk et al. 2021). This also aids in the extraction of a large amount of information by evaluating the random datasets' equality, diversity, adaptability, complexity, interactivity, and redundancy. To compensate for the weaknesses of the LBWA method, use of the multi-criteria decision-making (MCDM) approach has been utilised to compare and evaluate the various possibilities in order to choose the best solution (Patel et al. 2023). In the past years, machine learning (ML) strategies combined with MCDM have greatly expanded in order to address the issues of water resources, where these procedures are thought to be highly successful in solving issues related to water management (Trung 2022). These are frequently neglected by scientists who classify surface and subsurface water, and groundwater resources, and evaluate water quality (Keshavarz-Ghorabaee et al. 2021). As a result, this study suggests utilising an MCDM/ML method such as the Decision Tree (DT) algorithm. Several domains, including agriculture, water quality research, environmental disaster management, risk prioritisation, and human system reliability, have also made use of this kind of optimised machine learning approach (Zavadskas et al. 2012). This method was especially helpful for taking into account multiple linked random environmental variables at the same time. As a result, a new, smaller collection of uncorrelated variables that accounted for a significant amount of the variance in the original variables was identified. This approach is predicated on the same LBWA analysis, which is applied to assess the criterion's weight, and the DT technique will be utilised to determine the alternatives' preferred rankings and also evaluate which option is the best one (Adali and Tusisik 2016). The main goal seeks to assess environmental problems associated with water and to preserve and restore the health of aquatic resources in water systems. Moreover, by creating a linear equation, this method shows a link connecting two or more factors and a predictor variable in a model. As a result, it is essential to put into practise a workable and affordable strategy for trustworthy water quality assessment (Goswami and Mitra 2020). On the other hand, Geographical Information System (GIS) is employed to analyse and present spatial data, making resource planning and environmental protection easier (Kadam et al. 2021). Inverse distance weighting (IDW) and Kriging and Co-Kriging are the most used techniques for spatial interpolation. It is a precise technique that ensures that interpolated points closer to a variable, that itself possess a bigger impact on its evaluated value, than those ones, which are farther away from the interpolated region (Zhang et al. 2021). The weights are given different characteristics at every place, depending on distance and were computed by accounting for the closest designated locations. Further, the GIS may be used to manage natural resources at both the temporal and spatial scales. Many authors examined the role that GIS played in the analysis of surface water distribution in space. Gupta (2022) integrated MCDM and GIS techniques to provide decision-makers with information on drinking water system appropriateness assessments, by creating weights for the various layers that the GIS system has provided. The principal concept in this investigation is the process of utilising LBWA to determine weight coefficients depending on field data (Akhtar et al. 2021). Thus, these associations can help generate hypotheses for the interpretation of various hydro-chemical processes occurring in a given area, but they do not always prove cause-and-effect relationships. Rather, they present the information in a concise format as the first step in a thorough analysis of the data. Hence, smoothing out distortions generated by inherent data transformations in each approach is possible by the integration of different methods with varied logic for making quantitative evaluations (Deveci et al. 2021). So, WQI, weighted technique, namely LBWA and DT methods are a few of the state-of-the-art methods that scientists have determined necessary to give a comprehensive picture of surface water quality, which is required for effectively managing and safeguarding these essential resources. In view of this, the purpose of this work is to investigate whether surface water is suitable and its focuses on creating a novel hybrid framework by integrating firstly with WQI, to find the latent components that account for the database's structure, secondly, implementing the LBWA technique to examine the impact of potential pollution sources, both man-made and natural, on the criteria pertaining to water quality, and, thirdly, the Decision Tree (DT)-based approach, that comprises a powerful computer instrument for estimating, is applied to acquire a better comprehension of the causes and temporal fluctuations of water contamination in the rural–urban reach of Odisha' major river, i.e., Mahanadi Basin, during the summer period, by taking monthly mean of data from 2015 till 2023, so as to facilitate emerging issues. It is thought that the allocation's outcomes could be quite beneficial, to make room for its local government to have authority over its future pollution control and improved preservation of vital riverine water quality. Hence, the interrelationship of different ions and their surface water chemistry was understood through the application of these different approaches. Therefore, it serves as an additional instrument to identify regions in the research area where the water's quality is getting worse, and, also, it evaluates the potential sources of contamination.

3.2 Study Area

The Mahanadi River is a valuable natural resource that gives the majority of Odisha people access to drinking water, hydropower, food, jobs, transportation, and tourism. Also, more than 80% of the fish produced in Odisha comes from this significant interstate river, which flows eastward in Peninsular India. It is also a major source of inland freshwater fish. The river begins at Pharsiya village in the Dhamtari district of Chhattisgarh, at a height of 442 m above mean sea level (MSL). This catchment is situated between 19°21′N and 23°35′N latitude and longitude comprised of a range, i.e., 80°30′E–86°50′E. Before it meets the Bay of Bengal, it passes through the plains of Chhattisgarh and Odisha and then gets smaller yet, forming a sizable deltaic area in Puri and Cuttack, Odisha. The river's whole length is spotted as 851 km. From this, about 357 km belong to Chhattisgarh State and the rest, i.e., 494 km lie in Odisha. It is observed that the average yearly temperature in the tropical monsoon environment ranges from 15.8 to 28.7 °C that predominate within the river basin. The drainage basin's average elevation is exhibited at 426 m, with a 193 m at minimum and about 877 m is found as the highest value (Das 2022). To aid research on marine biology and hydrology, the catchment area was separated into the following three subbasins: Upper region resolves around 21.34%, Middle encompasses about 37.16%, and, finally, 41.5% covered under Lower Mahanadi region. This river also provides a significant amount of water for an irrigated area that is about 13590 Km^2 that prevails inside the study region. Agriculture represents the principal financial operations within the basin, and also the usage of agricultural land thereby represents major important factors as compared to the other type of land use (Mohanty and Samanta 2016). The agricultural regions with nearby stores about nearly 69655 Km^2 of the basin constitutes 49.39% of the basin's overall area, where 13% of the basin is farmed more than once annually. Mahanadi's flow from the upper watershed into the river's downstream portion is regulated by the Hirakud Dam. After splitting into multiple distributaries and channels, the Mahanadi River creates a delta downstream of the Naraj Barrage. The lithology of the basin includes granite suite of about 34% of the basin's total area; the Khandalite suite consists of around 7%. While Charnockite covers around 15%, limestone in aid with shale of lower Gondwana holds of approximately 17%. Also, sandstone, together with shale of upper Gondwana grouped under 22% and finally, 5% goes to coastal alluvium. Within the basin, there is a section of the subcontinent's richest mineral belt, which includes deposits of limestone, Pb, bauxite, Cu, dolomite, coal, and iron ore (Panda et al. 2013). This river is constantly filled with stagnant water from January to May each year, which contributes to the buildup of pollutants in the surrounding area. Ultimately, during the rainy season, the contaminated water is released into the Bay of Bengal (Panda et al. 2006). For example, it is considered the biggest river in the State of Odisha and provides domestic water to numerous cities, including Sambalpur that contains population, equal to 0.2 million, Cuttack population stores around 0.5 million and the city is equivalent nearly 1000 years, and, finally, Paradeep maintains a significant port, a population of 0.15 million, as well as a large number of officially unreported rural and small urban villages (Das 2024). So, agriculture is the main land use activity, with the majority of farmers involved in both crop production and animal rearing. The specific details of the sample locations are provided in Fig. 3.1.

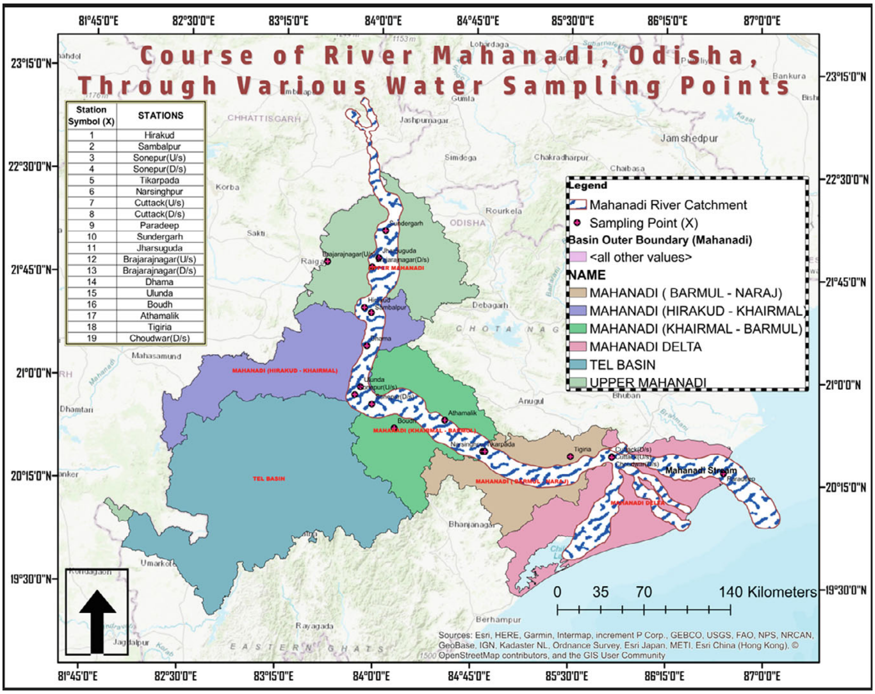


Fig. 3.1 Location of the study area with surface water sampling points

3.3 Sampling Methodology

Twenty water samples in total were taken from nineteen monitoring sites, during summer season: April–June, for the year 2015–2023. For this present study, all sites were selected, where human and industrial activities are conducted. The water from the first twenty to twenty-five strokes was carefully disposed of to reduce the impact of the iron pipes that the water was pumped through. Styrofoam boxes were used to hold the samples. The samples were taken at almost the same depth (15–20 m). The samples were likewise kept in an ice bucket for examination, with the temperature kept at or above 4 °C, brought to the lab and chilled to prevent contamination and the effects of light and temperature. Hence, the analysis was carried out in a lab while adhering to standards (APHA 2017). For a few factors, in situ observations were conducted, i.e., pH, electrical conductivity (EC), total dissolved solids (TDS), and alkalinity (A) Mini titrator were employed to gauge pH, EC, and alkalinity onsite. The Hanna standard is used to calibrate peristaltic pumps and measure total titratable alkalinity. Sulphate $\left(SO_4^{2-}\right)$ was assessed using the practicality of UV spectrophotometer. The DO concentration was determined using the Winkler iodometric titration method. The nitrate $\left(NO_3^-\right)$ is evaluated by spectrophotometer, while the hardness is executed by the ethyl diamine tetra acetic acid (EDTA) titration method.

Coliform is examined by the most probable number (MPN) test approach, chloride (Cl^-) by Mohr's method, and BOD by employing Winkler's method in the laboratory. Fluoride (F^-) is analysed using advanced research grade benchtop ion selective electrode (Hanna, HI5522). Boron (B^+) is quantified using ion chromatography. Different samples were gathered into 300 ml plain glass bottles for dissolved oxygen (DO) determinations, and the Azide adaptation of Winkler's method was used to fix DO. The remaining parameters were established, utilising the methods developed in the lab by the standard protocol suggested by American Public Health Association (APHA) (2017). The units of the parameters were addressed in milligrams per litre (mg/l) except pH (non-dimensional) and EC (μS/cm at 25 °C). Analytical grade chemicals (purity > 97%, from Sigma Aldrich) were employed for all analytical processes, to persist the quality control and assurance (QA/QC) standards. Further, every glass item was submerged in water for an hour in diluted nitric acid (a 1% nitric acid solution) and then given a distilled water rinse. For every sampling location, duplicate samples were gathered and examined in order to eliminate the analytical accuracy. The water samples were examined further with the use of calibrated apparatus and reasonable uncertainty. The ionic-balance error (X) was calculated, examining the connection between the total cations (B^+ and Fe^{2+}) and the total anions $\left(Cl^-,\ SO_4^{2-},\ NO_3^-\ \text{and}\ F^-\right)$ for each set of comprehensive water sample analyses, using $X = \left[\left(\sum \text{cations} - \sum \text{anions}\right)/\left(\sum \text{cations} + \sum \text{anions}\right)\right] * 100$ for their accuracy to interpret chemical data, where the cations and anions are expressed in milligram per litre (mg/L). Only specimens that fit within 5% were documented in this paper. In addition, the relative standard deviation (RSD) values were likewise inferior to 5%, as discovered through the dataset. Also, the spatial analyst programme extension makes use of interpolation to inverse distance weighted algorithm (IDW), as a useful instrument for creating maps of the spatial distribution of the physico-chemical characteristics of the surface water in this area. For this, survey of India topographic sheets were used to create the research area base map, which was then digitalised using the ArcGIS 10.3 program.

3.4 Methodology

The water quality index is by far the most efficient technique for analysing and tracking the general quality of drinking water; however there are other approaches as well. Considering the contrasts between the WHO guidelines, the quality of surface water was assessed for appropriateness. By using a modified multi-metric model on surface waters, it may be possible to assess the systems' chemical health. For calculations of relative weights, a Level Based Weight Assessment (LBWA/L) WQI approach has been adopted. This method is a development, based on the current entropy method, meant for analysis of single decisions. Weightage-related information quantifies the dataset's unpredictability or uncertainty (Shannon, 1948). Numerous scientific and technical fields, such as biology, genetics, chemistry, physics, quantum mechanics, statistical mechanics, reservoir engineering, and transportation engineering, have effectively used these. Apart from the novel algorithm offering a multi-criteria analysis with multiple decision-making (DM), through the correlation of the weights of the negative and null criterion, a process of matrix standardisation was incorporated, improving the consistency of the model (Žižović and Pamucar 2019). This idea involves quantifying the degree of disorderliness and randomness in the data. The deviation brought on by human factors can be minimised, and the index weight is determined based on the degree of fluctuation of each index value (Mishra and Rani 2021). This method comprises three procedures: in the preliminary stage, it is necessary to do the transformation of ordinal preference between criteria, which is represented by a vector that carries the weights of the criterion. Next, within a specified set of criteria, the ordinal transformation of the preference between options is made and expressed by a matrix (Das 2023a, b, c, d, e, f). The individual preference information of each decision-maker is indicated by a series of pairwise comparisons of variables, whether criteria or alternatives within a particular criterion. By evaluating the equality, diversity, flexibility, complexity, interaction, and redundancy of the random datasets, this aids in the extraction of a sufficient amount of information. Thus, it is a productive method of presenting probability and uncertainty. The weight of the indicators should be bigger if the examined parameters indicate a significant difference from one another on a particular indicator. Conversely, if the difference between the evaluated parameters is lower, the weighted score will be larger. Therefore, it can be viewed as an object-emancipating technique that subverts the conventional models, namely Delphi and AHP. They typically take a lot of time, are repetitive, and rely on expert and subjective judgments, which causes important information to be lost. It also takes into account the fluctuations in water quality metrics. It is computed using the subsequent formulas, as addressed by Wu et al. (2011) and Marghade (2020). Then the ultimate index is contrasted with a normal table that has numbers between 0 and 100, having received a score of excellent (<50), good (50–100), average (100–150), poor (150–200), and >200 signifying extremely poor. There are six steps in this water quality procedure, and the stages are described in detail as follows in Fig. 3.2.

An important mechanism, namely Decision Tree (DT), was incorporated (Valera et al. 2020) in the current work, that illustrates basically as a multi-criteria decision-making method along with a machine learning approach, was initially proposed by Li et al. (2020). Given the ambiguity, a weighted normalised matrix is calculated that relied on LBWA weights and its user-defined criteria (Huang 2022). However, it is important to note that by evaluating each parameter's weight independently, the process of constructing WQI for water quality evaluation may be made simpler, which addresses both its advantages and disadvantages (Ehsan et al. 2022; Nong et al. 2020). Since the beginning, this approach is becoming more and more popular for handling a variety of difficult decision-making issues, such as managing resources and evaluating security and water resource quality (Torkayesh et al. 2021). These models could produce trustworthy survey site rating outcomes once the obtained data has been normalised (Valkova et al. 2021). The benefit of normalising each qualitative element in this method is that it allows one to observe the impact of each

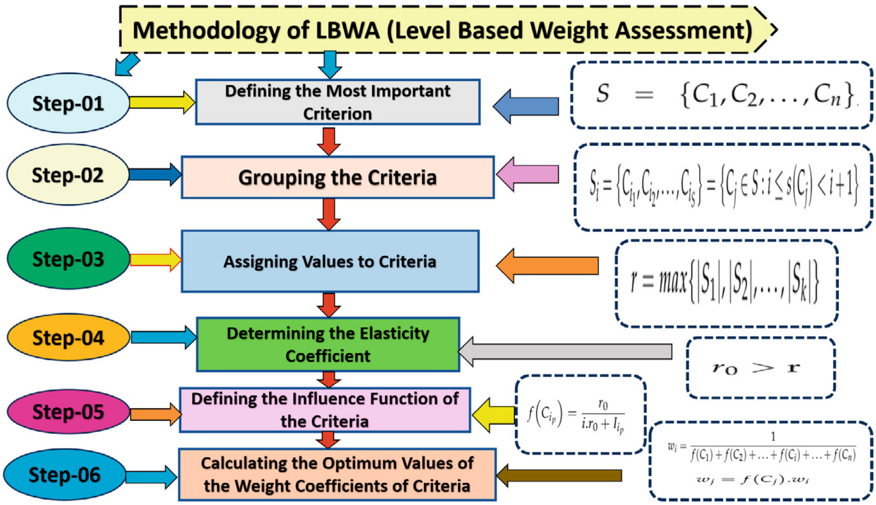


Fig. 3.2 Stages of LBWA model in determining the weights for 20 chosen indicators

individual parameter in addition to the overall influence on location ratings (He et al. 2022). The suggested computational procedures include identifying and ordering the choice criteria, figuring out each criterion's relative importance, estimating its coefficient, determining the revised weight, and, lastly, calculating the relative weight as addressed by Li et al. (2020). Figure 3.3 displays the sources and the various parameter-choosing steps. As demonstrated by the previously cited references, either the LBWA or DT algorithm, it was effectively used to interpret extensive and intricate water quality data. However, the two approaches together have not been used before. It is anticipated that combining these two techniques will offer a simple means of characterising extremely complex water quality data while mitigating the drawbacks of each technique, i.e., LBWA is a method of weighing that can handle the passive nature of environmental data, while, to describe each group, more interpretation is needed. In the later part, DT is useful for ranking purposes, but it also aids in understanding the non-linear relationship between the variables via visualisation. Hence, by adopting together, these strategies help to improve urban surface water management policies and provide a practical and effective network for surface water quality monitoring.

3.5 Results and Discussions

Twenty water samples and 19 sites were selected and analysed to ascertain the hydrochemical characteristics of water and assess the quality of surface water for irrigation and drinking. In our experiment, the pH value ranged from 7.738 to 7.915 that shows that the experimental sites' water was in perfect drinking condition, given that the

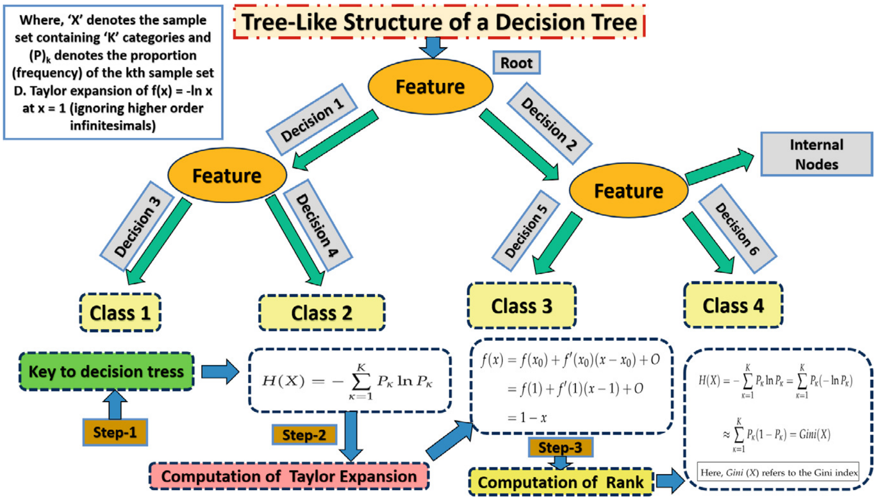


Fig. 3.3 Flowchart of a decision tree model, incorporated in the study area

values fall within the acceptable range of 6.5–8.5. Considering the pH value range, in the research area, surface water is classified as somewhat alkaline. Further, DO is essential to aquatic life's development, reproduction, and survival; its lack is a sign of sewage pollution. Therefore, it is essential to the water ecology. The estimated values (7.258–7.828) were more than the standard limit of DO of 6.0 mg/l. The results show that the condition of DO is significantly greater than the standard condition and is at a satisfactory level. The following findings show that during the study time phase, aquatic plants did not produce higher DO in river water by mixing industrial wastewater. Afterwards, BOD is a very essential water quality parameter that is required to assess the pollution of surface and ground water where contamination occurred due to the disposal of domestic and industrial effluents (Eid et al. 2023; Das 2023a, b, c, d, e, f). The aquatic ecosystem experiences an increase in BOD due to the burning of oxygen by numerous chemical reactions, microbial respiration, aquatic animals, and the breakdown of organic pollutants. Also, poor water quality is indicated by the increased BOD level. It is evident from the results that the readings (1.06–2.38) were well under the standard limit of 5 mg/l. The results show that there has been little to no mixing of organic compounds, which has contributed to the reduction of BOD in this river water. The presence of coliform (TC) bacteria guarantees faecal contamination in the water body, indicating a higher danger to health and unfitness for human consumption (Subba Rao et al. 2020). The values in the present study lie between 1211.5 and 42530. At Sites (X-8, 9 & 19), its presence is getting accompanied by a lot of homes, which suggests that a lot of non-point sources, such as washing, bathing, and animal husbandry, could be the likely cause of high coliform levels there (>5000 MPN/100 ml). Due to elevated TSS, the DO level drops and the water's clarity decreases as a result of less light penetration and delayed photosynthesis (Khadr et al. 2021). However, the value (28.64–74.98) was well below the threshold of 200 mg/l as per WHO (2017), which indicates it is for drinking and agricultural purposes. Alkalinity is the buffering capacity of water to neutralise acids which maintains a stable pH. The desirable limit of alkalinity in potable water is 200 mg/l, above which the taste of water becomes unpleasant. All values (70.38–101) come within the limitations that have been established by WHO (2017). However, each site possess a value that fits under the permissible limit of 200 mg/l. COD is a sign of organic pollution coming from sources such as partly or untreated urban residential and industrial wastewater. Because of high COD, it may be attributed to the production of organic acids as a result of the pH falling and anaerobic conditions developing from a high concentration of dissolved organic materials. The existing values (6.80–21.86) in the study area were below the WHO recommendation of 30 mg/l, and the concentration in the river was at a level not posing a health concern. Residents' open-land trash disposal, sewage disposal, and use of chemical fertilisers were the main causes of NH_3–N contamination of surface water. This might be caused by the filthy habits of open defecation, runoff from surrounding areas, and contaminated water that seeps from the neighbourhood drains (Tiyasha et al. 2020). The obtained range in the current work is between 0.512 and 1.940. Every physico-chemical characteristic of the water that was examined was well within the allowable bounds of 2 mg/l in drinking water, as given by WHO. Hence, it is noted that surface water can get contaminated with free-NH_3, because of a number of factors, including the usage of nitrogen-dependent fertilisers like nitrogen, phosphorus, and potassium (NPK), inappropriate handling of human and animal waste, and unlined and drainage lines. The recommended limit for drinking water is 2.0 mg/l (WHO 2017). However, all the observations were within the prescribed limits for all sampling locations. TKN is one of the important parameters present in surface water. Leaching from farmland, solid waste disposal sites, or ammonia oxidation results in TKN contamination in surface water. In light of this, soil phosphate was introduced to the soil via fertiliser phosphate leaching, weathered rock organic matter breakdown, and other human activities. In the present study, it ranges from 3.285 to 11.796 mg/l, which is well above the acceptable limits of 5 mg/l. However, a high concentration at most of the locations showed signs of anthropogenic contamination, agricultural runoff, and the mingling of human and animal waste. High TKN could have a negative impact on health and be classified as a non-carcinogenic danger to people. It is evident from the readings that silicate weathering may, in the event of an extremely alkaline climate, have a secondary impact on the quality of surface water, as the alkaline circumstances may increase the solubility of silica in surface water samples. EC is directly correlated with the temperature and salinity of the water. High EC values indicate a high level of mineralisation in water as a result of human and geogenic activity (Islam Khan et al. 2022). As the EC and TDS values increase, the amount of mineral salt soluble in water increases. A very slight variation of EC was found as 137.60–7779.78 during the study period. It is recommended that the highest amount of EC that is safe for humans to eat does not surpass the 2250 μS/cm reading. At X-(9), an abundance of cations and anions in the surface water is indicated by a higher EC value. The higher the EC, greater is the enrichment of salts. SAR is one of the characteristics that must typically be examined in order to determine whether surface water is suitable for use in agricultural irrigation. When surface water with a high sodium content is applied for irrigation, it may enhance the soil's exchange of sodium, which may reduce the soil's permeability and structure. This is also an important agent to assess the appropriateness of the water quality since a higher content encourages the exchange of Mg^{2+} and Ca^{2+} ions, which reduces the soil permeability and thereby damages the drainage system (Jiang et al. 2020). The limit set for drinking water is 10 mg/l as per WHO (2017). The recorded values ranged from 0.401 to 16.49. Excess concentration at X-9 (>10 mg/l) in water is frequently not suitable for drinking and irrigation, which degrades the soil's qualities and changes their structure, making the soil alkaline. It has been seen that increased ingestion amounts result in hypertension, i.e., high blood pressure. A specific quantity of B^+ is crucial for preserving good health, whereas if the maximum allowable amounts are surpassed, there are negative health hazards, like vomiting and hypertension. Therefore, it is the most important component of the nutrition. The results revealed that the values fell within the band of 0.031–0.561 mg/l. It is observed that concentration in all the water samples is below the permitted threshold of 2.0 mg/l. The TDS in surface water comprises all of the existing solid materials, whether or not they are ionised. Numerous inorganic solutes, mostly ions, trace element solutes, and dissolved gases, are found in water. Its primary constituents are inorganic salts; only a small amount of organic compounds, such as Na^+, Mg^{2+}, Ca^{2+}, K^+, SO_4^{2-}, Cl^-, and HCO_3^-, dissolve in water. A high TDS value may result in serious health concerns such as kidney stones, heart disease, and gastrointestinal troubles. In the investigation, the recorded values ranged from 82.28 to 13229, indicating well within the limits (100 mg/l) except at X-9. Higher value noticed in water can alter the taste and hardness of water. Hence, it indicates that water is highly mineralised at location X-9. Moreover, increased TDS values rise with altitude variation, which is explained by increased evapotranspiration in low-altitude regions and perhaps by surface water dissolving mineral components as it passes through geologic surfaces. When evaluating surface water's appropriateness for residential and commercial uses, hardness (TH) is a vital requirement, since it contributes to the hardness of the water; yet, it increases the need for detergents during cleaning and there is some evidence linking it to heart disease (Xu et al. 2020). It is a result of Ca^{2+} and Mg^{2+} ions in the river and possesses a score that fluctuates between 51.18 and 2195.12. The values in the current investigation were less than the allowable threshold of 250 mg/l except at site, i.e., X-(9). According to the TH, the surface water samples are categorised as soft/moderately soft as established by $CaCO_3$ guidelines, across all 18 locations. Greater values seen at X-(9) arise due to pollution from untreated effluents as well as unplanned development of a few industries and local housing in those locations (Jamei et al. 2022). Another dominant anion acknowledged for having a conservative inclination when evaluating chemicals is termed as Cl^-. In contrast to other primary ions, this is a very good indicator of surface water age. In WHO standards, a Cl^- content of above 250 mg/L in drinking water is suitable. The Cl^- content of each surface water sample collected from the research region was found to be a minimum of 9.64 and a maximum of 4904.92 mg/L, respectively. The reported reading substantially within the allowed range of Cl^- is around 250 mg/l, based on WHO (2017), except for one site, i.e., X-9.

However, sewage discharge and runoff from inorganic fertilisers from agricultural areas are its primary sources of contribution. It is necessary to evaluate the SO_4^{2-} level in surface water found in nature before it is suitable for human consumption. This indicator may get into water streams as a result of surface runoff from contaminated areas and sewage discharge. The maximum allowable concentration of sulphate in drinking water is 200 mg/L, according to WHO. The value of sulphate was considered to be in the range of 4.965–375.98 mg/l in the present study. In all surface water samples, X-(9) possessed the maximum sulphate content, while X-(13) holds a value of 26.43 mg/L. This investigation showed that all 18 samples fell within the WHO-recommended ranges for potable water. A rise in the concentration of sulphate at X-9 (>200 mg/l) may be connected to runoff from agricultural, given the research area's high level of activity induced by agriculture. Leachate from closed mines, air deposition from burning fossil fuels, and industrial wastewater could be additional sources. F^- mostly discovered in water is due to geological process. Because of their salinity and fluoride contents, 30% of Odisha's surface and ground water sources are deemed fit for human consumption. These ions have both positive and negative effects on human health. It is essential for human health, as consuming water that contains less than 0.6 mg/L of fluoride encourages dental caries. When fluoride levels are higher than 1.5 mg/L, children's teeth become discoloured. Furthermore, teeth exhibit severe mottling and defamation at concentrations of F^- greater than 6 mg/L. It has also been shown that the high fluoride level of surface water may contribute to fluorosis of the teeth and bones. In this study, the value was found to be between 0.256 and 1.0 mg/l. At all sites, the concentration were acceptable, and following disinfection, the water may be used for drinking. NO_3^- reflects the contributions of hydrological elements, household, agricultural, and industrial wastewater. It is observed that agricultural cultivation and industrial production are two important regional activities that also drew migration; hence, they can be identified as two potential sources of pollution in the region (Ghoderao et al. 2022). High nitrate levels in surface water are usually caused by excessive use of agricultural fertilisers, waste from animals and humans, and plant debris. The results revealed that nitrate value was between 1.279 and 2.689 mg/l. The highest amount of nitrate that can be present in drinking water is 45 mg/L. All the water samples within the research domain found that the nitrate amounts fell within a reasonable limit. The Fe^{2+} presence in this study is suggestive of industrial effluents, which originate from the pigment and corrosion inhibitors produced, both of which may be hazardous to aquatic life. The effect of Fe^{2+} on human health depends on its oxidation state. It is an essential nutrient for the human body but too much uptake can cause liver, DNA, and kidney problems. High value of Fe^{2+} may be of excessive industrial discharge from industries like iron, steel, fertilisers, pesticides, heavy vehicles as well as discharge of domestic sewage coupled with natural geogenic processes. In sampling stations of the study area, concentrations (0.59–2.612) are within the threshold of drinking water limits (3 mg/l). In this river water, the predominant cation trend was in the order of $Fe^{2+} > B^+$ with iron being the dominant cation and the predominant anion trend in the order of $Cl^- > SO_4^{2-} > NO_3^- > F^-$ with Cl^- being the dominant anion. An appropriate diagram for every parameter was created using a spatial analysis technique to provide a clear visual representation of the areas classified under various water quality indicators as represented in Fig. 3.4a–t. From the maps, it is visualised that the sites at the upstream area provide better drinking water than those at the downstream side.

Comprehensive water quality degradation is necessary to determine whether the water is suitable for drinking, agriculture, industry, residential, municipal, and public recreation. For further analysis, L-WQI has been employed to evaluate the water's suitability for drinking. There are three components to water quality: chemical, biological, and physical. In this study, the main cations and anions were examined to assess the water quality. This encompasses all physical characteristics as well as the overall ranking of the sampling sites provided by the DT methodology. Hence, it functions as an improvement over conventional WQIs, which assign weights to factors based on expert opinion and subjective judgement (Zhou et al. 2020). Water utilisation has a close relationship with water quality. The maximum weight was determined and made available to TC, TKN, EC, TDS, and Cl^-, which pose a serious risk to human health and according to their occurrence over a specific critical concentration that might restrict the surface water's suitability for drinking. The values are given for each sample in Table 3.1. Their L-WQI values varied in the range 23–412 in the ongoing work. These measurements showed that the quality of the water was excellent to extremely poor. About a portion of 36.84% of sites fell inside the zone of the excellent category, suggesting that drinking water is available from the surface water. Remaining 31.58, 15.79 and 5.26% of the testing places, grouped under poor/very poor/unsuitable poor category and thus are not advised to be consumed by local residents, residing along the study region. Further, the greatest value was assessed at X-(9), which had elevated levels of Cl^-, EC, TH, SAR, TDS, TKN SO_4^{2-}, and TC, compared to the typical time period. The fresh information about the leaching and runoff from roadways, agricultural lands, and roadside dumps is provided by the location that follows, i.e., consequently, the river was contaminated by a variety of substances due to coal mining operations and the hazardous chemical waste from sponge iron factories. SO_4^{2-} illustrates how human activity has a detrimental effect on the quality of surface water. The river's water quality is substantially contaminated due to the regular release of highly polluted waste solid and liquid effluents from thermal power plants, chemical companies, and the iron and steel industries. These releases raise the river's TDS and TKN values. EC shows that the processes of rock–water contact have a greater contribution than the evaporation of percolating water. Elevated concentration of TH, then came both Ca^{2+} and Mg^{2+}, may have been the consequence of silicate and carbonate mineral breakdown. The research area is made up of Kankars (calcium-rich encrustations) and alluvium which contribute to these ions in water and are abundant in feldspar. The Ca^{2+} present in the water could have come from minerals dissolving in rainwater or irrigation water during percolation. Also, Na^+ ion in SAR can be added to surface water by adding NaCl or dissolving sodic-rich minerals like plagioclase feldspars, or they can enter through rainwater seeping through. Saline soils are created by high salt content and are the main reason for crop loss. The danger of salinity further lowers plants' osmotic activity, which

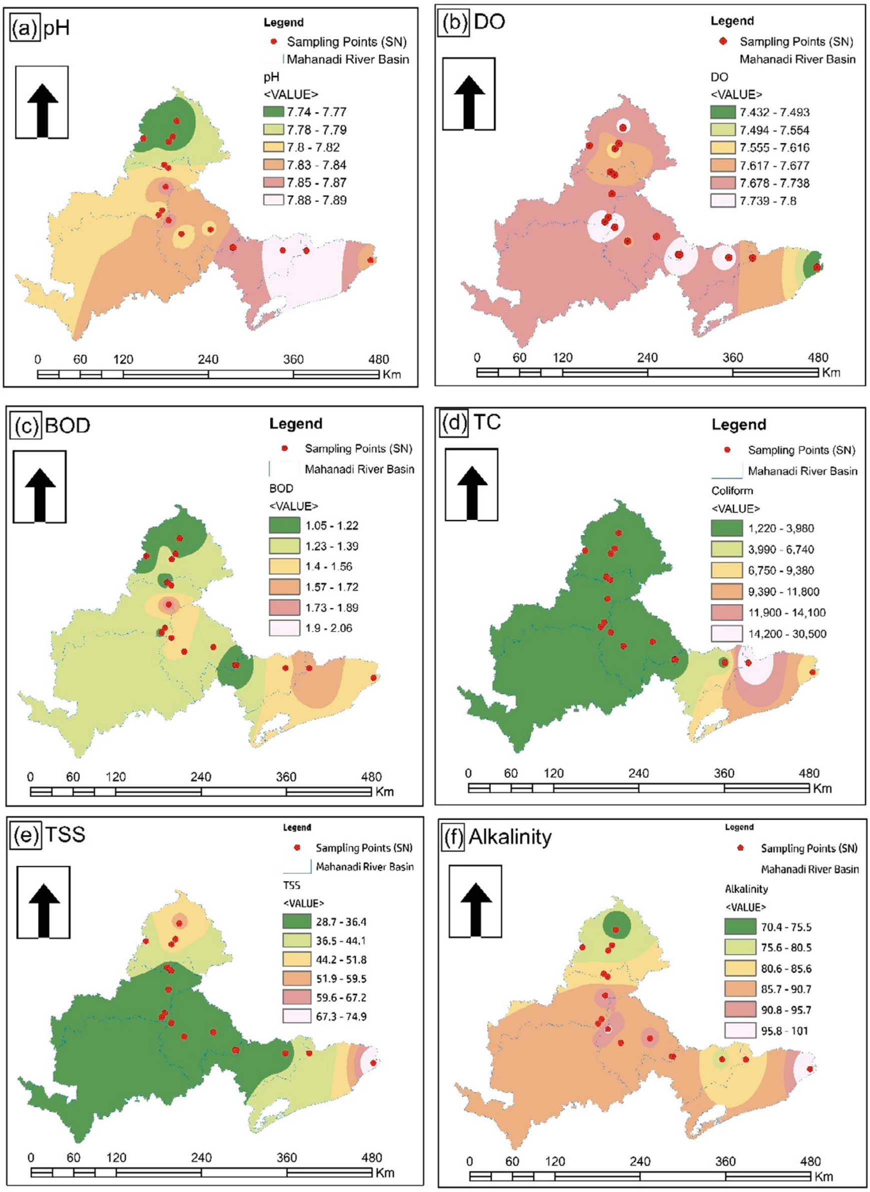


Fig. 3.4 A water quality parameter's spatial map of **a** pH, **b** DO, **c** BOD, **d** TC, **e** TSS, **f** TA, **g** COD, **h** NH_3–N, **i** free NH_3, **j** TKN, **k** EC, **l** SAR, **m** B, **n** TDS, **o** TH, **p** Cl^-, **q** SO_4^{2-}, **r** F^-, **s** NO_3^- and **t** Fe^{2+}

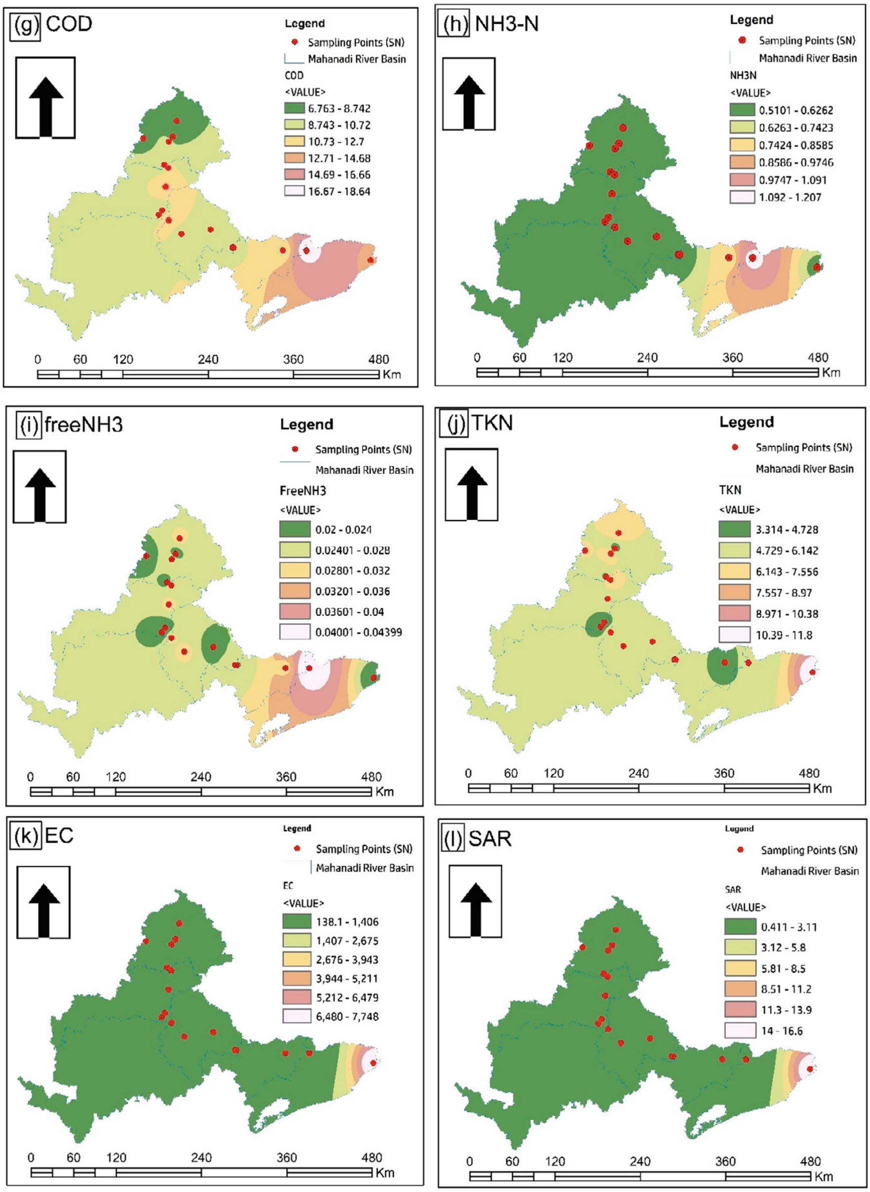
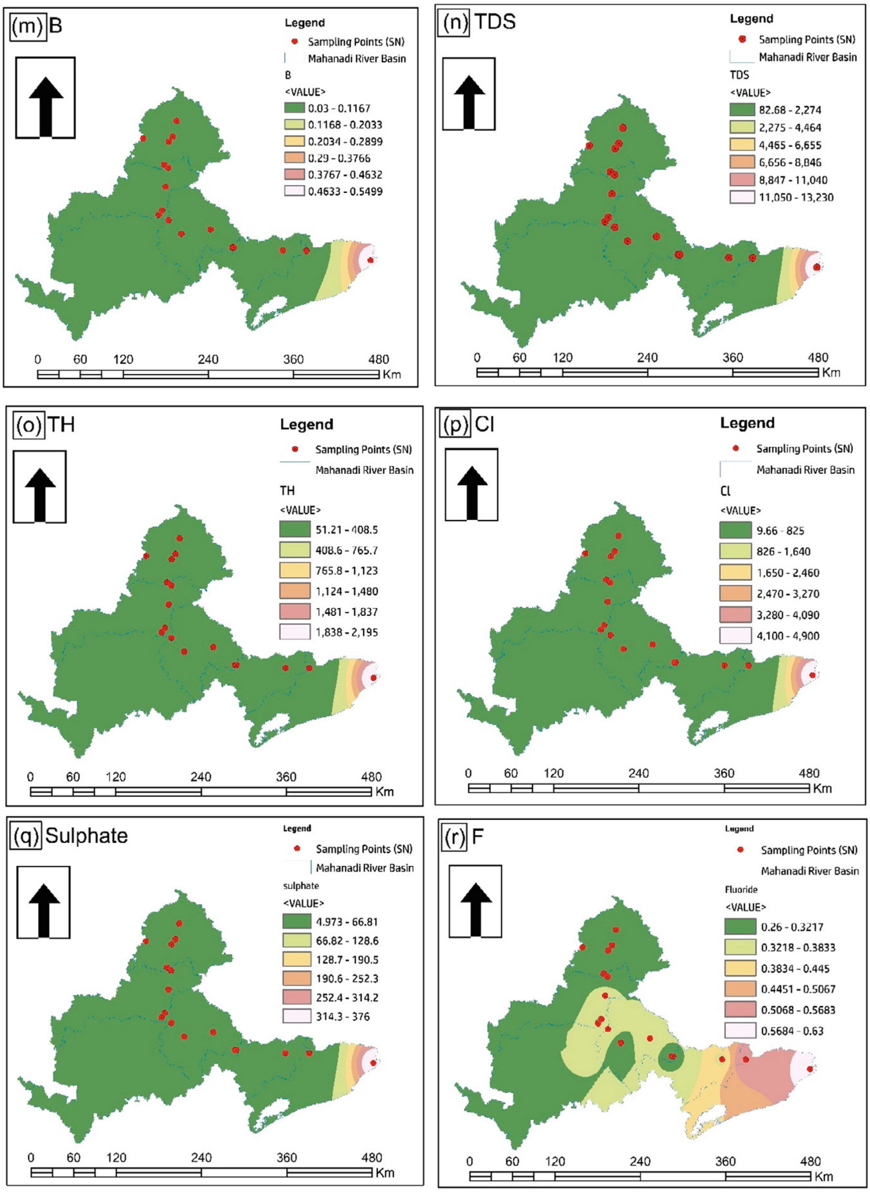


Fig. 3.4 (continued)



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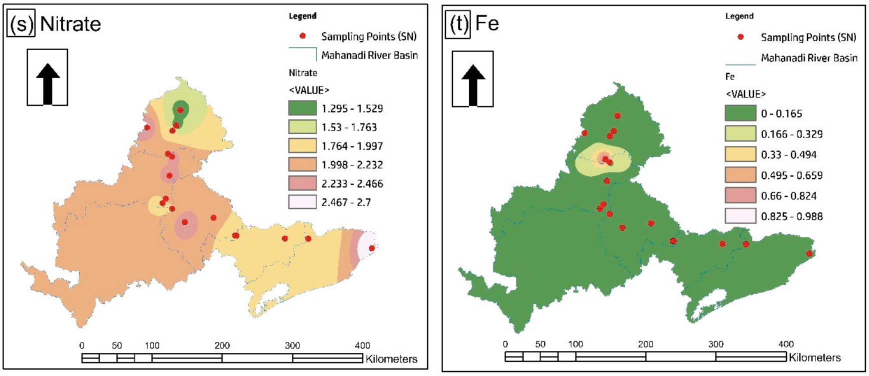

Fig. 3.4 (continued)

hinders water and nutrient adsorption from the soil. Because of the diluting effect and deeper water, on the U/S side of the river, the water quality was superior. Hence, out of 19 sites, 10 sites (52.63%) recorded poor/unsuitable WQ values and this may be due to various natural phenomena and anthropogenic activities. The very poor water quality at X-(2), (8), (9), (10), (11), (12), and (13) is caused by the position of the barrage and the significant volume of industrial effluents that are dumped into the main stream through the tributaries that link to the lower portion of the stream. Remaining nine sites display good quality water because the riverbank's cement mill and mining operations have been closed, which has improved the water's purity (Das 2023a, b, c, d, e, f). The L-WQI displayed significant anthropogenic activity in the populous zone and modest biogenic input, with values fluctuating around >50%, indicating a sign of extreme pollution. So, the industrial activity developed in this zone would be indicated by this index score. Each water quality parameter's concentration could be viewed in the form of spatial maps by employing ArcGIS 10.8 and thus, explained in Fig. 3.5.

To deal with ambiguities in systems for water quality, the use of DT is necessary for gathering extensive spatial and temporal data. However, DT method gives them their total ranks, which makes the relative pollution level easy to identify. Therefore, such ranking is useful in supporting decision-makers with both technical and non-technical backgrounds in making well-informed decisions. This technique provides insightful information on the water quality system, boosting the applicability of mitigation and adaptation measures to changing climate circumstances and supplementing observational data for streamflow modelling (Das 2023a, b, c, d, e, f). In this study (Fig. 3.6a), all 20 parameters were taken into consideration when selecting the optimal locations along the river stretch, where the criteria for drinking water quality were compared and validated. The performance score and DT ranks of the sampling sites are displayed in Table 3.1. Additionally, the DT ranks' spatial variability is displayed in Fig. 3.7. While studying the ongoing work in Fig. 3.6b, the sampling location X-9 ($H(x) = 0.95$) was believed to be the most infected place.

Table 3.1 Summary of LBWA-WQI and decision tree (DT) performance values and their final ranking at all sampling locations

Station symbol (X)	LBWA/L-WQI value	Interpretation of water	DT scores ($H(x)$)	Ranking by DT algorithm
1	41	Excellent	0.025316763	16
2	189	Very poor	0.0314	4
3	46	Good	0.025324999	15
4	89	Good	0.030916264	7
5	85	Poor	0.028862878	11
6	106	Poor	0.028995632	10
7	176	Very poor	0.028154884	12
8	267	Unsuitable	0.073639815	2
9	412	Unsuitable	0.959170482	1
10	165	Very poor	0.024809966	17
11	184	Very poor	0.024331042	19
12	169	Very poor	0.024559488	18
13	263	Very poor	0.026993471	13
14	32	Excellent	0.030458399	8
15	41	Excellent	0.026987596	14
16	23	Excellent	0.031372466	5
17	44	Excellent	0.03039229	9
18	39	Excellent	0.031004894	6
19	288	Unsuitable	0.046246425	3

The riverbed could be the cause that tends to progressively collect nutrients from many non-point sources (industrial and contemporary agriculture systems), and the massive amounts of nutrients require more oxygen to break down. Yet in most of the sites towards upstream, due to the closure of the majority of companies, the river stretch's eutrophic zone has transitioned into an oligotrophic and mesotrophic stage (Gao et al. 2021). This is a typical stage for aquatic life, bringing excellent water quality or river health to aquatic plants and animals (Das 2023a, b, c, d, e, f). While in comparison with other locations, the sites, namely X-8 ($H(x) = 0.073$), X-19 ($H(x) = 0.046$), and X-2 ($H(x) = 0.0314$) also tend to be of poor water quality. This follows about abundance of TDS, TH, Cl^-, TKN, and SO_4^{2-} in the river water which is the main factor causing the decline in water quality, which has an impact on both human health and the ecosystem's ability to function in rivers. Presence of TKN and Cl^- suggests that the weathering and disintegration of minerals is how these elements are obtained naturally. Also, the TDS parameter suggeststhat the weathering and dissolving of minerals is the natural source of these elements. SO_4^{2-} suggests both a natural and maybe human origins. Hence, during the study period, these parameters are determined to be higher than the allowable limit. The previous twenty years have seen a decline in the river's water quality due to industrial effluents from

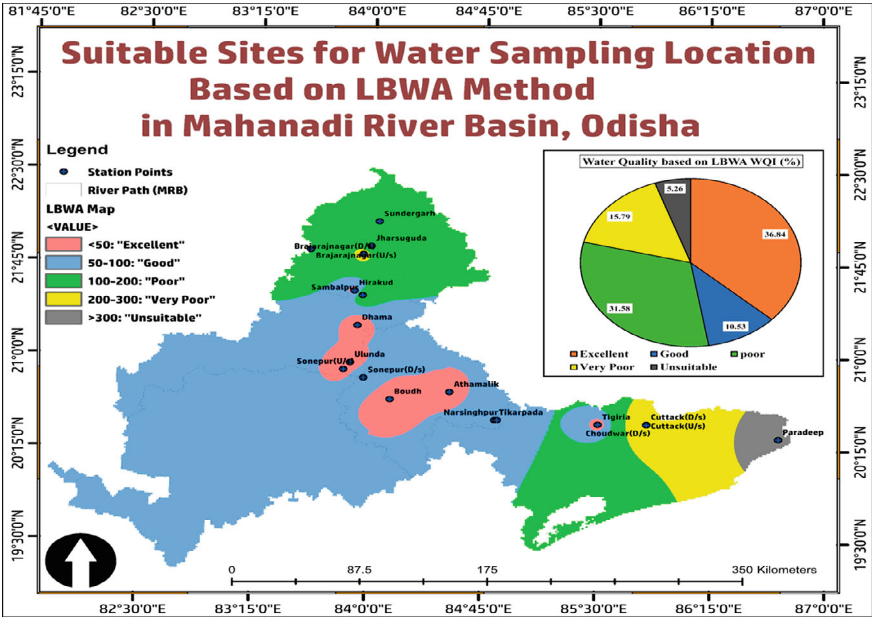

Fig. 3.5 Spatial distribution map of LBWA/L-WQI of all locations

neighbouring coal mining operations, thermal power plants, cement factories, and chemical companies. So, the employed methodology provides a trustworthy analysis using different parameter weights and is based on level-based weights and rough set theory. It is observed from the study's findings that resembles how extremely susceptible these stations are to activity caused by humans (Oladipo et al. 2021). Following this, the effects of human activity on water quality outweighed the effects of natural phenomena (Kabiri et al. 2021b; Das 2023a, b, c, d, e, f). Also, the river runs through the city's outskirts, and significantly high TC and TKN readings were found at every location, pointing to the careless use of fertilisers and agrochemicals in rural areas as well as the incorrect disposal of household garbage. Ultimately, these findings can provide insightful information for managing water resources and making well-informed decisions, helping stakeholders and policy makers deal with water-related issues and guarantee the sustainable use of water resources in the river basin and other hydrological contexts across the globe.

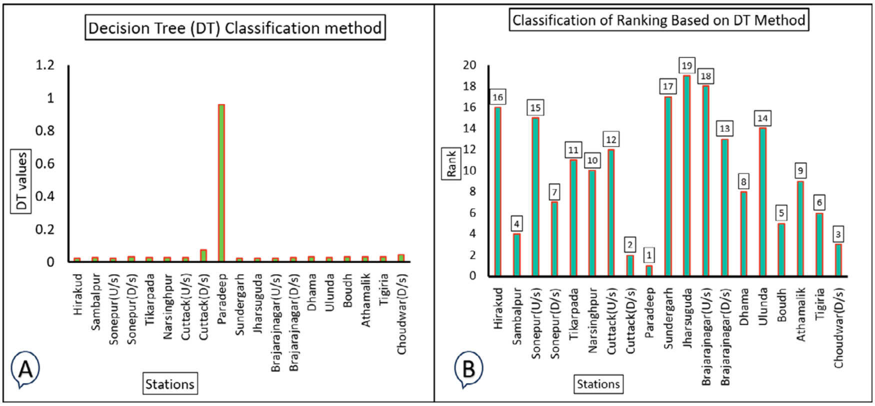

Fig. 3.6 Classification of surface water samples of the study area based on DT approach

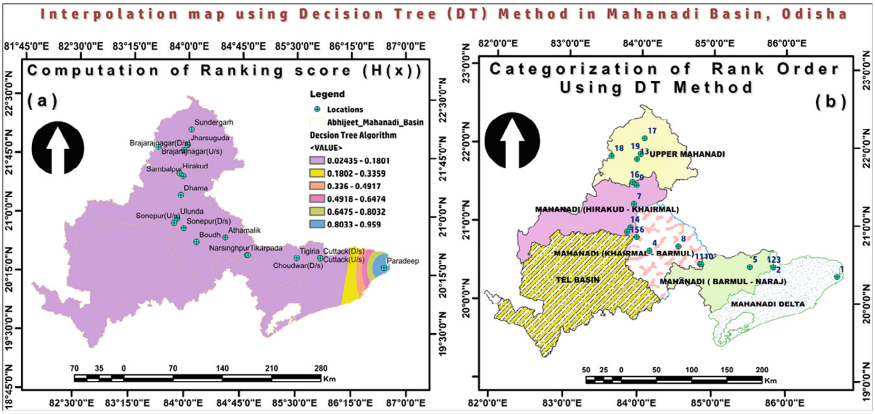

Fig. 3.7 Spatial distribution map of DT methodology adopted for all locations

3.6 Conclusions

The results are summed up as follows

The present study successfully developed a refined predictive model for surface water potentiality in the watershed, and investigated surface water quality using Level Based Weight Assessment Water Quality Index (L-WQI) and the MCDM method, in association with Machine Learning (ML) model, namely Decision Tree (DT) analysis, aimed at optimizing site selection and promoting sustainable water resource management. From this study, the regions with surface water quality issue were identified using the integrated approach. pH of all the samples shows a mild-alkaline condition in surface water. The values of TC and TKN are found to be above the acceptable limits, as given by WHO guidelines. This indicates one reason for the

WQI value to be impacted in the surface water. The advantage of this approach is that it combines data from numerous surface water quality parameters into a mathematical equation that depicts the water's ecological state. The classification of L-WQI suggests five categories namely: "excellent", "good", "poor", "very poor", and "unsuitable", which represents 36.84, 10.53, 31.58, 15.79, and 5.26% of the total samples. The spatial map of L-WQI illustrates that locations X-(2), (8), (9), (10), (11), (13), and (19) falls under poor/extremely poor zone, thus, unsuitable for drinking purpose. The cause might be due to large-scale farming and intensive industrial activities. These areas are also affected by domestic sewage discharge, garbage disposal, irrational use of pesticides, and landfill activities. Therefore, the approach shows the significance that each parameter has in the evaluation and control of the aulaity of water and can be used to define whether a source of surface water is fit for human use. Further, DT algorithm results match the water quality computation findings of the level-based weightage method, which additionally demonstrates the suitability and dependability of these two models. DT can offer ranks to increase the accuracy of the LBWA technique calculation. Simultaneously, the weight-based approach is employed to assess the water quality, and additional calculations and analysis are performed on the data. It is noticed from the DT results that the water quality at X-(9) is regarded as the most contaminated location since it is impacted by anthropogenic activities, and industrial, agricultural, and excessive surface water extraction in the research region. Based on the observed outcomes, this study behaves as an integrated approach to protect the surface water from deteriorating, and it promotes wholesome water resource management. It is strongly advised to put in place safe working procedures, such as sewage treatment facilities and safety precautions when drinking, watering, and working in the sector without harming the environment. The findings underscore the importance of integrating multi-criteria decision-making tools with geospatial technologies to effectively address water resource management challenges. This approach provides valuable insights for policy makers and stakeholders, guiding the development of effective water resource strategies tailored to the unique needs of arids environment. Thus, the present study limits to the thoughtful identification and integration of criteria that support the identification and integration of safe surface water site appropriateness with site reality. Therefore, this procedure can be modified to identify susceptible water locations where surface water depletion is a recurring concern. Artificial recharge techniques can then be used in these places, with minor adjustments made to account for site-specific requirements. From all of these, it demonstrates that this model works well and has a good impact when applied to quantify the quality of drinking environment at several sampling sites.

Acknowledgements The author is thankful to C.V. Raman Global University (CGU), Bhubaneswar, Odisha, India, for providing support and lab facility to conduct the present study. I would also acknowledge the support, in terms of logistics during data collection and chemical reagents for sample test, by State Pollution Control Board, Odisha, India. The author extends their sincere thanks and gratitude to the Ranu Prativa Research Group, Ruchika Square, Bhubaneswar, for its scientific and technical support in completing this research project.

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Chapter 4
Impact of a Major Water Pollutant, Endocrine Disrupting Chemicals (EDCs), on Aquatic Organisms with Special Emphasis in Fish Reproduction

Akash Acharyya, Sayan Mukherjee, Joydeep Das, and Kazi Nurul Hasan

Abstract Endocrine disrupting chemicals (EDCs) are naturally occurring or synthetic substances which affect living organisms by altering the natural pattern of hormone synthesis by the endocrine glands and various biological functions at environmentally relevant concentrations. EDCs are nowadays regarded as an ever-emerging major water pollutant which possesses a significant threat to aquatic life. At present, a lot of researches are going on about the impact of EDCs on human health but very few focused on the effects on physiological functions including reproduction of aquatic organisms especially in fish. Fish are affected on a large scale by increasing the degree of water contamination by EDCs from different sources like pharmaceuticals, personal care products, organic pollutants, and heavy metals. Chronic exposure to EDCs causes adverse affects on aquatic ecosystems even at their low concentrations in water bodies. The deleterious effects of EDCs on fish reproduction vary greatly depending on the "period and duration" of exposure. Various types of EDCs affect the growth and development of gonads, gametogenesis, and steroidogenesis in both male and female aquatic organisms. EDCs are categorized into xenoestrogens and xenoandrogens which cause endocrine dysfunction related to changes in fertility and the sex ratio of fish. It acts by mimicking or antagonizing the endogenously synthesized hormones. It results into feminization and musculinization of male and female fish respectively which impose a greater threat for fish culture and reduce the yield of fishery industry. In the present chapter, we tried to provide a link between endocrine disruption by a water pollutant, EDCs, and the impairment of fish reproduction on the basis of recent works which will help future research on aquaculture.

Keywords EDCs · Water pollution · Fish · Reproduction · Hormone · Gametogenesis

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S. Dey and M. P. Shah (eds.), *Biotechnological Removal of Emerging Pollutants from Wastewater Systems*, Advances in Wastewater Research,
https://doi.org/10.1007/978-981-96-3945-8_4

4.1 Introduction

Endocrine disrupting chemicals (EDCs) are a group of naturally or artificially produced compounds that potentially incite or suppress hormone synthesis and metabolism by binding to various receptors for steroid (nuclear and non-nuclear), non-steroid, neurotransmitter, and orphan receptors like the aryl hydrocarbon (Goksøyr 2006; Diamanti-Kandarakis et al. 2009). EDCs exert the influence not only through interaction with hormone receptors but also via epigenetic mechanisms, thereby altering the expression of pivotal genes integral to reproduction and normal developmental processes (Bhandari et al. 2015). It encompass a diverse array of substances including pesticides, hormone analogs, heavy metals, polychlorinated biphenyls (PCBs), phthalates, organic solvents, flame retardants, surfactants, and pharmaceuticals. Additionally, certain EDCs occur naturally, such as phytoestrogens and mycoestrogens which are synthesized by plants and fungi, respectively (Liu et al. 2010). Conversely, polycyclic aromatic hydrocarbons (PAHs), industrial byproducts resulting from chemical degradation processes, are also effective EDCs. To date, hundreds of EDCs have been identified but the mechanisms of action for many of these chemicals are largely untouched, and combinatorial studies remain notably scarce. Extensive investigation into the impact of EDC exposure has predominantly focused on aquatic organisms, notably fish, which serve as prominent bio-indicators due to the capacity for sexual plasticity and heightened sensitivity to sex steroids and xenobiotic compounds (Hutchinson et al. 2006). EDCs exhibiting pronounced hydrophobicity tend to adhere to suspended particulate matter, deposit in sediment, and accrue within organisms to concentrations often surpassing those observed in sediment, thereby posing a significant risk of ecotoxicological harm to aquatic organisms, particularly economically valuable fish species (Yan et al. 2022). The inherent lipid affinity of EDCs facilitates their accumulation within fish through ingestion and absorption via the gills and skin, subsequently undergoing biomagnification, rendering fish a valuable study model for evaluating both the immediate impacts and their transmission of environmental contaminants through the food chain (Schäfer et al. 2015; Yan et al. 2022). The synergistic inhibitory effect of insecticide, endosulfan, and a non-steroidal anti-androgenic drug, flutamide, manifested in the development of both testicular (Rajakumar et al. 2012) and ovarian tissues (Chakrabarty et al. 2012) in catfish. Another study also elucidated the combined disruptive effects of fenvalerate and triadimefon on embryonic development in the Chinese rare minnow, *Gobiocypris rarus* (Wu et al. 2018). Numerous sex steroid analogues and pesticides have been identified to induce estrogenic effects on diverse physiological systems in fish, wherein the structural similarity of certain molecular configurations of EDCs to endogenous steroid hormones is frequently adequate for targeting the gonads, although several EDCs frequently disrupt the hypothalamic-pituitary-gonadal (HPG) axis, leading to detrimental effects on gonadal functions over time. Within this exhaustive article, we have discussed invaluable insights concerning the origins and physiological consequences of assorted categorized EDCs, complemented by a concise overview on their environmental risk assessments.

4.2 Classification and Sources of EDCs

4.2.1 Persistent Organo-Chlorine Pollutants (POPs)

Polychlorinated biphenyls (PCBs), most studied POPs, characterized by a minimum of four chlorine atoms situated at ortho (mono-ortho) or non-ortho positions, exhibit remarkable inertness and resistance to degradation by acid, base, and heat, rendering them sparingly soluble in water but readily soluble in fats. They were extensively utilized in various applications including heat transfer systems, electrical equipment, transformers, capacitors, and plastics (e.g., Aroclor 1221 and 1254) (Baars et al. 2004). PCBs persist in electronic materials and older installations, as well as in thermal insulation and motor oil, despite their discontinued usage (Vieira et al. 2021). These compounds exert detrimental effects on cognitive development, primarily impacting spatial functions, while also exhibiting carcinogenic (targeting breast, prostate, thyroid, and testis), neurotoxic, hepatotoxic, immunotoxic, and nephrotoxic properties (Klocke and Lein 2020). Other POPs act as endocrine disruptors are polychlorinated dibenzodioxins (PCDD), polychlorinated dibenzofurans (PCDF), and 2,3,7,8-tetrachlorodi-benzodioxin (TCDD) (Fig. 4.1).

4.2.2 Organo-Chlorine Pesticides (OCPs)

Pesticides, constituting the predominant category of endocrine disruptors, find widespread application in agricultural practices, with residual traces detectable in certain food items and potable water sources (Vieira et al., 2021). A pre-emergent herbicide atrazine (2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine), utilized for inhibiting the growth of grassy and broadleaf weeds on crops such as sorghum grass, wheat, corn, and sugar cane, is documented to exert endocrine-disrupting effects (Wirbisky and Freeman 2015). Owing to its notable attributes including high-water solubility, prolonged half-life, soil mobility, and pervasive water contamination, it faced prohibition in the European Union in 2004 (Vonberg et al., 2014). Conversely, the World Health Organization (WHO) recently revised the permissible threshold of atrazine in drinking water is 100 μg/L (Wirbisky and Freeman 2015). Chlorpyrifos, an extensively utilized broad-spectrum organophosphate pesticide, finds application in both agricultural pest management and residential contexts (Ventura et al. 2016). Dichlorodiphenyltrichloroethane (DDT), a ubiquitous pesticide utilized extensively after World War II, faced global prohibition in the 1970s across numerous nations due to its adverse implications for both human and wildlife health, although its continued usage persists in certain underdeveloped regions for malaria control purposes (Meeker 2012). The organochlorine pesticide endosulfan employed in numerous countries as a broad-spectrum insecticide targeting high-value crops. However, owing to its considerable toxicity to non-target organisms, persistent environmental presence, and capacity to function as an endocrine-disrupting agent in

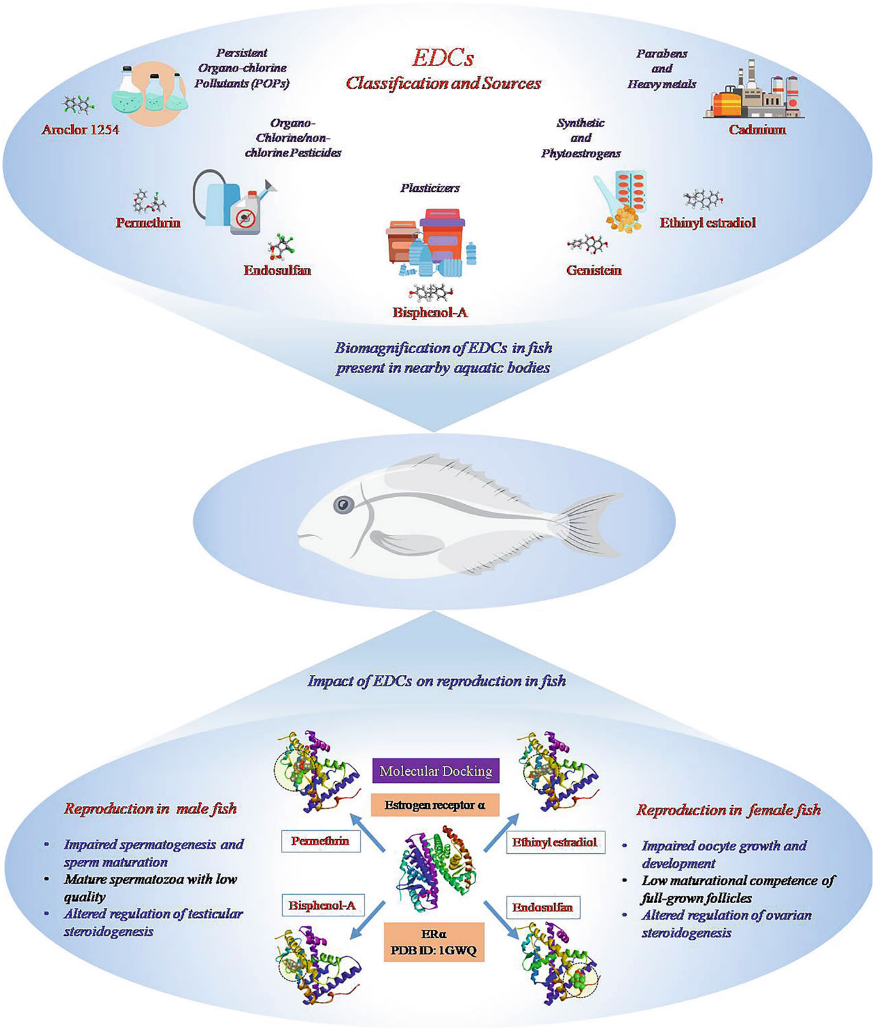
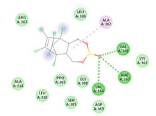
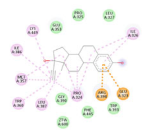
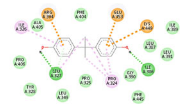


Fig. 4.1 Miscellaneous sources and assorted classification of endocrine disrupting chemicals (EDCs), originating as persistent organic pollutants, organo-chlorine or non-chlorinated pesticides, plasticizers, synthetic and phytoestrogen, and heavy metals, contaminate aquatic bodies and species, particularly fish. These chemicals have potential influence on natural reproductive homeostasis. It desynchronizes hormonal synthesis and activity, ultimately resulting in disruption of hormone-regulated germ cell development and maturational competence in both male and female fish. Moreover, emerging bioinformatics approach can demonstrate potential binding affinity of any EDC toward a particular putative hormone receptor. Here, we represented 3D molecular docking structures of estrogen receptor α (ERα) bound with different EDCs, viz. permethrine, ethinyl estradiol, Bisphenol-A and endosulfan (details of docking parameters are presented in Table 4.1)

Table 4.1 Parameters retrieved from molecular docking of different ligands with estrogen receptor (ERα) are binding energy (Kcal/Mol), ligand efficiency, inhibition constant (Ki) (μM), reference root mean square deviation (RMSD), number of hydrogen bonds and 2D interaction of participating amino acids in receptor-ligand complex

Receptor protein	EDC classes	Ligands	Binding energy (Kcal/Mol)	Ligand efficiency	Inhibition constant (Ki) (μM)	Reference RMSD	No. of hydrogen bonds	2D Interaction of participating amino acids in receptor-ligand complex
Estrogen receptor α (ERα) PDB ID: 1GWQ	Organo-chlorine pesticides	Endosulfan	–6.06	–0.32	35.98	43.41	3	
	Non-chlorine pesticides	Permethrin	–8.83	–0.34	0.334	40.01	3	
	Synthetic estrogen	Ethinyl estradiol	–8.80	–0.40	0.357	38.22	0	
	Plasticizer	Bisphenol-A	–7.11	–0.42	6.1	38.29	2	

fish, the utilization of endosulfan is presently either prohibited or subject to stringent restrictions across various nations (Da Cuña et al. 2013). Malathion, a ubiquitously employed organophosphate pesticide globally in addition to its agricultural application, is utilized for mosquito control in aquatic environments, thereby amplifying its adverse impact on non-target aquatic organisms (Karmakar et al. 2016). 3-(3,5-dichlorophenyl)-5-methyl-5-vinyloxazolidine-2,4-dione or vinclozolin, a dicarboximide fungicide, undergoes degradation in the field to yield two metabolites, M1 and M2, both characterized by extensive half-lives exceeding 180 days and presumed to exhibit significant mobility within the aqueous phase (Bayley et al. 2003). Notably, while vinclozolin itself demonstrates non-persistence, these metabolites possess a prominent affinity for the androgen receptor, thereby exerting anti-androgenic effects by impeding gene expression (Sperry and Thomas 1999).

4.2.3 Plasticizers

One of the extensively researched plasticizers with endocrine-disrupting properties is bisphenol A (BPA, 4,4′-isopropylidene diphenol), a chemically significant compound widely manufactured worldwide (Cantonwine et al. 2013) (Fig. 4.1). BPA is found as an effective plasticizer due to its cross-linking capabilities (Alonso-Magdalena et al. 2012). Roughly 90% of the aggregate BPA production is allocated to the fabrication of plastics and plastic-derived merchandise, encompassing water and infant bottles, food and beverage containers, toys, helmets, impact-resistant eyeglass lenses, and compact disks (Eladak et al. 2015). Additionally, BPA finds application in dental sealants as dimethacrylate (BIS-DMA), thermal paper, and medical equipment (Acharyya et al. 2024). BPA exerts deleterious effects on reproductive organs by modulating hormonal components within the brain-pituitary-gonadal axis, acting as a xenoestrogen, thereby disrupting the production of male and female gametes in fish (Park et al. 2020). Another important plasticizer phthalates employed as additives in PVC (polyvinyl chloride) production are prevalent in children's products and packaging materials, as well as cosmetics, medical devices, food, and building materials, with the three most common types being di-2-ethylhexyl phthalate (DEHP), diisononyl phthalate (DINP), and dibutyl phthalate (DBP) (Vieira et al. 2021). Nonylphenol, a significant non-ionic plasticizer found in lubricating oil additives, dish detergents, emulsifiers, paints, personal care products, and plastics, elicits notable biological effects (Careghini et al. 2015). It acts as an estrogen agonist in females, while concurrently inhibiting androgenic function in males. Its influence extends to the developmental processes of the male reproductive system, particularly targeting the testes and epididymis.

4.2.4 Heavy Metals

Heavy metals represent another category of endocrine disruptors, as they possess the ability to emulate certain hormonal functions within organisms, impeding the activity of specific enzymes, thereby inducing dysregulation within the endocrine systems (Gore et al. 2014). Cadmium is employed in battery production, pigment formulation, electroplating, and as a stabilizer for plastics and non-ferrous alloys, while lead is commonly utilized in the manufacturing of plastics, glass, batteries, ceramic enamels, and metal alloys, and mercury serves roles in pigment production, hydrochloric gas synthesis, thermometers, manometers, dental products, and intermediate chemical compounds (Friberg et al. 2019) (Fig. 4.1).

4.2.5 Synthetic- and Phyto-Estrogens

Ethinyl estradiol (EE2), a synthetic estrogen prevalent in contraceptive pills and pharmaceuticals, is also commonly found in surface water due to its extensive use. This compound acts both as an agonist and antagonist for estrogen receptors (Bakker 2022). Another notable synthetic estrogen, diethylstilbestrol (DES), is associated with testicular and ovarian cancers and infertility. DES disrupts the neuroendocrine axis by inhibiting the hypothalamic-pituitary-gonadal axis through its action on both ERα and ERβ (Lauretta et al. 2019). Phytoestrogens are found in legumes, soy-based infant formulas, and dietary soy supplements including lignans and genistein (Fig. 4.1).

4.2.6 Parabens

Parabens, compounds employed as preservatives primarily in cosmetics but also utilized in pharmaceuticals, personal care, and food items, encompass methylparaben as the most prevalent variant, alongside ethylparaben, butylparaben, and other derivatives found in food, cosmetics, and personal care products (Towers et al. 2015). Parabens classified as 4-hydroxybenzoic acid and its salts and esters are subjected to a maximum allowable concentration of 0.4% (as acid) for individual esters and 0.8% (as acid) for mixtures of esters to comply with regulatory standards for use in cosmetics.

4.3 Degree of Water Pollution by EDCs

Water constitutes a dynamic system, subject to various mechanisms for pollutant distribution, including sorption to sediments, which can serve as a long-term source of pollution. Over recent years, EDCs have pervaded aquatic environments via multiple pathways, such as pharmaceutical and hospital waste disposal, wastewater treatment plants, leaching from industrial and household items, and pesticide residues from agricultural activities (Kar et al. 2021). EDC contamination affects surface and groundwater, marine ecosystems, wastewater, and, rivers and lakes (Pironti et al. 2021; Acharyya et al. 2024).The water cycle predominantly influenced by rainfall plays a crucial role in contaminant transport. During heavy rainfall, sewer systems may become overwhelmed, resulting in discharge of stormwater, untreated waste, and toxic materials into nearby surface water bodies. Precipitation also leaches contaminants from various sources such as buildings, streets, land surfaces, and agricultural fields, contributing to surface water pollution. Runoff from rainwater has been identified as a significant source of contaminants, especially in areas with combined sewer systems that collect rainwater runoff, sewage, and industrial wastewater (Pironti et al. 2021). Household and commercial wastewater, collected in sewer systems, undergo treatment before release into surface waters. Throughout the water cycle, surface water and groundwater facilitate natural purification processes, known as natural attenuation, which include dilution, sorption, volatilization, and chemical or biological degradation, attenuating contaminant concentrations below detection limits (Pal et al. 2014). Despite this treatment effort, pollutants may still persist in surface waters, leading to chronic source of aquatic ecosystems. Notably, sewer leakages contribute significantly to groundwater pollution within the sewershed (Bunting et al. 2021). Pesticides as EDCs can also infiltrate soil eventually contaminating ground and surface waters (Pal et al. 2014).

4.4 Ecological Relevance of EDCs

The ecological risk assessment of EDCs evaluates the probability of adverse effects resulting from the exposure of the chemicals, with numerous studies establishing their dose-response relationships with the decline of aquatic fauna productivity (Lubick 2011). These assessments often involve various ecotoxicity tests, like mortality assessment, growth reduction, reproductive impairment, and determination of lethal concentration (LC_{50}) and half-maximal effective concentration (EC_{50}) in test populations, as well as bioaccumulation studies in target and non-target tissues. Short-term reproductive assays, embryo toxicity tests using fish, and bioconcentration and biomagnification toxicity tests in aquatic systems are examples of studies evaluating risks at early life stages and full life cycles (Ayobahan et al. 2020). In vivo screening assays have also been proposed to comprehensively assess hormonal functions (Hutchinson et al. 2006). Such investigations are crucial for understanding

EDC persistence and transformation in the environment. Exposure characterization, a key step in risk analysis, evaluates the ecological interaction of concerned EDC residues in various environmental media such as food, water, air, and soil. It estimates the frequency, magnitude, and duration of exposure, as well as the characteristics of the exposed population. "Quantitative structure activity relationship" and other integrated computational models have emerged for high throughput screening of compounds (Cohen et al. 2010), complemented by field studies providing realistic insights into the fate of EDC and their byproducts in the environment. Aquatic organisms are particularly susceptible to EDC contamination, compounded by other chemicals. Furthermore, EDCs can also bio-accumulate in fish-consuming higher vertebrates and mammals, leading to adverse effects on wildlife and potentially human health. Aquatic ecosystems worldwide are significantly affected by EDC and heavy metal contamination, resulting in intersex, gonadal aberrations, and altered reproductive responses in fish species (Lubick 2011; Müller et al. 2020).

4.5 Physiological Relevance of EDCs in Aquatic Inhabitants

4.5.1 Molecular Mechanism of Action of EDCs at Cellular Level

EDCs primarily target nuclear receptors, pivotal regulators of gene expression, thereby instigating enduring alterations at the cellular level, although they also exert effects on membrane-bound receptors and it tends to be transient. The diverse array of receptors influenced by EDCs underscores their potential to perturb various physiological functions (Guarnotta et al. 2022). Bisphenol-A demonstrates a heightened affinity for GPER in comparison to nuclear ER α/β receptors (Acharyya et al. 2024). Xenobiotics bind to nuclear receptors at flexible hormone-binding sites, accommodating various synthetic and natural organic compounds, modulating their activity (Sever and Glass 2013) and also significantly influence target cell phenotypes by modulating receptor transcriptional activity. Nonetheless, certain endocrine disrupting chemicals (EDCs) interact with membrane receptors as well (Guarnotta et al. 2022). A subset of hormone-like compounds exhibits the ability to engage receptors and induce an inactive state, thereby disrupting the physiological functions of endogenous hormones. EDCs often circumvent hormone receptors, instead of directly engaging with downstream endocrine regulators, triggering a cascade of adverse effects. Despite structural disparities from natural hormones, EDCs retain the capacity to disturb endocrine balance, manifesting various detrimental effects on organisms (Combarnous and Nguyen 2019). Certain bisphenols interact with Ras proteins, activating the Ras signaling cascade and increasing pERK and pAKT levels (Schaffert et al. 2022). Atrazine, a common herbicide, disrupts the endocrine system by inhibiting PDE4, leading to intracellular cAMP accumulation (Kucka et al. 2012).

DEHP, a plasticizer, acts as both an endocrine disruptor and obesogen, phosphorylating AMPK, ERK1, ERK2, and ACC via interaction with PPARs (Schaffert et al. 2022).

4.5.2 Biotechnological Study to Demonstrate the Molecular Pathway of EDC

We aimed to explore the molecular interaction between different EDCs (endosulfan, ethinyl estradiol, permethrin and BPA) with estrogen receptor (ERα) protein using molecular docking to demonstrate probable mode of action of these EDCs as estrogen agonists (Fig. 4.1). We utilized the Autodock 4.2 software to perform the docking studies between the key ligand molecules and the receptor. The 3D structure of the target protein ERα (PDB ID: 1GWQ) was obtained in PDB format from the RCSB Protein Data Bank. The structures of different ligands were sourced from the PubChem database in SDF format and subsequently converted to PDB format. The preparation of the target protein included adding Kollman charges and removing water molecules, also using Autodock tools. For the docking process, we employed Autogrid to generate grid maps, positioning the center of the docking grid box at the original ligand binding site of the templates, with dimensions set to 60 Å × 60 Å × 60 Å and a grid spacing of 0.375 Å. The docking simulations utilized the Lamarckian Genetic Algorithm (LGA) as the search method, setting the energy evaluations and generations to 2,500,000 (Acharyya et al. 2023a). This allowed us to investigate the potential binding interactions and affinities of endosulfan, ethinyl estradiol, permethrin, and BPA with the ERα protein. An important molecular docking parameter revealed that permethrin and ethinyl estradiol were the most potent EDCs with significant affinity toward ERα followed by BPA and endosulfan, highlighting the role of these molecules as potent estrogen agonists (Table 4.1).

4.6 Impact of EDCs on Fish Reproduction

Reproduction in fish is intricately regulated by the neuroendocrine system, which coordinates the functional relationship between the brain and the endocrine system, thus linking environmental changes to reproductive physiology (Hasan et al. 2020; Das et al. 2022). In fish, oocyte growth and the resumption of meiosis are primarily controlled by pituitary-derived gonadotropins (GTH) and ovarian maturation-inducing steroid (MIS), which is 17,20β-dihydroxy-4-pregnen-3-one (DHP) or 17,20β,21-trihydroxy-4-pregnen-3-one (20β-S) (Maitra and Hasan 2016). In fish, the processes spermiogenesis and spermiation are believed to be predominantly regulated by male sex steroids, 11-ketotestosterone (11-KT), and progestins (Maitra et al. 2015) (Fig. 4.1).

4.6.1 Impact of EDCs on Reproduction in Male Fish

In vertebrates, the evaluation of sperm motility and velocity stands as pivotal determinants of male fertility once spermatozoa are released into the environment (Linhart et al. 2008). Androgens play a crucial role in regulating testicular functioning, spermatogenesis, development of secondary sexual characteristics, and behavioral traits, with their effects mediated by androgen receptors (Acharyya et al. 2023b). Exposure to EDCs has been linked to inhibition of testes growth, alterations in male sex cell types, delays in maturation, occurrence of ovotestis, reduced semen quality, and fluctuations in estrogen and testosterone levels across various teleost models (Kime 1999). Notably, the adverse impacts of EDCs tend to manifest at lower concentrations with prolonged exposure durations (Wang et al. 2016). EDC toxicity remains challenging due to technical and biological variations among studies; evidence suggests that heavy metals may pose a greater risk in impairing the functions of spermatozoa and exhibit adverse effects compared to different organic EDCs (Gore et al. 2014).

4.6.1.1 Spermatogenesis and Sperm Maturation

The effects of chronic exposure to environmentally relevant concentrations of DEHP (0.2 and 20 μg/L) in zebrafish were analyzed, revealing its capacity to disrupt reproduction by inducing mitotic arrest during spermatogenesis and reducing embryo production by up to 90%. These alterations were correlated with increased DNA fragmentation of spermatozoa (Corradetti et al. 2013). Exposure of zebrafish to a combination of environmentally significant concentrations of triclocarban and inorganic mercury similarly resulted in severe histological lesions in the testes. When compared to fish exposed to the compounds individually, there was a reduction in testis size and mature sperm abundance, highlighting the adverse effects of combined exposure (Wang et al. 2016). Similarly, exposure to diethylstilbestrol (DES), flutamide (FLU), and their combination resulted in impaired spermatogenesis. This impairment manifested as a decreased sperm concentration and disruptions in both meiotic and apoptotic processes (Yin et al. 2017). Exposure of male (*Cyprinus carpio*), to 2 mg/L of perfluorooctanoic acid (PFOA) for 56 days led to an increased proportion of spermatogonia and spermatocytes in the testes, indicating a possible disruption or delay in the normal progression of spermatogenesis (Giari et al. 2016). Also in this fish species, a 14-day exposure to graded concentrations of BPA, ranging from 1 to 1000 μg/L, resulted in severe alterations of the lobular structure and spermatogenic cysts and free spermatozoa frequently degenerated within the lumen (Mandich et al. 2007). In goldfish exposed to BPA, there was an induction of hepatic vitellogenin, yet the gonadosomatic index (GSI), hepatosomatic index (HSI), and estrogen (E_2) levels remained unaffected. This suggests that BPA may influence testicular spermatogenesis, leading to alterations in sperm maturation (Hatef et al. 2013).

4.6.1.2 Quality of Sperm

Sperm velocity, encompassing curvilinear (VCL), straight-line (VSL), and average path (VAP) velocities, serves as a vital biomarker of sperm functionality and is notably sensitive to perturbations induced by EDCs. Exposure to cadmium, mercury, BPA, zinc, and tributyltin caused species-specific decrease of VCL and VSL in fish spermatozoa (Hatef et al. 2013). In African catfish (*Clarias gariepinus*), burbot (*Lota lota*), and European chub (*Leuciscus cephalus*), a decrease in sperm motility was observed immediately after exposure to copper or cadmium. In contrast, brown trout (*Salmo trutta*) spermatozoa showed no evident effects when exposed to the same metals (Lahnsteiner et al. 2005). Comparative studies have shown varied results regarding the effects of different contaminants on spermatozoa motility among various fish species. In seabass, African catfish, burbot, and European chub, spermatozoa were exposed to mercury, zinc, lead, nickel, cyclohexane, and 2,4-dichlorophenol, and distinct differences in sperm motility were observed (Lahnsteiner et al. 2005). Exposure to cadmium has been shown to adversely impact sperm quality in *Danio rerio*, resulting in decreased motility, and changes in VCL, VAP, and VSL. These alterations have the potential to diminish the fertility rate of the organism (Acosta et al. 2016). Mercury chloride ($HgCl_2$) decreased sperm velocity by affecting the structures of plasma membrane, axoneme, and midpiece in *Perca fluviatilis*, leading to decreased stored ATP levels (Hatef et al. 2013). In the same fish species, an in vitro treatment of sperm with BPA resulted in decreased motility and velocity, along with a demonstrated capacity to damage the flagellar structure, causing a change in shape from the straight position to a C-shaped configuration (Hatef et al. 2013). Exposure of brown trout, *Salmo trutta*, to environmentally relevant concentrations of BPA (1.75, 2.4, and 5 μg/L) resulted in impaired spermatogenesis, with lowered density and motility rate of sperm, and swimming velocity during pre-spawning and spawning seasons (Lahnsteiner et al. 2005). Recent findings in sterlet (*Acipenser ruthenus*) have shown that sperm exposure to nonylphenol (NP) and diethylstilbestrol (DES) triggered the generation of reactive oxygen species within spermatozoa, resulting in compromised sperm quality, notably characterized by a decrease in the percentage of intact sperm cells (Shaliutina et al. 2017).

4.6.1.3 Testicular Steroidogenesis

Testicular steroidogenesis is the source of male sex steroid hormone testosterone from cholesterol. Di n-butyl phthalate (DBP) acts as an endocrine disruptor in sexually mature male three-spined sticklebacks, *Gasterosteus aculeatus,* by increasing plasma testosterone levels (Aoki et al. 2011). The variation in testis morphology observed in zebrafish following exposure to inorganic mercury was correlated with changes in the transcriptional activity of several steroidogenic genes, including cyp19a, 3β-HSD, cyp17, and 17β-HSD (Wang et al. 2016). In *Gobiocypris rarus*, BPA (15 μg/L) increased mRNA expression of testicular genes encoding steroidogenic enzymes that resulted the up-regulation of androgen levels (Liu et al. 2014). The inhibition of steroidogenic gene expression by 25 ng/L ethinylestradiol (EE2) parallels the impact observed with BPA, indicating that this effect could potentially stem from a negative feedback loop of EE2 on pituitary FSH or possibly be mediated through direct effects of EE2 on the testis (Liu et al. 2014). In goldfish, the endocrine disruptive activity of DEHP revealed that it decreased levels of 11-KT and LH, implying a potential link between reduced sperm quality and hormone concentrations, as its absence of estrogenic activity and non-engagement with sex steroid receptors (Golshan et al. 2015). Exposure of zebrafish to DES and FLU disrupted spermatogenesis, correlating with reduced plasma 11-KT levels and the altered expression of genes associated with steroidogenesis (Yin et al. 2017).

4.6.2 Impact of EDCs on Reproduction in Female Fish

The majority of the studies delineated thus far have elucidated the response of EDCs to ovarian morphology, oocyte growth and maturation, thereby perturbing the normal functions of the endocrine and reproductive systems through the modulation of endogenous hormone production, mimicry of its action, or alteration of its receptor populations (Acharyya et al. 2024). A prominent mechanism underlying endocrine disruption involves the binding of EDCs to hormone receptors. Additionally, mechanisms beyond receptor-mediated events may encompass the inhibition or stimulation of hormone metabolism, as well as alterations in serum hormone-binding proteins.

4.6.2.1 Germ Cell Status in the Ovary

In fish ovary, relative population of different germ cell stages is evidenced in histological study as it depends upon the reproductive status of the organism (Hasan et al. 2014, 2023). The chronic exposure of female zebrafish (*Danio rerio*) to EE2 and DEHP markedly impaired vitellogenesis, and the abundance of previtellogenic oocytes and subsequent mating performances also revealed a substantial decline in fecundity rate and the number of embryos produced (Carnevali et al. 2010). In *Gobiocypris rarus*, bisphenol A (BPA) treatment increased occurrence of premature oocytes and numerous atretic follicles (Liu et al. 2014). Furthermore, EE2 and DES caused precocious oocyte development and follicular atresia in catfish (*Clarias gariepinus*) (Sridevi et al. 2015).

4.6.2.2 Oocyte Growth and Development

The principal events responsible for the enormous growth of fish oocytes occur predominantly during the phase of development termed vitellogenesis, and involve the sequestration and packaging of a hepatically derived plasma precursor, vitellogenin (VTG), into yolk protein (Acharyya et al. 2021; Das et al. 2022; Mondal et al. 2017). In zebrafish (*Danio rerio*), tris (1,3-dichloro-2-propyl) phosphate (TDCPP) showed a notable augmentation in the proportion of late vitellogenic/ mature oocytes and consequent oocyte maturation (Wang et al. 2015). In a recent investigation involving zebrafish (*Danio rerio*), the protracted exposure to various concentrations of di-isononyl phthalate (DiNP) was scrutinized, particularly emphasizing reproductive parameters, encompassing size distribution, follicular abundance, and the intricate macromolecular makeup of vitellogenic oocytes (Santangeli et al. 2017). In the ovaries of marine medaka (*Oryzias latipes*), treatment of 8.5 μg/L 3,3′-diindolylmethane (DIM) resulted in an increased accumulation of VTG, but a concomitant reduction in cathepsin enzyme activities, suggesting an impediment in VTG uptake by growing oocytes. This reduction was accompanied by decreased levels of eggshell proteins, leading to inhibited primary oocyte maturation and subsequently diminished fecundity (Chen et al. 2017).

4.6.2.3 Oocyte Maturation

The term "oocyte maturation" designates a succession of complex cellular processes corresponding to meiosis resumption up to the second metaphase arrest in most vertebrates (Hasan et al. 2016; Moniruzzaman et al. 2016). In vitro administration of prochloraz, either alone or in combination with LH, resulted in alterations in germinal vesicle breakdown (GVBD) in post-vitellogenic rainbow trout follicles. Independently, prochloraz could induce oocyte maturation by stimulating the transcription of specific genes implicated in pre-ovulatory follicular recruitment and differentiation, including igf1, igf2, and hsd20β (Rime et al. 2010). Furthermore, an in vitro maturation assay corroborated inhibitory impact of DEHP on germinal vesicle breakdown (Carnevali et al. 2010). In zebrafish, it has been demonstrated that low concentrations of BPA (10–200 nM) and three alkylphenols, namely tetrabromobisphenol A, 4-nonylphenol, and tetrachlorobisphenol A (5–100 nM), disrupted oocyte maturation through a non-genomic mechanism of action involving the activation of the GPER/ EGFR/MAPK3/1 pathway (Fitzgerald et al. 2015).

4.6.2.4 Ovarian Steroidogenesis

Exposure of *Gobiocypris rarus* to varying concentrations of BPA resulted in differential effects on the expression of steroidogenic enzymes, including star, cyp11a1, cyp17a1, hsd3b, hsd11b2, and cyp19. The fluctuations in steroidogenic gene expression were likely associated with alterations in *ER* and *AR* transcript levels, which have the potential to impact both steroid hormone signaling and nr5a1s expression, thus suggesting a possible mechanism of epigenetic regulation (Zhang et al. 2014). Exposure to EE2 and DES in catfish resulted in significant alterations of transcript and activity of the enzyme aromatase, crucial for estrogen biosynthesis (Sridevi et al. 2015). Exposure of zebrafish to di-isononyl phthalate (DiNP) resulted in dose-dependent modulation of genes associated with steroidogenesis, demonstrating a non-monotonic response (Santangeli et al. 2017).

4.7 Conclusions

The extensive array of research elucidated in the present article underscores the profound consequences of EDCs on the reproductive functions of both male and female fish. These compounds, comprising substances like bisphenol A (BPA), diethylstilbestrol (DES), phthalates, heavy metals and many others, exert intricate effects on various facets of reproductive biology, ranging from the structural makeup of ovaries and the maturation of eggs to the hormonal synthesis in testes and the quality of sperm. In females, continual exposure to EDCs precipitates notable changes in ovarian structure, impeding critical functions like oocyte development, ovulation, and its competence for fertilization and the disruptions lead to diminished reproductive capacity. Mechanistically, it interferes with the binding, metabolism, and the genetic expression of hormones, which in turn disrupts the normal functioning of gonads. Moreover, alternative pathways of hormonal action mediated by receptors like GPR30 contribute to the adverse effects of EDCs on the maturation of egg cells. Similarly, in males, exposure to EDCs derails the process of sperm formation and its maturation, and the synthesis of hormones in testes, culminating in compromised quality of semen and reduced fertility. However, EDCs alter the morphology of testes, expression of genes responsible for hormone synthesis, and also the movement and appearance of sperm cells. It is noteworthy that EDCs exhibit properties that antagonize the effects of male hormones, disrupting the signaling pathways activated by these hormones and reducing the production of testosterone, thereby exacerbating reproductive dysfunction in males. Taken together, these findings underscore the intricate and detrimental consequences of EDC exposure on the reproductive biology of fish, emphasizing the urgent need for stringent regulatory measures to mitigate environmental pollution and safeguard aquatic ecosystems. Furthermore, there is a pressing necessity for further exploration into the molecular mechanisms that underlie the reproductive toxicity induced by EDCs, with the ultimate goal of developing effective strategies to counteract their adverse effects on fish culture.

Acknowledgements Financial assistance from WB-DSTBT (2075(Sanc.)/STBT-11012(27)/2/2024-ST SEC) to KNH is thankfully acknowledged. The award of Senior Research Fellow (SRF) [F. No. 09/1156(0006)/2018-EMR-I] to AA from the Council of Scientific and Industrial Research (CSIR), Govt. of India, and Swami Vivekananda Merit cum Means Fellowship (WBP191602488458), Govt. of West Bengal, to JD is appreciatively acknowledged.

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Chapter 5
Algae-Based Systems for Removal of Emerging Pollutant from Sewage Sludge

Iman Dey, Anwesha Mondal, and Ruma Pal

Abstract The growing population has resulted in a substantial burden on water supplies and a corresponding increase in wastewater generation. Consequently, releasing untreated wastewater into receiving bodies of water has deleterious consequences. The efficient wastewater treatment in this situation requires ongoing effort. Owing to its increased treatment efficiency, the algae-based treatment system has gained attention lately. Algae cultivation in wastewater is an environmentally friendly remediation method that can replace traditional technologies. The reason behind this is its capacity to photosynthesize and its rapid growth in low-cost nutrient source of wastewater. Algae in wastewater lowers both the organic loads and the inorganic nutrients. Unlike traditional treatment methods that generate hazardous sludge, algae-mediated treatment methods yield nutrient-loaded biomass that can be utilized for the manufacture of value-added products such as biofuels and fertilizers. Nevertheless, this approach has some significant drawbacks because the biological method needs a lot of land and more time to operate. This chapter outlines the benefits and drawbacks of the various biological wastewater treatment techniques as well as their many applications along with prospects.

Keywords Algae · Pollution loads · Sewage sludge · Treatment · Wastewater

5.1 Introduction

Algae-based systems are increasingly recognized for their potential to remove emerging pollutants from sewage sludge, offering an eco-friendly and innovative solution to modern wastewater treatment challenges. According to the research,

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https://doi.org/10.1007/978-981-96-3945-8_5

almost 525,000 children perished as a consequence of sewage disposal, specifically due to diarrhea and other water-borne diseases. The World Health Organization has estimated that almost 135 million individuals will perish by 2020 as a result of illnesses connected to water. Wastewater treatment sludge comprises a complex mix of organic and inorganic elements, including new contaminants such medicines, personal care products, and industrial chemicals. Humans pollute surface (rivers, lakes, aquifers, sea) and ground (wells and springs) waters. Home, industrial, agricultural, green, and urban runoff, and atmospheric precipitation cause this pollution (Singh et al. 2022). Fertilizers, biocides, manure, etc. come from agriculture (Mazurkiewicz et al. 2020). In the past, sewage was released into rivers and beaches, altering the biotic environment. Consequently, this diminishes the usability of the watercourse. Therefore, sewage treatment is necessary to restrict water pollution and establish certain standards for the use of water by humans, industries, and agriculture (Kesari et al. 2021). Natural degradation processes in any environmental compartment are sluggish; thus removing or reducing initial loadings requires an appropriate treatment. In sewage treatment plants (STPs), also known as wastewater treatment plants (WWTPs), physical, chemical, and biological processes are used to purify wastewater from urban areas and industries (Patel et al. 2021). However, several techniques and steps remove pollutants from residence sewage during sewage treatment. Each level of treatment guarantees that wastewater is safe for release or reuse, meeting strict environmental regulations (Borah et al. 2020; Capodaglio 2021). Conventional treatment technologies have a negative impact on the environment because they produce a large quantity of sludge. This sludge requires further costly and time-consuming chemical treatment before it can be disposed of, which further increases operational expenses (Rodriguez-Mozaz et al. 2020). These drawbacks prompt the exploration of cost-efficient, economically viable, and environmentally benign solutions. Biological wastewater treatment systems are successful and sustainable due to numerous advantages. Activated sludge, trickling filters, and engineered wetlands use microorganisms to breakdown organic materials and remove impurities. Affordable and effective, these approaches reduce biochemical oxygen demand (BOD) and suspended solids (Musa and Idrus 2021; Ahmad et al. 2022).

Adding algae to sewage treatment has additional benefits (Fig. 5.1). Algae efficiently remove nitrogen and phosphate, reducing water eutrophication as well as heavy metals and other contaminants by biosorption and bioaccumulation (Ahmed et al. 2022). Raceway ponds and photobioreactors can improve efficiency when combined with standard treatment procedures. Moreover, algae produce oxygen, helping other aerobic microorganisms break down organic materials and minimizing mechanical aeration system energy needs. After treatment, these algal biomasses may be utilized to produce biofuel, animal feed, and fertilizer, which not only adds economic value but also supports the concept of a circular economy (Fig. 5.2). Thus, sustainable development goals are met by algal treatment's natural processes and renewable resources (Sharma et al. 2021; Zabochnicka et al. 2022). This overview of algae-based systems emphasizes their promise as a versatile and eco-friendly approach for tackling the issue of developing contaminants in sewage sludge.

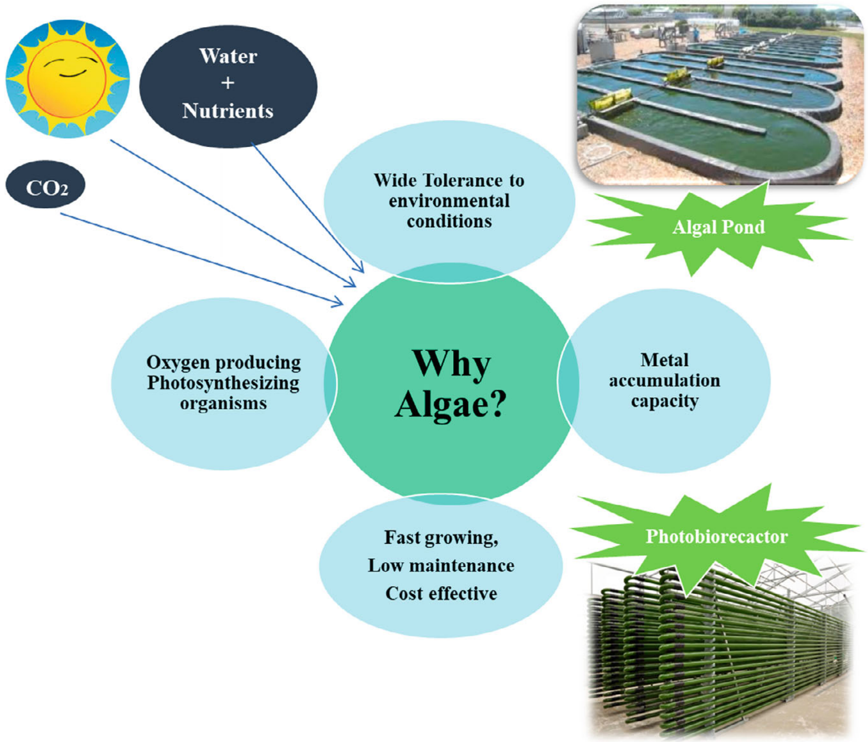

Fig. 5.1 Benefits of using algae as wastewater remediation

5.2 Removal of Organic and Inorganic Load from Sewage Sludge

Sewage sludge is composed of a complicated and varied combination of inorganic and organic burdens, each of which contributes to its overall pollution profile. The organic load in sewage sludge is primarily composed of biodegradable materials, such as proteins, carbohydrates, fats, and oils, which are derived from human refuse, dietary residues, and other biological sources. The biochemical oxygen demand (BOD) and chemical oxygen demand (COD) of the sediment are significantly influenced by these organic substances, which demonstrate the quantity of oxygen necessary for microbial decomposition (Rulkens 2008; Raheem et al. 2018). Furthermore, sewage sediment contains a diverse array of microorganisms, including bacteria, viruses, and protozoa that may pose health hazards if not adequately addressed. In addition, it contains emerging pollutants such as pharmaceuticals, hormones, and personal care products, which are not eliminated by conventional wastewater treatment procedures and may remain in the environment (Akpor et al. 2014; Ahmed et al. 2019). The inorganic load of sewage sludge includes a range of metals and heavy

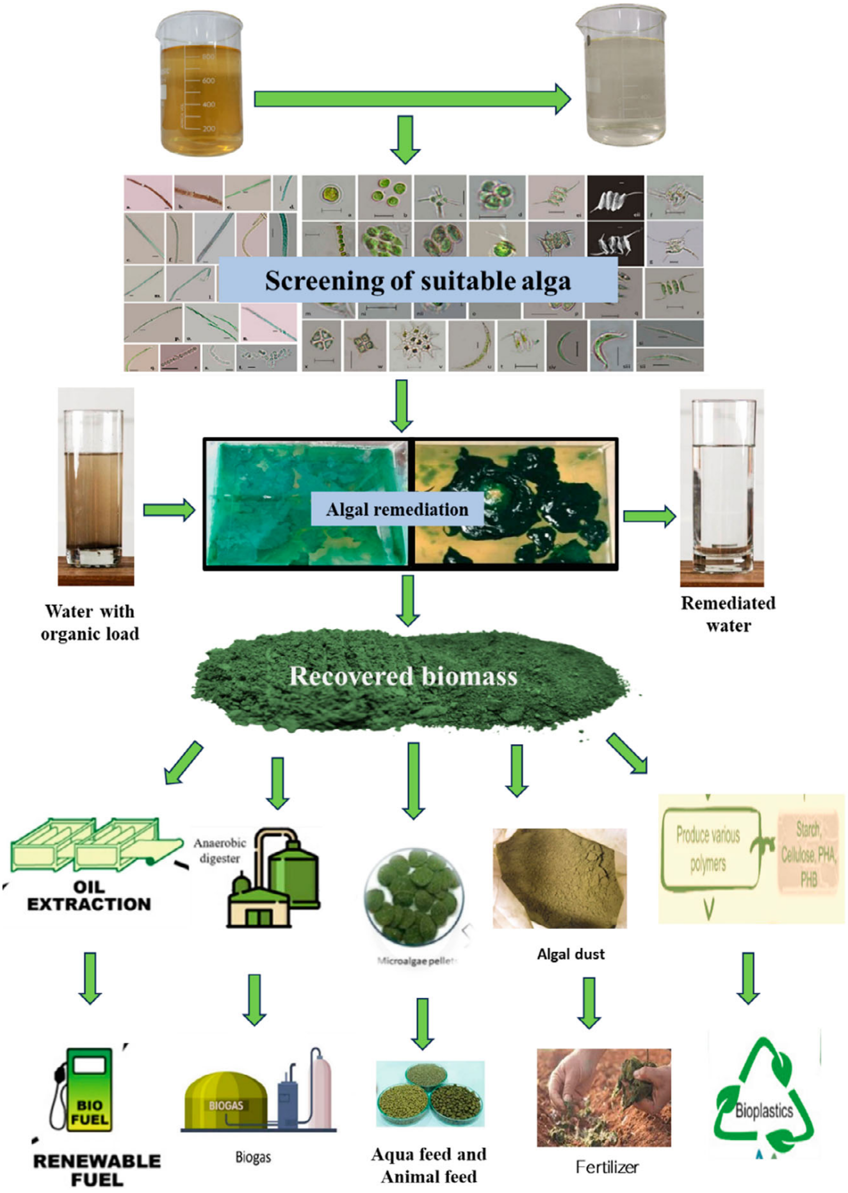

Fig. 5.2 Algae as a tool of sewage treatment and post treatment product production

metals, such as lead, mercury, cadmium, chromium, copper, and zinc. These metals often originate from industrial discharges, household chemicals, and the corrosion of plumbing systems. Inorganic pollutants also encompass essential nutrients like nitrogen and phosphorus, which, if released into water bodies, can contribute to eutrophication, leading to excessive growth of algae and other aquatic plants, thus disrupting aquatic ecosystems (Garcia-Delgado et al. 1994; Spanos et al. 2015). Furthermore, minerals, salts, and grit are inorganic components that are typically eliminated during the initial phases of effluent treatment. The safe disposal or reuse of treated sludge, the protection of public health and ecosystems, and the reduction of the environmental impact of sewage sludge are all contingent upon the effective management and treatment of both organic and inorganic burdens (Mishra et al. 2023). Algae effectively remove both organic and inorganic pollutants from effluent sediment through biosorption, biodegradation, and bioaccumulation mechanisms, enhancing water quality and ecosystem health.

5.3 Algal Bioremediation Mechanism in Sewage Treatment

The organic load that is present in sewage wastewater is effectively removed by algae through a number of different methods (Fig. 5.3). These mechanisms include the absorption of nutrients and organic compounds directly from the wastewater, which includes nitrogen, phosphorus, and carbon. They are able to transform light energy into chemical energy through the process of photosynthesis, which results in the release of oxygen and the establishment of an aerobic environment that is suitable for bacteria (Silva et al. 2019; Chan et al. 2022). The enzymes that algae make are responsible for the breakdown of complex organic compounds into simpler forms, which they then ingest in order to continue their development. As they multiply, algae drain nitrogen and phosphorus, which results in a decrease in the amount of nutrients that are present in the water (Lewis et al. 2011). Their biomass serves as a repository for organic materials, which may be extracted in order to ensure that the wastewater is thoroughly purified. Not only does this all-encompassing procedure oxygenate and clarify the wastewater, but it also makes a contribution to the biological balance that exists in aquatic systems. By leveraging the natural affinity of certain algae species for metals like zinc, iron, cadmium, lead, copper etc., these organisms can effectively absorb and accumulate metals from wastewater. This process, known as biosorption, involves the binding of metal ions onto the cell walls or within the cellular structure of algae (Danouche et al. 2021). Algae offer a promising avenue for remediating metals in sewage treatment due to their intricate molecular mechanisms. Certain algae species possess specialized cell wall components, such as polysaccharides and proteins, which have high affinity for metal ions. These components contain functional groups like carboxyl, hydroxyl, and amino groups that bind strongly to metals through ion exchange, complexation, and chelation processes (Priyadarshini et al. 2019). Additionally, algae can modify their biochemical composition in response to metal exposure, upregulating metal-binding proteins and enzymes to enhance metal uptake and detoxification (Ayele et al. 2021). This molecular sophistication enables algae to efficiently sequester metals from sewage, making them effective and environmentally sustainable agents for wastewater treatment and metal recovery efforts.

5.4 Selection of Algal Strain in Sewage Treatment

The selection of an appropriate algal strain for pollutant remediation in sewage treatment is crucially influenced by both the specific types of pollutants present and the prevailing climatic conditions. Different algae species exhibit varying affinities and capabilities for absorbing different pollutants such as heavy metals, organic compounds, and excess nutrients (Tables 5.1 and 5.2). For instance, green algae like *Chlorella* and *Scenedesmus* are adept at removing heavy metals, while diatoms such as *Navicula* and *Cyclotella* excel in organic load uptake (Marinova et al. 2018; Manzoor et al. 2019; Rai et al. 2022). Climatic factors such as temperature, light intensity, and nutrient availability also play a significant role in determining the optimal algal strain for a given location. Tropical and subtropical regions might favor algae that thrive in warmer temperatures and higher light intensities, such as *Spirulina* and *Dunaliella*, whereas cooler climates might be better suited for species like *Chlorella* and *Microcystis* (Hernando et al. 2022). Therefore, selecting the right algal strain involves a careful assessment of pollutant profiles in the wastewater and an understanding of local climatic conditions to ensure efficient and effective remediation and treatment processes. Both microalgae and macroalgae offer unique advantages in the context of pollutant remediation in sewage treatment, each suited to different environmental and operational conditions. Microalgae are single-celled organisms that possess high surface area-to-volume ratios, facilitating efficient absorption of dissolved pollutants like heavy metals and nutrients. They can be cultivated in controlled environments, making them adaptable to varying climatic conditions and operational scales. Most of the microalgae species have rapid growth rates, allowing for quick biomass accumulation and pollutant uptake (Iasimone 2018; Novoveská et al. 2023). On the other hand, macroalgae are multicellular and typically larger in size. They excel in nutrient uptake, particularly nitrogen and phosphorus, and can thrive in marine or brackish water environments. Macroalgae offer additional benefits such as habitat provision and shoreline stabilization, contributing to ecosystem health while simultaneously enhancing sewage treatment efficiency (Den Haan et al. 2016; Martínez et al. 2012; Macreadie et al. 2017; Lelis et al. 2024).

Using both microalgae and macroalgae in wastewater treatment has its drawbacks, including operational costs, environmental sensitivity, and potential risks to water quality and aquatic ecosystems. Using microalgae in wastewater treatment needs high operational costs due to energy-intensive cultivation and maintenance, and challenges in efficiently harvesting microalgae from treated water, which often requires expensive techniques (Mathimani and Mallick 2018). Nutrient imbalances in wastewater can limit microalgal growth, and large-scale cultivation systems demand

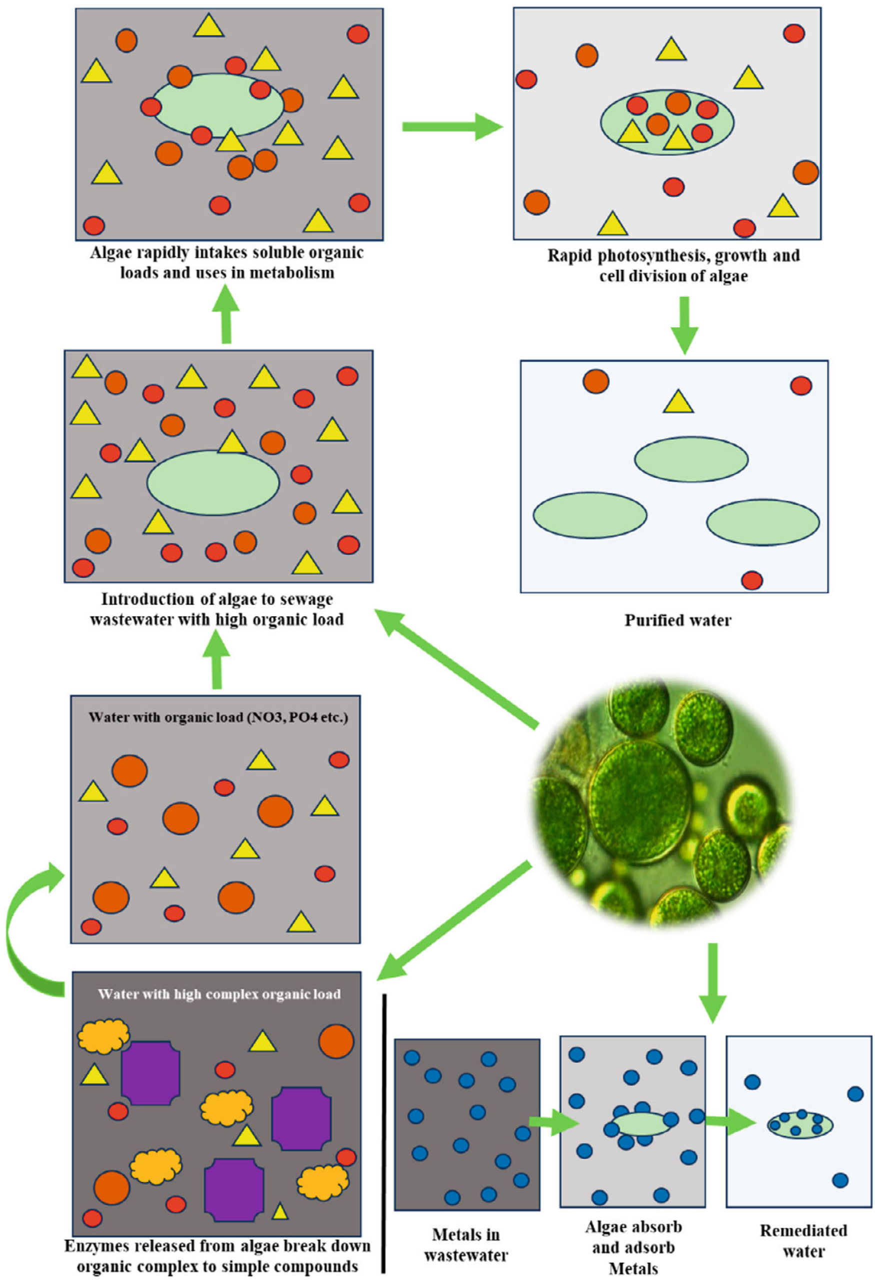

Fig. 5.3 Processes of algal remediation of wastewater treatment

Table 5.1 Some algal strains used for wastewater remediation

Name of algae or cyanobacteria used to reduce BOD and COD	Reduction %	Concentration of wastewater in which reduction took place (in %)	Days required for reduction (days)	Individual or consortium	References
Leptolyngbya valderiana, *Anabaena sphaerica*, *Arthrospira platensis*	BOD—93% COD—94%	50%	21	Individually	Dey and Pal (2023)
Chlorella vulgaris and *Scenedesmus obliquus*	COD—40% BOD—37%	5, 7, 9 gL^{-1}	6	Individually	Mirza et al. (2021)
Chlorella sp.	76% COD and 85% BOD	50%	16	Individually	Santhosh et al. (2020)
Scenedesmus sp., *Chlorella variabilis* and *Chlorella sorokiniana*	COD—80%	25%, 40%	16	Individually	Nagi et al. (2020)
Chlorella marina and *Nannochloropsis marina*	COD—78%	–	12	Consortium	Nambukrishnan and Singaram (2020)
Tetraselmis sp.	COD—50% BOD—35%	25, 50, 100%	21	Consortium	Pena et al. (2019)
Lyngbya sp.	BOD—18.5% COD—29%	100%	30	Consortium with Coir pith, Nava Rasa Karaisal	Mohamed et al. (2019)
Chlorella vulgaris and *Pseudochlorella pringsheimii*	COD—65%	10, 20, 30, 40, 50, 100%	16	Individually	Saranya and Shanthakumar (2019)
Chlorella sp. and *Phormidium* sp.	BOD—93.5% COD—93%	100%	20	Individually and also in consortium	Das et al. (2018)
Scenedesmus sp.	COD—80.33%	88.4%	25	Individually	da Fontoura et al. (2017)

(continued)

Table 5.1 (continued)

Name of algae or cyanobacteria used to reduce BOD and COD	Reduction %	Concentration of wastewater in which reduction took place (in %)	Days required for reduction (days)	Individual or consortium	References
Scenedesmus sp.	BOD—35% COD—37%	50%	12	Individually	Ajayan et al. (2015)
Chlorella vulgaris	COD—88.5%, BOD—90.17%	100%	21	Individually	Begum et al. (2015)
Lyngbya sp.	BOD—79.31% COD—70%	100%	14	Individually and also in consortium with Coir pith	Lakshmi and Malliga (2014)
Nostoc sp.	BOD—67% COD—75%	100%	7	Individually and also in consortium with aquatic plants	Jahan et al. (2014)
Spirulina fusiformis	BOD—75% COD—81%	100, 200, and 300 ppm	15	Individually	Pandi et al. (2009)
Oscillatoria sp.	BOD—66.35% COD—52.80%	100%	30	Individually	Dhamotharan et al. (2016)
Spirulina platensis	COD—23% BOD—25%	100 ppm	1	Individually	Shashirekha et al. (2008)

Table 5.2 Some algal strains used for Ammoniacal nitrogen removal

Name of algae or cyanobacteria used to reduce Ammonia	Reduction %	Concentration of wastewater in which reduction took place (in %)	Days required	Individual or consortium	References
Leptolyngbya valderiana, *Anabaena sphaerica*, and *Arthrospira platensis*	Ammoniacal nitrogen—93%	50	21	Individually	Dey and Pal (2023)
Scenedesmus sp., *Chlorella variabilis*, and *Chlorella sorokiniana*	Ammoniacal nitrogen—74%, PO_4–P—93%	25 and 40	16	Individually	Nagi et al. (2020)
Tetraselmis sp.	Ammoniacal nitrogen—99%, Total nitrogen—82%, PO_4–P—92%	100, 50, 25	21	Consortium	Pena et al. (2019)
Lyngbya sp.	N—55% P—75%	100	30	Consortium with Coir pith, Nava Rasa Karaisal	Mohamed et al. (2019)
Chlorella vulgaris and *Pseudochlorella pringsheimii*	NH_3–N—65%, PO_4–P—100%	10, 20, 30, 40, 50, 100	16	Individually	Saranya and Shanthakumar (2019)
Chlorella sp. and *Phormidium* sp.	TN—91% TP—89%	100	20	Individually and also in consortium	Das et al. (2018)
Scenedesmus sp.	Ammoniacal nitrogen—85.631%, phosphorus—96.78%	88.4	25	Individually	da Fontoura et al. (2017)
Scenedesmus sp.	NO_3—44.3%, PO_4—95%	50	12	Individually	Ajayan et al. (2015)
Oscillatoria sp.	Nitrate—96.36%	100	30	Individually	Dhamotharan et al. (2016)

considerable space, making them less feasible in urban areas. Microalgae are also sensitive to environmental conditions such as temperature, pH, and light availability, which can affect their effectiveness (Gonçalves et al. 2017). Additionally, the presence of contaminants or pathogens in wastewater can inhibit microalgal growth and pose health risks (Amaro et al. 2023). Moreover, there is a risk of uncontrolled microalgal growth leading to harmful algal blooms, which can negatively impact water quality and aquatic life (Igwaran et al. 2024). Similarly, cultivating macroalgae also often requires substantial space and specific environmental conditions, such as adequate light and water flow, which can be challenging to maintain consistently. The harvesting process can be labor-intensive and costly, as macroalgae need to be manually collected or require specialized equipment (Fernand et al. 2017). Additionally, macroalgae can be susceptible to diseases and pests, which can compromise their effectiveness and increase maintenance efforts (Sangha et al. 2014). Sometimes, the introduction of non-native macroalgae species for wastewater treatment can disrupt local ecosystems and biodiversity. The decomposition of dead macroalgae can release nutrients back into the water, potentially negating some of the treatment benefits (Murphy et al. 2015).

The choice between microalgae and macroalgae for pollutant remediation hinges on the specific pollutants, environmental conditions, and desired outcomes of the treatment process. Both types are effective in fresh water, alkaline, marine or brackish water pollutants where they stabilize sediments and improve water clarity. Eventually, the particular contaminants, surrounding circumstances, and treatment goals will determine whether microalgae or macroalgae are more suited for pollutant remediation, and both varieties work well to stabilize sediments and make the water more transparent.

5.5 Algal Cultivation Systems

To cultivate algae for this purpose, it is necessary to produce a significant amount of biomass. This may be accomplished using many methods, each with their own distinct benefits and difficulties. Algal culture systems are crucial for efficient wastewater treatment, employing several designs specifically designed to maximize growth and eliminate pollutants (Arutselvan et al. 2022). Raceway ponds, which are shallow and constantly agitated, offer an economical approach for cultivating algae on a big scale. This method makes use of natural sunlight and requires no infrastructure (Kumar et al. 2024). Photobioreactors are enclosed devices often constructed from transparent materials. They provide a means to exert exact control over environmental factors such as light, temperature, and nutrient levels. This control enhances the productivity and uniformity of algae growth (Huang et al. 2017). When comparing open ponds, such as raceway ponds, to closed systems, it is evident that open ponds are more cost-effective and simpler to build. However, they are susceptible to pollution, variations in the environment, and reduced production (Lage et al. 2021). Photobioreactors, which are closed systems, provide superior efficiency and safeguard against external pollutants. However, they entail more expenses for both installation and operation (Olivieri et al. 2014). The selection of a system depends on the specific aims of wastewater treatment, available budget, and environmental circumstances, since each system has its own benefits and constraints.

5.6 Basic Stages of Algal Sewage Treatment

Algal wastewater treatment uses algae to filter water in a novel, eco-friendly method. As urbanization and industrialization increase, wastewater volume increases, requiring effective and sustainable treatment technologies. Traditional wastewater treatment uses chemical and energy-intensive methods, which are expensive and harmful (Abuhasel et al. 2021). Algal treatment systems use algae's metabolic activities to remove toxins, making them cost-effective and ecologically friendly. This method involves several stages, beginning with pre-treatment to remove large debris and solid particles that can impede algal growth. In the main treatment stage, algae photosynthesize to reduce organic matter and nutrients in wastewater. Algal biomass is produced and biochemical oxygen demand (BOD) is reduced. To fulfill strict regulatory criteria for safe discharge or reuse, the secondary and tertiary treatment phases use additional biological, chemical, and physical processes to improve water quality (Heaven et al. 2012; Mohsenpour et al. 2021).

5.6.1 Pre-treatment Requirements

Prior to the efficient utilization of algae in sewage treatment, it is imperative to carry out pre-treatment procedures to eliminate sizable debris and grit that have the potential to cause harm or disrupt succeeding operations. This stage often includes the process of screening and sedimentation to remove big solids and particle debris. Properly pre-treating the wastewater is essential to maximize the circumstances for algal development. Excessive contaminants or solid materials might hinder algal activity and decrease the overall effectiveness of treatment (Paul et al. 2016; Kadir et al. 2018).

5.6.2 Primary Treatment with Algae

During the initial treatment phase, algae play a crucial role in effectively eliminating organic matter and nutrients from the wastewater. Algal ponds or photobioreactors are utilized to facilitate the consumption of carbon dioxide and nutrients, such as nitrogen and phosphorus, by algae through the process of photosynthesis. This procedure not only decreases the biochemical oxygen demand (BOD) and nitrogen burden but also produces biomass that may be collected for diverse applications, such as biofuel generation, fertilizer, and animal feed. The presence of algae in the water also contributes to the oxygenation of the water, hence improving the treatment process (Henderson et al. 2008; Shokoohi et al. 2023).

5.6.3 Secondary and Tertiary Treatments

After the initial algal treatment, additional secondary and tertiary treatments are used to refine the effluent and meet more stringent water quality requirements (Dammak et al. 2023). Secondary treatment often incorporates further biological processes, such as bacterial breakdown, to further decrease biochemical oxygen demand (BOD) and suspended solids. Tertiary treatment involves the implementation of enhanced filtration, chemical coagulation, and disinfection techniques to eliminate any residual pollutants, pathogens, and trace organics (Dhanker et al. 2023). By integrating these processes, the treated wastewater is guaranteed to fulfill the necessary legal criteria for either release or reuse. This approach to sewage treatment is both sustainable and efficient, with the added advantage of using algal biomass.

However, site-specific features and modifications must be considered to deploy algal sewage treatment systems successfully. Climate, wastewater composition, and space affect algae treatment facility design and operation. To increase efficiency, algae species selection, pond or photobioreactor setups, and integration with other treatment technologies may be modified. Algal sewage treatment may be used to solve a variety of wastewater management problems by customizing these systems to each instance.

5.7 Utilization of Spent Algal Biomass After Treatment

The spent algal biomass, which is a byproduct of the algal sewage treatment process, has considerable potential for many uses, effectively converting waste into useful resources (Table 5.3). A key use is in the manufacturing of biofuels, such as biodiesel and bioethanol, which offer a sustainable energy alternative and diminish reliance on non-renewable fossil fuels (El-Sheekh et al. 2023; Vasistha et al. 2023; Vickram et al. 2023). In addition, the biomass may be converted into fertilizers and soil conditioners, which will improve the quality of agricultural soils by adding vital nutrients and promoting soil health (Dey and Pal 2023; Khan et al. 2023; Ferreira et al. 2023). Additionally, algae may be used to remove metals from wastewater (Ordóñez et al. 2023; Ramesh et al. 2023; Gouda and Taha 2023). The leftover biomass from this process can also be used in phytoremediation, which involves using it to clean up polluted soil by either stabilizing or removing heavy metals (Liu et al. 2023; Mahtab et al. 2024). Within the field of aquaculture, the biomass is utilized as a nutrient-rich food source for fish and cattle, hence encouraging the adoption of sustainable methods in animal husbandry (Bhatti et al. 2023; Rifna et al. 2023; Ma et al. 2022). Furthermore, the algal biomass has the potential to be transformed into bioplastics and other materials that can naturally decompose, thereby aiding in the mitigation of plastic pollution (Mehariya et al. 2023; Mehmood et al. 2024). Through the exploration of various reuse paths, the full potential of algal biomass in terms of environmental and economic advantages may be achieved. This will contribute to the establishment of a circular economy and the promotion of sustainable resource management.

5.8 Utilization of Phyco-Treated Water

Following the process of algal purification, the treated water generally attains a commendable standard of purity, rendering it appropriate for a wide range of advantageous applications. Subject to regional laws and the level of processing, the decontaminated water can be released into natural water sources, such as rivers, lakes, and oceans, to support and maintain aquatic ecosystems. In urban and agricultural environments, this processed water may be reused for irrigation, offering a dependable water supply for crops and green areas, thereby preserving freshwater supplies (Cunha-Chiamolera et al. 2024). Moreover, treated water may be utilized in industrial operations, such as the act of chilling and washing, hence decreasing the need for drinkable water in the manufacturing and other sectors (Song et al. 2024). Additional treatment phases in certain sophisticated systems can render the water drinkable, enabling its reuse in the drinking water distribution network. Communities may improve water sustainability, minimize environmental harm, and promote effective water resource management by discovering inventive methods to repurpose treated water (Satpati et al. 2024a; Ethiraj et al. 2024).

5.9 Challenges and Limitations

The utilization of algae for wastewater treatment shows considerable promise, although it is impeded by several obstacles and constraints. The variety in the content of wastewater presents a considerable challenge, as changes in the quantities of nutrients, pH levels, and the existence of harmful compounds can have a substantial effect on the development of algae and the effectiveness of treatment processes (Raghuraman Rengarajan et al. 2024). The presence of heavy metals and other pollutants commonly present in industrial effluents can have a significant negative impact, as they can hinder the process of photosynthesis and result in unpredictable treatment results (Maity et al. 2024). Attaining and sustaining ideal development conditions for algae, including sufficient illumination, suitable temperatures, and well-balanced nutrient levels, is an intricate process that needs meticulous supervision and regulation (Dey et al. 2021, 2023). Maintaining these conditions requires a significant

Table 5.3 Uses of algal biomass after wastewater remediation

	Name of algae or cyanobacteria	Application	References
1	*Leptolyngbya valderiana*, *Arthrospira platensis*	Fertilizer	Dey and Pal (2023)
2	*Chlorella marina*	Biodiesel	Nambukrishnan and Singaram (2020)
3	*Lyngbya* Consortium	Fertilizer	Mohamed et al. (2019)
4	*Synechococcus subsalsus* *Spirulina* sp.	Bioplastic	Khan et al. (2022)
5	*Desmodesmus communis*	Polyhydroxybutyrate (PHB)	Pezzolesi et al. (2023)
6	*Chlorella vulgaris* *Microcystis aeruginosa*, *Haematococcus pluvialis* *Phaeodactylum tricornutum* *Botryococcus braunii* *Nannochloropsis gaditana*	Bioplastic (PHB)	Arora et al. (2023)
7	*Nannochloropsis gaditana*	Biogas	Capson-Tojo et al. (2017)
8	*Oscillatoria sp.*	Biobutanol	Kallarakkal et al. (2021)
9	*Dunaliella salina*	Biobutanol	Tekin et al. (2024)
10	*Scenedesmus sp.*	Bioethanol	Yirgu et al. (2023)
11	*Chlorella sp.* *Chromochloris zofingiensis*	Biobutanol	Onay (2020)
12	*Chlorococcum sp.*	Biopolymer	Mehariya et al. (2023)
13	*Scenedesmus dimorphus* *Arthrospira platensis*	Cattle feed	Cicci et al. (2024)
14	*Scenedesmus sp.* *Chlorella pyrenoidosa* *Chlorella vulgaris*	Animal feed	Ma et al. (2022)
15	*Chlorella sp.*	Livestock feed	Luzzi et al. (2024)
16	*Chlorella* sp. *Coelastrella cogersae* *Arthrospira platensis*	Cattle feed	Blanco-Vieites et al. (2024)
17	*Scenedesmus* sp. *Limnothrix* sp.	Biodisel and Cattle feed	Devi et al. (2023)
18	*Extremophilic algae*	Animal feed	Öztürk and Satpati (2024)
19	*Chlorella sorokiniana* *Scenedesmus* sp.	Fish feed	Bhatti et al. (2023)
20	*Chlorella vulgaris*	Fish feed	Barnharst et al. (2023)
21	*Chlorella minutissima*	Fertilizer	Sharma et al. (2021)

(continued)

Table 5.3 (continued)

	Name of algae or cyanobacteria	Application	References
22	*Scenedesmus* sp.	Fertilizer	Álvarez-González et al. (2022)
23	*Chlorella* and *Scenedesmus consortium*	Fertilizer	Silambarasan et al. (2021)
24	*Nostoc* sp. *Chlorella sp.* *Scenedesmus sp.*	Fertilizer	Khan et al. (2019)
25	*Desertifilum tharense*	Fertilizer	Usman et al. (2024)
26	*Micro algal consortia*	Fertilizer	Rojo et al. (2023)
27	*Aphanothece* sp. *Aphanocapsa* sp., *Chlorella* sp. *Scenedesmus* sp. *Chlamydomonas* sp	Fertilizer	Ferreira et al. (2023)
28	*Microalgae*	Fertilizer	Othman et al. (2024)
29	*Chlamydomonas reinhardtii, Monoraphidium braunii, Scenedesmus obliquus*	Biodiesel	El-Sheekh et al. (2023)
30	*Chlamydocapsa bacillus, Ankistrodesmus fusiformis*	Biodiesel	Vickram et al. (2023)
31	*Chlorella vulgaris*	Biofuel	Fathi et al. (2013)
32	*Chlorella vulgaris*	Biodiesel	Houser et al. (2014)
33	*Chlamydomonas reinhardtii,* *Chlorella* sp. *Parachlorella kessleri* *Nannochloropsis gaditana*	Biofuel	Singh et al. (2017)
34	*Chlorella sp.*	Biofuel	Cho et al. (2011)
35	*Chlorella vulgaris*	Biofuel	Sarpal et al. (2024)
36	*Chlorococcum humicola* *Tetradesmus* sp. *Chlorococcum humicola* *Scenedesmus vacuolatus* *Tetradesmus* sp.	Biofuel	Singh and Singh (2024)
37	*Chlorella pyrenoidosa*	Biogas	Kumari et al. (2021)
38	*Tetradesmus obliquus*	Biogas	Miyawaki et al. (2021)
39	*Chlorella vulgaris*	Bioethanol	Condor et al. (2024)
40	*Chlorella sorokiniana*	Biochar	Rawat et al. (2024)

amount of energy, which might partially negate the environmental advantages of employing algae (Öztürk and Satpati 2024). Moreover, the extraction of algae from processed wastewater poses practical and financial difficulties. Efficient methods of separating algae, such as centrifugation, filtration, and flocculation, are necessary for algae recovery. However, these techniques may be costly and demand a significant amount of energy. The elevated water content of algal biomass further complicates its manipulation and processing. In addition, the widespread use of algae treatment systems requires significant amounts of land and water resources, which might potentially conflict with agricultural and urban land uses, especially in densely populated regions (Borah et al. 2024). The presence of seasonal fluctuations in algal growth adds complexity and uncertainty to the consistency and dependability of wastewater treatment procedures. These constraints collectively hinder the ability of algal-based wastewater treatment systems to be scaled up and widely used, despite their promised environmental advantages (Satpati et al. 2024b). So, despite these challenges, algae-based wastewater treatment remains a valuable and beneficial approach, offering sustainable and eco-friendly solutions for pollutant removal and nutrient recovery.

5.10 Regulatory and Policy Aspects

Algae-based wastewater remediation requires environmental compliance and governmental incentives. By requiring good effluent quality and pollutant reduction, strict environmental laws can spur innovation in treatment methods (Yan et al. 2024; Wen et al. 2024). Grants, subsidies, and tax incentives for algal technology research and development can boost innovation and minimize implementation costs. Regulations that acknowledge algae-based systems' environmental advantages, such as carbon sequestration and nutrient recycling, might further encourage their use (Zhong et al. 2024). Algal systems may be integrated into wastewater treatment infrastructures through government, business, and research collaborations (Kumar et al. 2024). Compliance with these standards and policy support can speed algae-based wastewater treatment, making it more sustainable and efficient.

5.11 Future Prospects and Research Directions

The future prospects for algae-based wastewater treatment are promising, driven by ongoing innovations in algal biotechnology and potential improvements in efficiency and scalability. Research is focused on enhancing algal strains through genetic engineering to increase their resilience to variable wastewater conditions and improve their nutrient uptake and pollutant degradation capabilities. Advances in photobioreactor design and optimization of raceway ponds aim to maximize light penetration and nutrient distribution, thereby boosting algal productivity. The integration of artificial intelligence and machine learning can enhance system monitoring and control, enabling real-time adjustments to maintain optimal conditions. Additionally, co-cultivation with other microorganisms and the use of tailored consortia can enhance treatment efficiency and broaden the range of contaminants addressed. Efforts to reduce the costs and energy requirements of algal harvesting and processing are also critical, with innovations such as bio-flocculation and low-energy dewatering technologies showing promise. As these research directions progress, the scalability of algae-based wastewater treatment systems is expected to improve, paving the way for their broader adoption and contribution to sustainable water management.

5.12 Conclusion

Algae-based sewage wastewater treatment is a promising and new method for reducing water pollution and providing many environmental advantages. Algae possess the ability to efficiently eliminate nutrients, heavy metals, and other pollutants from wastewater, aiding in the process of water purification and mitigating the environmental consequences of effluents. In addition, the biomass generated may be used for the production of biofuels, animal feed, and biofertilizers, thereby establishing a circular economy that optimizes the extraction of resources. The future holds great potential in the advancement of algae biotechnology, enhancing the efficiency and cost-effectiveness of growth and harvesting techniques, and expanding the scale of systems for wider use. Although there are difficulties in maintaining ideal development conditions and dealing with expensive operations, continuous research and technology advancements are leading to stronger and more scalable solutions. Algae-based wastewater treatment has significant potential for improving the sustainability of water management techniques, in line with worldwide initiatives to tackle environmental and resource conservation issues.

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Chapter 6
Seaweed Biosorption: A Sustainable Approach to Wastewater Treatment

Sasmita Das, Maheswari Behera, Prateek Ranjan Behera, Varanasi Adarsh, and Lakshmi Singh

Abstract Our country's environmental pollution has seriously threatened the natural world. Among all the pollution, water pollution is becoming a great concern as it accumulates unwanted toxic contaminants in water bodies. Insufficiently treated or untreated wastewater greatly contributes to releasing contaminants into the water bodies that are being used for different purposes. These pollutants are becoming bioaccumulated and causing serious threats to the aquatic ecosystem. Many wastewater treatment technologies are working to overcome this problem. Despite all the technologies, seaweed adsorption technology has an excellent impact on various industrial sectors because of its substantial significance. i.e., low cost, easy availability, large biomass, easy handling, obvious, and high efficiency with a low-cost investment compared to other artificial techniques used and also used for sewage treatment management. Hence, seaweed adsorption is an obvious technique to remove all the pollutants. However, biosorption is also an efficient method for trapping the contaminants in water bodies by using naturally available seaweed such as removing disinfection byproducts, heavy metals like copper and zinc, phenolic compounds, various inorganic dyes, and nitrites from water bodies. Seaweeds have been used as a low-cost adsorbent. The biosorption by seaweeds should be used as an alternative to other wastewater techniques. So, this book chapter highlights the importance of seaweed biosorption as a promising technique for treating contaminated water because of its eco-friendly nature.

Keywords Algae · Seaweed · Adsorption · Biosorption · Wastewater · Wastewater treatment

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S. Dey and M. P. Shah (eds.), *Biotechnological Removal of Emerging Pollutants from Wastewater Systems*, Advances in Wastewater Research,
https://doi.org/10.1007/978-981-96-3945-8_6

6.1 Introduction

Nature presents many obstacles to human endeavors, including population growth, food shortages, climate change, and the increasing need for naturally occurring bioactive substances (Chen et al. 2022). Replacing fossil fuels with renewable biomass can address these challenges by cutting adverse environmental impacts and protecting natural bioresources simultaneously. This process calls for quick adoption procedures and broad support (Osman et al. 2021). To live life there is an absolute need for food, clothes, and habitat is necessary. Water is considered vital to life on Earth for several reasons. It is necessary for plant growth, essential for drinking, and serves as a habitat for animals. Wastewater, conversely, refers to the polluted and hazardous water frequently utilized by humans various conventional causes interfere with water pollution, including anthropogenic sources, textile industries, religious places and agrochemical industries, etc.

Algae are a broad class of photosynthetic organisms that inhabit an array of aquatic, terrestrial, and exotic ecosystems (Wang et al. 2020). Among them, algae are essential for partially or completely purifying water found in aquatic ecosystems including freshwater, marine water, and moist terrestrial places. They can range from simple single-celled (microalgae) to complex multi-celled (macroalgae) such as seaweeds. Seaweed is a type of macroalgae that thrives in marine environments. It can be categorized into three main families based on pigmentation and other traits: brown seaweeds (Pheophyta), green seaweeds (Chlorophyta), and red seaweeds (Rhodophyta). Each seaweed plays a crucial role in the marine ecosystem providing habitat, food, and protection for other marine life. They also have various commercial uses, such as producing food products (e.g., nori for sushi), agar, and carrageenan (used in food processing), as food stabilizers and texture modifiers (Chopin and Tacon 2021), pharmaceutical products (cosmetics, drugs), and agricultural bioproducts (Sugumaran et al. 2022). Seaweeds are rapidly developing plant-like organisms that may grow up to 60 m in length in certain species. Owing to their numerous natural traits, they are utilized in a variety of industrial procedures, including bioremediation and eutrophication balancing, which manage nutrients in aquatic settings (Holdt and Edwards 2014; Kim et al. 2017). Inadequate or untreated wastewater treatment results in the discharge of contaminants that are used for different purposes in water bodies. These pollutants are becoming bioaccumulated and causing serious threats to the aquatic ecosystem. Despite all the technologies that are working to overcome this problem, seaweed adsorption technology has an excellent impact on various industrial sectors because of its substantial significance. In marine ecosystems, biosorption has been advocated as a waste-water treatment technique because of its advantages for the environment, accessibility, abundance, enormous biomass, ease of handling, obviousness, and high efficiency at a low cost of investment (Arumugam et al. 2018). To avoid nutrient contamination, improve water quality, and increase the seaweed's economic worth, it is also essential to select the right species of seaweed for use as a biofilter. Furthermore, a great deal of research has been done on the use of seaweed, such as *Palmaria palmata*, *Ulva*, *Kappa phycus*, *Hypnea aspera*, and, *Gracilaria* as

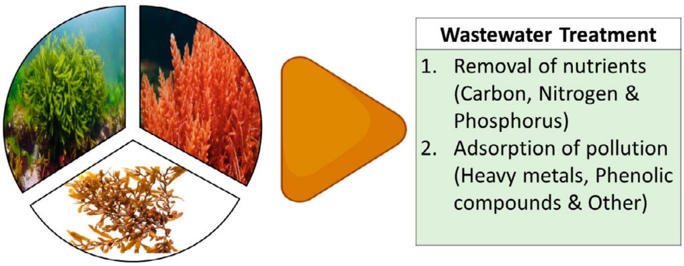

Fig. 6.1 Seaweeds used against wastewater treatment

a biofilter and biosorption (Trianti and Adharini 2020; Andayani et al. 2016; Aníbal et al. 2014; Carneiro et al. 2011; Castelar et al. 2015; Elizondo-González et al. 2018; Hayashi et al. 2008; Kang et al. 2011; Laramore et al. 2018; Neori et al. 2003; Ribeiro et al. 2017; Tremblay-Gratton et al. 2018). It has been reported that seaweeds may decrease nutrient contamination in the water shown in Fig. 6.1. Every seaweed species has a different level of biofilter efficacy (Kang et al. 2011). Seaweed physiology, water quality, beginning biomass, and water volume and circulation may all be factors (Hayashi et al. 2008). The life-suitable tolerance varies across seaweeds, affecting their ability to remove nutrients, endure, and expand. Figure 6.1 shows the activities of seaweeds against wastewater treatment.

Growing seaweed as a viable agent to treat wastewater by adsorption has recently attracted more attention. Recent research has focused a great deal of effort on the use of fungi and bacteria in bioremediation approaches. But for the best development, developing microbes could need outside carbon sources (Wang et al. 2019). Seaweeds make good bioremediation agents since they grow autotrophically. A range of polymers, such as pectin cellulose, arabino-galactan proteins, and hemicellulose, make up their cell walls. The main functional groups in the seaweed's cell walls—phosphoryl, amines, and carboxyl give them negative charges. This causes the sorption process depicted in Fig. 6.2 to begin and attracts pollutants with cationic groups to the seaweed's surface. The main reason why seaweed, or macroalgae, has such an exceptional capacity to bind impurities like trace metals is that its cellular wall contains sulphated polysaccharides, especially in the fibril matrix and intercellular gaps. The polysaccharide groups that are hydroxyl, sulfate, and carboxyl are potent ion exchangers and are crucial locations for the complexation of metal cations (Vasconcelos and Leal 2001). The preferred type of seaweed depends on its intended application. The chemical compositions of the cell walls of various kinds of seaweeds varied greatly from those previously described.

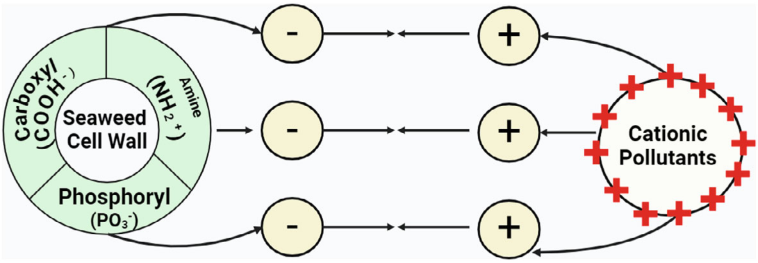

Fig. 6.2 Attraction of cationic pollutants against seaweed cell wall

6.2 Causes of Global Wastewater Production and Treatments

Wastewater is the term used globally to describe "conventionally used" water that has been degraded by human activities. The main sources of wastewater creation include commercial activities such as food processing, industrial sectors, and runoff from agriculture and domestic drinks. Even though agricultural runoff is rarely managed or handled. The term "wastewater" refers to urban (or municipal) runoff, encompassing stormwater and other urban runoff, commercial establishments, and institutions' water, industrial effluents from hospitals, and domestic effluent made up of greywater and blackwater from kitchens and baths. Wastewater can be gathered and utilized directly, or it can be dumped into a body of water, where it can be indirectly reused later on or used to assist natural flow processes. Another issue that can be seen in the water body is eutrophication, which is the result of inadequate nutrient enrichment that leads to the unintended development of simple plants. This causes water bodies to become dead zones due to the reduction of dissolved oxygen and a decrease in water quality.

6.2.1 Domestic Wastewater Treatment

Wastewater output has grown as a result of the growing urban population and the expanding footprint of residential water supplies and sewage systems. Municipal wastewater treatment should be handled properly to minimize challenges with surface water pollution and to prepare it for reuse. Domestic wastewater can be processed using a variety of techniques, including, septic tanks, soil-absorption trenches, aerated wastewater treatment (AWT) systems, and reticulated sewerage systems (Dutta et al. 2021).

6.2.2 Industrial Wastewater Treatment

Industrial wastewater has significant impacts on human health and water quality, making it a major environmental concern (Dutta et al. 2021). Many companies still lack the infrastructure and technology necessary to properly treat their wastewater, which leads to the discharge of untreated water into aquatic bodies, according to the United Nations Environment Programme (2017). Industrial wastewater treatment may be identified into five categories, according to Environmental Health and Safety (EHS): physical treatment, chemical treatment, biological treatment, advanced treatment, and disinfection including reuse and disposal etc. There are situations when there is insufficient monitoring of industrial wastewater, which results in a constrained comprehension of the problem's scope and poor response to it (Rana et al. 2022).

6.2.3 Eutrophication of Water and Its Treatment

The problem of surface water eutrophication was initially identified in the 1970s and 1980s and is still a major global concern, leading to a notable decline in the ecosystem services that aquatic systems supply. Deepening eutrophication is closely associated with rising anthropogenic nutrient loads, mostly nitrogen and phosphorus discharged into surface waters from diverse sources. These restrictions, which have gotten increasingly strict concerning nutrient content, have led to the use of expensive and complex wastewater treatment systems that apply advanced nutrient removal methods (Bartosova et al. 2019).

6.3 Challenges of Wastewater Treatment Techniques

Because of this, modern scientists utilized a range of techniques, including chemical, biological, and physical ones, to clean wastewater. Every one of these strategies has advantages and disadvantages. Unfortunately, widely available information on the operation and protocols of each method utilized to eliminate different pollutants is still inadequate. Some explored challenges of wastewater treatment techniques are composing complex contaminants, energy demands, conventional methods, emerging contaminants, sludge management, public acceptance, legal aspects, water scarcity, climate change, and technological advancements. In summary, wastewater treatment faces multiple technological challenges, but ongoing research and innovations offer hope for more effective, easy processing and sustainable techniques in the future. The potential of seaweed biosorption to remove toxins from water and make it beneficial again has generated a lot of interest in the continuing study because of its accessibility, cost-effectiveness when compared to other options for treatment, and sustainability (Bartosova et al. 2019; Marinho-Soriano et al. 2011).

6.4 Potential Use of Seaweed for Wastewater Treatment

Reclamation of wastewater is a crucial purification process for the efficient use and handling of water resources. It also acts as a sustainable way to protect aquatic ecosystems from harmful pollution and eutrophication, as well as to raise the standards for water quality. Because aquaculture effluents have a high suspended particle content, the wastewater treatment procedures used today are costly, time-consuming, and inefficient. Growing seaweed seems to be a good alternative method of wastewater treatment. They absorb nitrogen and phosphorus from wastewater and retain it in their tissues, much like a sponge. Seaweeds employ these resources for growth by storing them as pigments and amino acids required in photosynthetic activities. Similar to other plants, seaweeds, macroalgae, and wastewater treatment all release oxygen and collect carbon dioxide. They also apply fertilizer derived from other metabolic waste products. The selection parameters for acceptable seaweed for phytoremediation include growth rate, adaptability to growing techniques, life cycle information, capability for nutrient storage, and filtering capacity. As a result, seaweeds are an effective stand-in method for cleaning aquaculture effluent, enhancing water quality, and giving farmers a source of revenue (Marinho-Soriano et al. 2011).

6.5 Seaweed Approaches in the Treatment of Wastewater

6.5.1 Removal of Nitrogen and Phosphorus

There are too many uses for nitrogen and phosphorus in human existence. Crop production, the extraction of fossil fuels, and the cultivation of leguminous plants are a few examples of human activity. Excess of phosphorus and nitrogen from anthropogenic sources aids in depletion in water bodies (Camargo and Alonso 2006; Sonarghare et al. 2020; Zhang et al. 2023). This results in a higher frequency of harmful algal blooms (Carpenter 2008; Glibert et al. 2018) and hypoxia. Since eutrophication increases the frequency of fish deaths, lowers water clarity, and weakens coral reef health and community structure, it has become a prevalent concern for water quality in most freshwater and marine ecological systems. In the future, these nutrients may also be utilized to promote the dense formation of seaweeds, an extremely profitable type of aquatic plant life (Kim et al. 2014). Demand is very high for seaweed's capability to sustain a high concentration of nitrogen in its tissue. The bio-extraction of inorganic nutrients from seaweeds has been the subject of much interest from several research organizations and investigators. A selection of the experiments conducted over the last ten years to eliminate inorganic nutrients are displayed in Table 6.1. The majority of the seaweeds on this list function as a biofilter between contaminants and wastewater. Nitrogen and phosphorus may be significantly biologically removed from wastewater by using seaweeds (Table 6.1). Nitrate and ammonia–nitrogen, two important nitrogen compounds found in sewage, industrial, and agricultural water discharges, may be used by seaweeds (Wang et al. 2020). They found that the amount of nitrogen and phosphorus removed by China's seaweed farms was around 75 and 9.5 megatonnes, respectively. Experts estimate that the seaweed industry will have eliminated 100% of the phosphorus from Chinese coastal waters by 2026 (Jagtap and Meena 2022). A culture of *Gracilaria lemaneiformis* can extract 12.10 tonnes of nitrogen, 1192.03 tonnes of carbon, and 15.89 tonnes of phosphorus from the waters of Yantian Bay, as reported by (Duan et al. 2019).

6.5.2 Removal of Heavy Metals

One of the primary environmental risks posed by recent events is the contamination from heavy metals and their absorption through water. These heavy metals, which are a result of both human and herbal operations, have an immediate negative impact on living things and human health. The advancement of technology has increased the amount of contaminants from heavy metals in the environment. Because heavy metals are hazardous to the environment and living things, removing them from wastewater is a huge environmental concern that has received a lot of attention lately (Fei et al. 2022). Numerous anthropogenic sources, such as metal smelters, paint producers, fertilizers, agricultural operations, leather tanning, electroplating, alloy and battery production, and the disposal of various industrial waste products, can contribute to the presence of heavy metals in wastewater (Arumugam et al. 2018; Ozay et al. 2009). Nickel (Ni), arsenic (As), chromium (Cr), copper (Cu), lead (Pb), cadmium (Cd), mercury (Hg), and arsenic (As) are among the heavy metals that are of great concern worldwide (Islam et al. 2015). Noncancer adverse health effects can also result from environmental exposure (Cohen et al. 2013). So far, a range of treatment methods, including flotation, coagulation, ion exchange, electrodialysis, ultrafiltration, reverse osmosis, nanofiltration, flocculation, and chemical precipitation procedures, have been used to achieve heavy metal decontamination. However, these tactics, in particular, have some shortcomings when compared to other alternatives. As the most used method to eliminate heavy metals, adsorption is cheap, efficient, straightforward, and adaptable. The list of common seaweeds used to remove heavy metals is compiled in Table 6.2.

6.5.3 Removal of Dyes

The most practical adsorption treatments that are employed as superior treatment procedures are required to handle the dissolved organic pollutants, such as dyes derived from the pulp manufacturing, paper, and textile, food coloring, and carpet and cosmetics sectors. Large amounts of dyes that are harmful to aquatic life and mammals, even potentially carcinogenic, are allegedly used in these sectors. Most dyes used in the textile industry are resistant to aerobic digestion and are not

Table 6.1 Approaches of seaweed for removing nitrogen and phosphorus

Seaweed category	Species	Type of wastewater	Contaminants	Treatment conditions	Reduction rate of pollutants	References
Red seaweed	*Gracilaria lemanaeformis*	Aquaculture	Nitrogen and phosphates	Co-culture with the fish *Pseudosciaena crocea* Cage aquaculture Seawater with a salinity of 26–29 for 20 days	$N = 21.0\%$ & $P = 28.6\%$	Wei et al. (2017)
	Gracilaria tikvahiae	Shrimp wastewater	Nitrogen	Co-cultured along pacific white shrimp *Litopenaues vannamei*	$N = 35\%$	Samocha et al. (2015)
	Gracilaria chouae	Aquaculture water (Bay water)	Nitrogen and Phosphate	co-cultured along *Sparus macrocephalus*, the black sea bream	N = 41.2% P = 46.2%	Wu et al. (2015)
	Chondrus crispus	Finfish culture effluent	Nitrogen	Land-based Atlantic halibut (*Hippoglossus hippoglossus*) farm	Net $N = 2.0\ kgm^{-2}$ (at $T = 6$ and 13 °C)	Kim et al. (2013)
	Palmaria palmata			Land-based Atlantic halibut farm $t = 28$ d each trial	Net $N = 2.0\ kgm^{-2}$ (at $T = 6$ °C) Net $N = 4.0\ kgm^{-2}$ (at $T = 16$ °C)	
	Gracilaria vermiculophylla	Aquaculture effluents	Nitrogen	Land-based pilot scale system	–	Abreu et al. (2011)
	Gracilaria birdiae	Shrimp wastewater	Phosphate and Nitrate	Salinity of 30.1–30.7 PSU	Phosphate = 93.5%	Marinho-Soriano et al. (2011)

(continued)

Table 6.1 (continued)

Seaweed category	Species	Type of wastewater	Contaminants	Treatment conditions	Reduction rate of pollutants	References
	Gracilaria verrucosa	–	–	Co-cultured with the fish *Pseudosciaena crocea*	–	Huo et al. (2012)
Green seaweed	*Ulva lactuca*	water from waste from sewage sludge that has undergone anaerobically digested	Nitrogen and phosphorus	Salinity of 20% from artificial seawater $T = 15$ °C pH = 7.9–8.9 $t = 18$ d	$N = 22.7$ mg N g DW^{-1} d^{-1} P = 2.7 mg P g DW^{-1} d^{-1}	Sode et al. (2013)

Table 6.2 Approaches of seaweed for removing heavy metals

Seaweed category	Species	Type of wastewater	Contaminants	Treatment conditions	Reduction rate of pollutants	References
Brown seaweed	*Sargassum muticum*	Simulated wastewater	Sb^{3+}	Adsorbent = 100 mg Ion concentration = 10 mg/L Adsorbent size = 5 mm rpm = 200 $T = 23$ °C $t = 6$ h	*Aschophyllum nodosum* is not equally successful at removal as *Sargassum muticum*	Ungureanu et al. (2015)
	Sargassum filipendula	Simulated wastewater	Pb^{2+}	Adsorbent = 0.49 g/L Ion concentration = 152.10 pH = 4.99 mg/L $T = 34.8$ °C	96%	Verma et al. (2016)
Red seaweed	*Osmundea pinnatifid*	Simulated wastewater	Cu^{2+} and Cd^{2+}	rpm = 500 $t = 60$ min Biomass = 1 g Biomass size = 0.5 mm pH = 5 Ion concentration $T = 25$ °C	Cd^{2+} = 57.29% (concentration = 20 mg/L, ion concntration = 100 mg/L t = 180 min), Cu^{2+} = 50.89% (pH = 5, biomass = 20 g/L, ion concentration = 100 mg/L, t = 180 min)	Hassouni et al. (2014)
	Chondracanthus chamissoi	Aqueous solution	Pb(II) and Cd(II)	Ion concentration = 70 mg/L Adsorbent = 20 mg t = 48 h pH = 4	Cd(II) = 0.76 mmol/g Pb(II) = 1.37 mmol/g	Yipmantin et al. (2011)
Green seaweed	*Ulva rigida*	Simulated wastewater	As^{3+}, As^{5+}, Sb^{3+}, Se^{4+} and Se^{6+}	Ion concentration = 25 Adsorbent size = 0.5 $T = 20$ °C mg/L Adsorbent = 0.5 g rpm = 180 cm t = 5 h	Se^{4+} = 0.5 mg/g (pH = 2–4) Se^{6+} = 0.2 mg/g (pH = 2–3)	Sode et al. (2013)

biodegradable. Methylene blue and malachite green are the two colors that appear most frequently in wastewater. Research was done on several low-cost adsorbents and their application in dye removal, along with a search for more affordable and readily available materials. Adsorbents used to remove methylene blue include activated carbons (AC) such as those based on olives (Berrios et al. 2012), Karanj fruit hulls (Islam et al. 2017), and waste-based ACs such as cashew nut shells (Spagnoli et al. 2017), *Ficus carica* bast fiber-based (Pathania et al. 2017), *Daucus carota* plant-based (Kushwaha et al. 2014), and *Salix psammophila* plant-based (Bao and Zhang 2012), potato peel-based (Sartape et al. 2017), and *Limonia acidissima* shell-based (Guechi and Hamdaoui 2016). Several waste-based adsorbents, notably ACs, are employed to remove the green color malachite. The common polluting colors found in wastewater are listed in Table 6.3, along with methylene blue and malachite green. Most of the removal strategies employed seaweed as an adsorbent, and some ongoing studies continue to use natural seaweeds. The presence of active functional groups in the seaweed's cell wall, such as amine, sulfate, carboxyl, hydroxyl, and carbonyl, that participated in the biosorption process is the main motivation to study the adsorption of dyes by seaweed. Kinetic reaction research showed that data fit the pseudo-second-order kinetic model well, demonstrating that the wastewater dye removal process utilized the chemisorption technique (Mokhtar et al. 2017).

6.5.4 Removal of Phenolic Compounds

Better for manufacturing, phenol is generated and employed gradually. It has several uses, such as an antimicrobial reagent and phenolic resin. It also finds use in the agrochemical, bioplastic, and petrochemical sectors as a pesticide. Additionally, phenol is a flexible precursor used in a wide range of medications, including pain relievers like aspirin, herbicides (which destroy undesired flora), perfumes, medicines, and cosmetics including skin lightening agents, hair colorants, sunscreens, and exfoliants. It is a fundamental commodity chemical that is used to create several important industrial compounds and polymers, such as phenolic resins and bisphenol A (Takkellapati et al. 2018). Thus, from the above investigations phenolic pollutants broadly exist in wastewater released from agrochemical industries, chemical plants, cooking plants, or petroleum refineries (Zhang et al. 2011). As phenolic chemicals have a significant potential for toxicity, carcinogenicity, teratogenicity, and mutagenicity in living things, they must be removed from wastewater. Nevertheless, phenolic chemicals found in aquatic environments are challenging to address with the current arsenal of conventional treatment techniques alone (Ahmaruzzaman et al. 2024). However, the wastewater treatment business has also looked at biological treatment and adsorption, particularly using macroalgae (Arumugam et al. 2018; Mahdizadeh et al. 2018). According to multiple studies, phenolic chemical biosorption caused by administering seaweeds involve a donor–acceptor mechanism and a hydrophobic connection (Arumugam et al. 2018; Rubín et al. 2006). Several methods for the removal of phenolic compounds have received an extensive amount of interest recently, including

Table 6.3 Approaches of seaweed for removing dyes

Seaweed category	Species	Type of wastewater	Contaminants	Treatment conditions	Reduction rate of pollutants	References
Brown seaweed	*Nizamuddinia zanardinii*	Pure textile methylene blue solution	Methylene blue	Concentration = 160 mg/L) pH = 6.5 dye	565.96 mg/g (*Nizamuddinia zanardinii*)	Kousha et al. (2012)
	Sargassum muticum	Aqueous solution	Methylene blue	Dye concentration = 50 mg/dm^3 Adsorbent size = 0.5–1 mm T = 25 °C rpm = 175 t = 4 h pH = 4 Biomass = 0.125 g	98.2% (Treated with HCl) 98.0% (Treated with H_2CO 97.4% (Treated with $CaCl_2$)	Rubín et al. (2006)
Red Seaweed	*Gracilaria parvispora*	Pure textile methylene blue solution	Methylene blue	Dye concentration = 160 mg/L) pH = 6.5	77.18 mg/g (*Gracilaria parvispora*)	Kousha et al. (2012)
Green seaweed	*Ulva lactuca*	Aqueous solution	Malachite green	Biomass size = 1.0 mm t = 150 T = 25 °C min pH = 8.0 Biomass = 2.0 g	94.5% (T = 25 °C) 93.8% (pH = 8.0) 97% (t = 150 min)	Omar et al. (2018)

the employment of fungi and bacteria in bioremediation. However, external carbon sources could be necessary for the optimum development of developing microorganisms (Wang et al. 2020). Because of their chemical makeup, pollutants discovered in the environment are positively charged, or cationic. However, these cationic contaminants are drawn to the negatively charged functional groups on the seaweed's cell walls. The removal of seaweed is a popular and practical technique investigated how the seaweed *Macrocystis integrifolia* and *Lessonia nigrescens* sorb phenol chemicals (Navarro et al. 2008). Because Macrocystis integrifolia exhibited both an electrostatic sorption process and a completely polar sorption pathway, the results revealed that it displayed the highest sorption efficiency of 35% at pH10. This study demonstrated that hydrogen bond interactions between the hydroxyl groups of the polysaccharides including alginates found in the seaweed's cell wall and phenol are accountable for the process of phenol adsorption onto the seaweed's surface. By using seaweed biomass to study the biosorption of toluene and benzene, common aromatic hydrocarbons were discovered. The findings revealed that Phaeophytes could extract benzene and toluene at rates of 28 and 112 mg/gram, respectively. The sorption process was ascribed to hydrophobic contact with lipids and, to a lesser extent, with carbohydrates and proteins, through non-specific Van der Waals connections.

6.6 Conclusion

Researchers' interest in the numerous uses of seaweeds in wastewater treatment has increased, underscoring the significance of seaweeds in modern times. The mentioned uses and functions of seaweeds will require the ongoing development and availability of quality raw seaweeds resources. It is anticipated that seaweed-based industries will likely improve socio-economic conditions. Since seaweeds are among the most intriguing and complicated living resources, there is no doubt that we still have a lot of opportunities to learn from these unusual yet resourceful species. The goal of this book chapter is to provide a general overview of seaweeds used in wastewater treatment. With naturally occurring raw materials and enhanced efficacy at a minimal treatment cost, biosorption with seaweeds is a promising technique. It is evident that the majority of research is simulations and that very few studies used actual wastewater for treatment. Therefore, it is advised that more attention be paid to treatment using actual wastewater in future research. Because seaweeds does not mimic the complicated properties of real wastewater, it may have certain drawbacks to treating synthetic or simulated. Furthermore, probably, the outcomes of wastewater simulations won't translate to actual wastewater treatment facilities (WWTP). By eliminating impurities and extra nutrients, seaweeds may turn wastewater into useful resources. Currently, wastewater receives therapy via seaweeds farming to eliminate uranium and plutonium. Pollution can be decreased by growing seaweeds on industrial effluents.

Funding No funding was received for this contribution.

Conflicts of Interest The author declares no conflict of interest.

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Chapter 7
Removal of Phosphate from Wastewater Using Natural Coagulants Prepared from Leaves of *Xanthium Strumarium*

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7.1 Introduction

7.1.1 Overview of Wastewater Pollution and Its Impact

Water is a crucial resource for the survival of mankind. According to UNESCO's (2021) World Water Development Report, globally freshwater use has increased sixfold over the last century and has been expanding at a pace of approximately 1% per year since 1980. Water quality is worsening as water demand increases. Industrialization, agricultural production, and urbanization have all contributed to environmental degradation and pollution, which has had a severe impact on water bodies (Lin et al. 2022).

Water contamination is the introduction of dangerous or undesired substances into water, making it unsafe for its intended use or hazardous to the environment. Contaminants might be biological, chemical, or physical. Water contamination can be detrimental to human health, ecosystems, and overall water quality.

In general, wastewater is divided into two categories: sewage wastewater and non-sewage wastewater (Schoen and Ashbolt 2010). Sewage wastewater includes outflow from household activities. Sewage wastewater is produced in places such as homes, schools, hospitals, hotels, restaurants, public toilets, and so on and contains bodily wastes (urine and feces). Non-sewage wastewater refers to all other types of wastewater generated by commercial activities, such as those from factories and industrial plants. Stormwater and rainwater generated by rainfall or flood events are also considered non-sewage wastewater (Ahmed et al. 2021).

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S. Dey and M. P. Shah (eds.), *Biotechnological Removal of Emerging Pollutants from Wastewater Systems*, Advances in Wastewater Research,
https://doi.org/10.1007/978-981-96-3945-8_7

The widespread industrialization and population density in urbanized civilizations have presented substantial issues in wastewater management. Household and commercial operations contribute to the pollution of water bodies by creating effluents with various contaminants. These contaminants include pathogenic bacteria, phosphate and nitrogen, hydrocarbons, heavy metals, endocrine disruptors, and organic materials. Water-related illnesses like cholera, typhoid fever, and diarrhea are usually caused by hazardous bacteria in contaminated water. Furthermore, excessive phosphorus and nitrogen can cause eutrophication, which promotes the growth of toxin-producing cyanobacteria. Exposure to these poisons can result in a variety of ailments. Furthermore, non-biodegradable and persistent contaminants represent a risk because they remain in natural ecosystems and accumulate in the food chain over time (Akpor et al. 2014).

One of the most serious hazards to aquatic organisms is the presence of contaminants in wastewater effluent. The principal contaminants in wastewater include nutrients (nitrogen and phosphorus), hydrocarbons, heavy metals, and microorganisms (Akpor et al. 2014).

7.2 Phosphate Pollution: A Critical Environmental Concern

Phosphates are a common water contaminant and a primary contributor to eutrophication in lakes and natural waters. Phosphorus, the eleventh most prevalent element on Earth, is commonly found as phosphate in ores such as fluorapatite and hydroxyapatite. Water quality issues resulting in higher purification costs, reduced recreational and conservation value of impoundments, livestock loss, and potential health risks from algal toxins in eutrophic water supplies have arisen due to the presence of phosphates. The earth's crust contains ores such as fluorapatite and hydroxyapatite (Badamasi et al. 2019).

Phosphorus is the primary nutrient responsible for eutrophication (Correll 1998), as it has a higher ratio in plant content compared to its availability in water (Badamasi et al. 2019). Algal growth is most likely to accelerate due to phosphorus additions in freshwater conditions. Nitrogen and phosphorus together stimulate growth the most (Elser et al. 1990). Eutrophication caused by high levels of phosphate and nitrate can lead to hypoxia and anoxia in aquatic life. Increased concentration of phytoplankton and zooplankton excreta may lead to phosphate increase. In 1974, an International Congress of Limnologists emphasized the critical role of phosphorus in eutrophication (Badamasi et al. 2019).

Natural water and wastewater hold most of the phosphorus in the form of orthophosphate ions. However, using the total phosphorus as a quantitative indicator in wastewater is not effective because various types of phosphorus have different mobility and availability. The Soluble Reactive Phosphorus (SRP) and the orthophosphate/SRP ratio are necessary to identify the accessible form of phosphorus in wastewater (González Medeiros et al. 2005; Comber et al. 2015; Maruo et al. 2016). To prevent eutrophication, the total P shouldn't go above 0.05 mg/L at the stream's admission point into a lake or reservoir, and 0.1 mg per liter in streams that do not directly flow into lakes or reservoirs (Nobaharan et al. 2021).

7.2.1 Challenges in Phosphate Removal from Waste Waster

To remove particles, organic matter, and nutrients, traditional wastewater treatment procedures use a combination of physical, chemical, and biological processes. Adsorption, photo-degradation, coagulation-flocculation, ionic exchange, precipitation, and biological and membrane separation (Zaher and Shehata 2021) are common sub-processes used to achieve treated wastewater with specific characteristics (Obaideen et al. 2022).

Water scarcity is a global concern because of urbanization, industry, and population increase, which causes pollution and economic, human, and environmental instability (Malik et al. 2015). Wastewater, formerly deemed inconsequential, is now a valuable supply of clean water for both non-potable and potable applications. Wastewater can be filtered and treated for human consumption, industrial usage, irrigation, and washing. Recycled wastewater provides numerous benefits to society in various ways. However, greater investigation of its application is required to maximize its benefits. Converting wastewater into reused water has enormous promise for many cultures, and stakeholders are looking at ways to make better use of it. Wastewater can be used to achieve the Sustainable Development by providing drinking water and sanitation (Obaideen et al. 2022).

Wastewater treatment decreases waste and protects natural resources, particularly in areas with acute water scarcity. Natural resources are depleting as the population and demand for water grow, and deforestation poses a significant threat to their sustainability (Gernaey et al. 2004). Wastewater treatment can help address these challenges by ensuring an adequate water supply for human and industrial usage. Climate change, drought effects, urbanization, farming, and population growth are all contributing to a decrease in clean water sources around the world, according to scientific studies. If no measure is taken, many of present-day sources of water will be depleted over the next decade. Treatment of wastewater is a key step toward regulating the supply and demand for clean water. Treatment of wastewater is a key step toward balancing the supply and requirement for clean water. Wastewater treatment is an important way to balance the supply and demand for clean water. Organic fertilizers from wastewater treatment are more environmentally friendly and provide rich nutrients to support growth and offer nutritional benefits to consumers. The use of natural fertilizers enhances soil sustainability by reducing the risk of acidification (Silva 2023).

Technology helps to discover weak points in the process and prevent future disasters. Furthermore, it promotes sustainability by providing policymakers with informed tools for making timely decisions (Van der Bruggen 2021; Brame et al.

2011; Palansooriya et al. 2020). The adoption of contemporary wastewater treatment technology increases its cost-effectiveness and efficiency. AI investments are crucial for automating activities, reducing waste, and enhancing overall operational efficiency (Łuczkiewicz et al. 2010; Vymazal 2010).

Sustainable resource management entails using technology to help make decisions and monitor natural resources in order to reduce potential hazards (Silva 2023).

Wastewater treatment is critical for maintaining sustainable cities and managing rising urban water demand. Industrial use accounts for 90% of overall water consumption, whereas families can contribute to water conservation by adopting water-saving habits. Wastewater treatment plants have been developed in many places throughout the world to improve water supply and hygiene. Decentralized wastewater treatment facilities offer long-term solutions, particularly in locations where water shortage is a serious concern. Such plants educate communities about the benefits of wastewater treatment and allow people to build up wastewater treatment facilities in their own houses. This is vital for maintaining high cleanliness standards and preventing dangerous infections (Silva 2023).

Sustainable wastewater treatment is critical for protecting both the environment and human health. By successfully managing wastewater, we reduce the release of dangerous chemicals into water bodies, safeguarding aquatic ecosystems and biodiversity. Furthermore, sustainable treatment methods enable the collection and reuse of valuable resources found in wastewater, minimizing pressure on natural resources and encouraging a circular economy.

7.3 Innovation in Wastewater Treatment Methods

Innovation in techniques for treating wastewater have been a critical area of focus due to increasing environmental concerns and the need for sustainable water management. In todays world, the presence of a group of pollutants, nominated as arising pollutants (ECs), has been honored as significant water adulterants that have adverse goods on mortal and wildlife endocrine systems. Several innovative approaches have emerged in recent years, leveraging advanced technologies and novel concepts to enhance efficiency, reduce costs, and minimize environmental impact. Over time, non-conventional water treatment procedures have changed because of new approaches being developed; they may be used to group these therapies: phase-changing technologies, improved oxidation processes, and biological treatment (Rout et al. 2021; Chen et al. 2022).

Advanced oxidation processes (AOPs) are considered a largely competitive technology regarding water treatments all for dumping of biotic pollutants classed as biodefiant and for the inactivation of pathogen microorganisms not treatable by usual ways. AOPs were first indicated for drinking water treatments in 1980 (NHMRC-NRMMC 2011; Chen et al. 2022). After moments, they were considerably studied as oxidizing treatments applied to different wastewaters, which are defined as the oxidation processes involving the generation of hydroxyl revolutionaries ($OH^{\bullet}$) in sufficient volume to sequel water sanctification. Advanced oxidation processes (AOPs) are methods that use strong oxidizing agents to break down pollutants. Among the strongest oxidizing revolutionaries exercised are the hydroxyl revolutionary ($^{\bullet}OH$) and sulfate revolutionary $\left(SO_4^{\cdot-}\right)$ (Rathi and Kumar 2021; Kumar et al. 2022). When AOPs are used to treat wastewater, these revolutionaries, as an important oxidizing agent, are anticipated to sufficiently destruct wastewater adulterants, and transfigure them to lower and indeed non-toxic productions, thereby furnishing an ultimate result for wastewater treatment (Acero et al. 2012; D = Garrido-Cardenas et al. 2020). AOPs are environmentally friendly chemical processes that can convert organic pollutants into inoffensive productions that do not transfer pollutants from one stage to another or produce large amounts of slush. This approach has several advantages, such as rapid-fire response classes that reduce retention times compared to other conventional treatment methods and the fact that it does not require a large area for recycling the system's required inflow rate. However, there are also several disadvantages, including high operating and conservation costs. It also has a daedal chemistry acclimatized to special pollutants which requires professed labor force to design the system (Varsha et al. 2022; Fernández-García et al. 2015; Amor et al. 2019).

Naturally, the primary and crucial stage among the wastewater treatment system is wastewater treatment, which handles wastewater from homes, businesses, etc. Exercise is a crucial component of the "Secondary Treatment Process," which aims to remove any toxins left behind after the initial therapy failed. Whereas biological treatment breaks down wastewater pollutants with microorganisms, chemical treatment employs chemicals to react with the poisons in the wastewater (Leichtweis et al. 2022). This therapy uses rotifers, algae, fungi, bacteria, worms, and protozoa to convert unstable organic wastes into stable inorganic forms. Wastewater that has undertaken biological treatment may be roughly divorced into two groups based on the methods involved: These are treatments that are biologically both aerobic and anaerobic (in the absence of oxygen) (Rekhate and Srivastava 2020).

Exploration of natural coagulants and adsorbents represents novel techniques for treating wastewater, providing long-term substitutes for conventional methods. By utilizing the inherent properties of both organic and inorganic materials, wastewater pollutants may be eliminated by employing natural coagulants, and adsorbents plants, minerals, and biomass are a few instances of their sources. Through a mix of physical and chemical processes, contaminants, suspended particles, and organic waste may be removed thanks to the coagulation and adsorption capabilities of these materials. References for natural coagulants include activated carbon, clay minerals, zeolites, and plant extracts derived from Moringa oleifera seeds. Other naturally occurring coagulants include chitosan from crab shells and tannins from tree bark. With natural coagulants and adsorbents being more affordable and ecologically friendly, and sustainable than synthetic chemicals—which are usually used in wastewater treatment—they are gaining popularity. These inventive techniques, which employ nature's inherent abilities, offer reassuring solutions for addressing water pollution and promoting environmental sustainability (Badawi et al 2023; Giannakis et al. 2018; Musa and Idrus 2021).

The use of natural coagulants and adsorbents rather than traditional chemical ones has several benefits. Most significantly, their biodegradability and regenerative nature lessen our dependency on scarce fossil fuels and impede environmental deterioration (Zaher and Shehata 2021). They have a variety of naturally occurring sources. Natural coagulants and adsorbents are readily available, reasonably priced alternatives during resource shortages. Most of these compounds leave little to no toxic residue, which lessens their impact on the environment and helps with extra control. By harnessing the power of nature, natural coagulants and adsorbents purify wastewater in an environmentally responsible and long-lasting way. Green chemistry and the circular economy are promoted by this approach (Du et al 2023; Khan et al. 2022; Bahrodin et al. 2021).

Nevertheless, there are several issues with using natural coagulants and adsorbents that need to be resolved to optimize their effectiveness and suitability for wastewater treatment. The variation in natural materials' composition and qualities, which might impact treatment efficacy and uniformity, is a major obstacle (Amor et al. 2019; Moreira et al. 2017). Standardization and quality control procedures must be implemented to guarantee consistent and repeatable outcomes across various waste types of compositions and treatment scenarios. Additionally, determining the optimal dosage of natural coagulants and adsorbents for specific applications may require extensive experimentation and optimization, adding complexity to treatment processes. Furthermore, some natural materials may exhibit degradation or loss of efficacy over time, necessitating periodic replenishment or replacement to maintain treatment efficiency (Muniz et al. 2020). To tackle these obstacles, multidisciplinary cooperation is a necessary investment in research and development, and the development of robust protocols and guidelines for the selection, utilization, and optimization of natural coagulants and adsorbents in wastewater treatment.

7.3.1 Advantages and Challenges of Using Biomass-Based Coagulants in Wastewater Treatment

Contaminant junking from wastewater utilizing natural biosorbents has been thoroughly investigated as an able and environmentally benign volition for usual ways. Biomass-grounded coagulants, deduced from organic accouterments such as agricultural residue, food waste, and algae, offer a sustainable and environmentally friendly alternative to synthetic chemicals (Yadav et al. 2021). These biomass-derived substances contain bioactive compounds capable of promoting coagulation and flocculation processes, facilitating the removal of suspended solids, organic matter, and pollutants from wastewater. Advantages of using biomass-based coagulants include their renewability, value addition to biomass residues, and biocompatibility, which minimize adverse effects on aquatic ecosystems and human health. However, challenges such as feedstock availability and quality, extraction and processing complexities, and performance optimization requirements must be addressed to maximize the efficacy and applicability of biomass-based coagulants in wastewater treatment (Kumar et al 2017, 2021). Future studies should look at new sources of biomass, extraction techniques, and formulation strategies, additionally integrating biomass-based coagulants into circular economy frameworks to enhance sustainability and resource efficiency (Loh et al. 2021).

This mainly takes into seat a wide range of biomass-grounded mixes like hydrogel mixes, essence oxide mixes, glamorous mixes, polymer mixes, carbon copy nanotubes (CNTs) and graphene mixes, essence organic frame mixes (MOFs), and complexion mixes for the junking of colorful pollutants from wastewater (Nasir et al. 2022). The review of the literature makes it clear that the process of compound manufacturing entails modifying the biomass's morphological and textural characteristics, which significantly increases the material's adsorption capability. By utilizing organic materials including food waste, algae, and agricultural wastes, biomass-based coagulants are an additional cutting-edge method of treating wastewater. By offering renewable and biodegradable alternatives to conventional chemical coagulants, these biomass-derived products support resource conservation and environmental sustainability. Resolving difficulties related to feedstock availability, processing complexity, and performance optimization is necessarily arranged to optimize the efficacy and practicality of biomass-based coagulants in wastewater treatment (Kurniawan et al. 2020). A major challenge is the difference in biomass content and quality, which may affect the coagulant's consistency and efficacy. Biomass-based coagulants may also require specialist equipment and skills to extract and process, which might increase manufacturing costs when compared to chemical coagulants. Moreover, optimizing dosage and application methods to achieve the desired treatment outcomes can be complex due to the diverse nature of biomass materials (López-Sánchez et al. 2022; Koul et al. 2022).

7.4 *Xanthium Strumarium* as a Natural Coagulant

The medicinal plant *Xanthium strumarium* (Common Cocklebur) belongs to the Asteraceae or Compositae family. *Xanthium strumarium* is used in traditional medicine for treating various ailments such as malaria, diabetes, and cancer. The plant also has anti-inflammatory, anti-nociceptive, and anti-oxidative activity which can help control arthritis.

X. strumarium is a perennial plant that can grow up to 1 m in height. In warmer climates, it can be found in landfills, on roadsides, and along riverbanks. The leaves are broadly alternating, light green in color, and 5–15 cm long, with uneven lobes and relatively little teeth. The plant has a short, robust, hairy stem, strongly veined leaves, and long petioles (Fan et al. 2019).

Anodyne, antirheumatic, antisyphilitic, appetizer, diaphoretic, diuretic, emollient, laxative, and sedative properties are among the medicinal uses for the plant's leaves and roots. The fruits are utilized both internally and externally to treat a variety of illnesses. They contain a variety of compounds, such as phytosterols and glycosides. The leaves are used as a tonic, diuretic, and sedative; the roots are used to treat cancer. The dried leaves have been used as blue body paint and are a source of tannin. The dried plant has an essential oil that keeps weevils away from stored wheat grain. Cocklebur, a leafy vegetable in China, is cultivated as a pot-herb in Assam. It is suspected to be poisonous, but toxic substances can be removed through washing and cooking. *Xanthium*, a toxic herb, is used for treating sinus congestion and has antitumor and anticancer properties. Pollens can cause asthma, rhinitis, and dermatitis in susceptible individuals. *Xanthium* is classified as a herb for dispelling wind chill or damp and is used mainly for allergy-type disorders (Fan et al. 2019).

The plant extract demonstrated antimicrobial activity against various bacteria and fungi due to the presence of xanthol. It also contains xanthinin, which acts as a plant growth regulator and has antibacterial properties. The extract has shown inhibition of human tumor cell proliferation and farnesylation process (Fan et al. 2019). Additionally, it exhibited strong antibacterial activity against gram-negative bacteria and fungi. The study also revealed its antitumor activities and cellular toxicities, showing promising results in comparison to existing antitumor agents (Little et al. 1950).

Furthermore, the plant extract showed significant in vitro antimycobacterium activities against *Mycobacterium tuberculosis* and *Mycobacterium smegmatis.* It also exhibited anticancer activity against various human cell lines (Fouché et al. 2008).

7.4.1 Rationale for Selecting **Xanthium Strumarium** *as a Coagulant*

Coagulation and flocculation are widely used methods for wastewater treatment due to their effectiveness and relatively low cost compared to other methods. These processes involve adding inorganic coagulants to promote the agglomeration of colloids. However, excessive use of these coagulants can pose health risks and lead to the production of non-biodegradable sludge. As a result, there is growing interest in exploring natural coagulants as a potential alternative to reduce or replace the use of inorganic coagulants. Natural coagulants can be classified as proteins, polyphenols, and polysaccharides. Protein-based coagulants like Moringa oleifera are widely studied, but face challenges in extraction and storage. Polyphenol-based coagulants have limited studies, while plant-based polysaccharides like starch and gums show potential for wastewater treatment. Microbial polysaccharides from sources like *Serratia marcescens* and xanthan gum from Xanthomonas campestris are also used for coagulation. Despite their high coagulation activity, challenges in production and purification persist, particularly for microbial polysaccharides. Xanthan gum has various environmental applications and has been used for water purification and flocculation, but its use for dye wastewater treatment is limited. The use of xanthan gum as a coagulant aid offers a viable alternative to potentially harmful polymeric flocculants such as polyacrylamide (PAM) and polydiallyldimethylammonium chloride (PDADMAC). Previous research has raised concerns regarding the toxicity of PAM and PDADMAC to a variety of taxa, including microbes, freshwater creatures, fish embryos, and humans. In contrast, xanthan gum has been approved for use with no safety concerns (Fouché et al. 2008).

Xanthium strumarium has the potential to be used as a natural adsorbent for textile wastewater treatment. The Freundlich model was found to best fit the adsorption data, with high R2 values and low errors. The adsorption process was shown to be endothermic, with a two-stage kinetic process resulting in 95% decoloration in 60 min. Research showed that *Xanthium strumarium* is a more cost-effective and efficient alternative to activated carbon for treating colorful effluents (Shraddha et al. 2020).

7.5 Methodology

7.5.1 Sample Collection and Preparation

Plant Material Collection

Xanthium strumarium, commonly known as Cockleburs, was gathered from the Sootea area in the Sonitpur district of Assam, Northeast India.

Water Sample Collection

(a) Water samples were obtained from Deepor Beel, situated southwest of Guwahati city in the Kamrup Metropolitan district of Assam, India.
(b) Another water sample was collected from a residential well near the Noonmati Oil Refinery in Guwahati City, Assam, India.

Sample Preparation

Water Samples

The collected water samples were filtered using filter paper to eliminate debris and large pollutants. The filtered samples were then stored at room temperature for subsequent analysis.

Plant samples

The leaves were plucked, collected, and washed multiple times with tap water followed by distilled water to remove dust and debris. After washing, the leaves were air-dried at room temperature until sufficiently dry to be ground into a fine powder. Once dried, the leaves were ground into fine powder using a grinder.

7.5.2 Preparation of Sample Extract

***Xanthium strumarium* (Cocklebur) sample extract** (Roghini and Vijayalakshmi 2018)

2.5 g of the plant powder was mixed with 50 ml of phenol solution (0.05 g/ml concentration). The mixture was stirred using a magnetic stirrer for four hours and then shaken overnight in a mechanical shaker. The mixture was filtered the next day using Whitman No. 1 filter paper, and the extract was collected and stored in centrifuge tubes at room temperature.

7.5.2.1 Qualitative Analysis for Phytochemicals

Standard protocols were adhered to for conducting preliminary phytochemical screening on the phenol extract to ascertain its constituents (Roghini and Vijayalakshmi 2018; Hazarika and Saha 2017). The procedures involved specific tests for various phytochemicals:

Flavonoid Test: A 2 ml portion of the extract was obtained and treated with a few drops of 2N sodium hydroxide solution in a test tube. The emergence of a yellow tint indicated the presence of flavonoids.

Alkaloid Test: Utilizing Wagner's reagent, 2 ml of the extract was placed in a test tube and subjected to a few drops of the reagent. The appearance of reddish-brown precipitation signified the presence of alkaloids.

Tannin Test: 1 ml of the extract was mixed with 2 ml of 5% ferric chloride solution in a test tube. The development of dark blue and greenish-black colors indicated the presence of tannins.

Saponin Test: By diluting 2 ml of the extract with an equal volume of distilled water, the mixture was shaken in a graduated cylinder for 15 min. The formation of approximately 1 cm layer of foam indicated the presence of saponins.

Phenol Test: 1 ml of the extract was combined with 2 ml of distilled water, followed by a few drops of 10% ferric chloride solution. The formation of a blue or green color indicated the presence of phenols.

Glycosides Test: 2 ml of the extract was mixed with 3 ml of chloroform and 10% ammonia solution in a test tube. The appearance of a pink color demonstrated the presence of glycosides.

Terpenoid Test: Treating 0.5 ml of the extract with 2 ml of chloroform and concentrated sulfuric acid, the formation of a red-brown color at the interface indicated the presence of terpenoids.

Quinones Test: Adding 1 ml of extract to 1 ml of concentrated sulfuric acid, the formation of a red color indicated the presence of quinones.

These tests provide valuable insights into the phytochemical composition of the phenol extract, enabling the identification of its various constituents.

7.5.2.2 Quantitative Analysis for Phytochemicals

Following the qualitative assessment of phytochemicals in *Xanthium strumarium*, a quantitative analysis was conducted to determine the concentration of these compounds in the plant sample. Quantitative analysis is done to determine the concentration of these phytochemicals in the plant sample.

Estimation of Alkaloid Content (Harborne Method): Using the Harborne method (Ananthalakshmi et al. 2019): 1.25 g of the specimen were precisely measured and transferred into a container. Subsequently, 50 ml of 10% acetic acid in ethanol was added, and the covered container was left undisturbed for four hours. After filtration, the resulting extract was concentrated on a water bath until its volume reduced to 1/4th of the original. Concentrated ammonia hydroxide was then added drop by drop until precipitation was complete. The precipitate was collected, washed with dilute ammonium hydroxide, filtered, and the residue was dried and weighed.

Estimation of Total Tannins Content (Folin-Ciocalteu Method): The quantity of tannins in the plant sample was determined using the Folin-Ciocalteu method (Ananthalakshmi et al. 2019). Initially, 0.1 ml of the sample extract was mixed with 0.5 ml of FC reagent, 7.5 ml of distilled water, and 1 ml of 35% sodium carbonate in a flask, and diluted to 10 ml with distilled water. The mixture was then left at room temperature for 30 min. Concurrently, a series of reference standard solutions of tannic acid were prepared. The absorbance of both test and standard solutions was measured at 700 nm against the blank.

Estimation of Total Phenolic Content: For determining the total phenolic content, 10 mg of gallic acid was dissolved in 10 ml of methanol to achieve a concentration of 1 mg/ml. Various concentrations ranging from 25 to 100 μg/ml were prepared. To each concentration, 5 ml of 10% FC reagent and 4 ml of 7% Na_2CO_3 were added. For the test procedure, 0.5 ml of plant extract was combined with 0.5 ml of diluted FC reagent and incubated for 5 min at 22 °C. Then, 2 ml of 20% Na_2CO_3 was added, and the mixture was further incubated at 22 °C for 90 min. The absorbance was measured at 650 nm (Ananthalakshmi et al. 2019; Bärlocher and Graça 2020).

Estimation of Total Terpenoids: For the estimation of total terpenoids, 9 ml of ethanol was used to immerse 100 mg of dried plant extract for a day. The extract was then subjected to extraction with 10 mL of petroleum ether after filtration. Pre-weighed glass vials containing the ether extract were isolated, and the product was allowed to dry thoroughly. The yield (%) of the total terpenoids content was calculated using the formula ($w_i - w_f/w_i \times 100$), where w_i represents the initial weight and w_f the final weight after complete evaporation of the ether (Malik 2017).

7.5.3 Phosphate Content Assessment in Water Sample

The examination of phosphate content in the filtered water samples obtained from Deepor Beel (designated as S_{db}) and a well adjacent to the Noonmati Oil Refinery (referred to as S_{ww}) was conducted through both qualitative and quantitative analyses.

7.5.3.1 Qualitative Analysis

For the qualitative analysis, 2 ml aliquots of both Sdb and Sww samples were treated with ammonium molybdate subsequent to acidification using concentrated nitric acid (HNO_3)[63]. The emergence of a brilliant yellow precipitate layer of ammonium phosphomolybdate was indicative of the presence of phosphate.

7.5.3.2 Quantitative Analysis

The quantification of phosphate present in the water samples (S_{db} and S_{ww}) was performed using the Ascorbic Acid procedure (Strickland 1968; WPCF, Washington 1992). In this procedure, in an acidic solution containing orthophosphate, potassium antimonyl tartrate and ammonium molybdate combine to make phosphomopydbic acid, a heteropolyic acid that may be reduced by ascorbic acid to produce a vivid blue color whose absorbance is then measured at 885 nm spectrums.

The method employed in this procedure utilized potassium dihydrogen phosphate (KH_2PO_4) as the standard. Initially, 0.816 g of anhydrous potassium dihydrogen phosphate was dissolved in 1000 ml of deionized water to create the primary standard solution with a concentration of 6 µmol/ml. Subsequently, 10.0 ml of the primary standard solution was diluted with 1000 ml of deionized water to generate the secondary standard with a concentration of 0.06 mmol/ml. Further dilution was carried out by mixing 5.0 ml of the secondary standard with 100 ml of deionized water to achieve a standard solution concentration of 3.0 µM.

The reagents required for the test were prepared as follows: Ammonium molybdate solution was created by mixing 15 g of ammonium paramolybdate with 500 ml of deionized water. Ascorbic acid solution was made by dissolving 27 g of ascorbic acid in 500 ml of deionized water. Sulfuric acid solution was prepared by mixing 140 ml of concentrated sulfuric acid with 900 ml of deionized water. Potassium antimonyl-tartrate solution was obtained by mixing 0.34 g of potassium antimonyl-tartrate with 250 ml of deionized water. Finally, the final reagent was prepared by combining 250 ml of sulfuric acid solution, 100 ml of ascorbic acid solution, 50 ml of potassium antimonyl-tartrate solution, and 100 ml of ammonium molybdate solution.

For spectrophotometer analysis, 10 ml of the standard solution was taken in a test tube, and 1 ml of the final reagent was added. After an incubation period of 5 min, the absorbance was measured at 885 nm using a spectrophotometer.

The analysis of water samples involved taking 10 ml of each water sample (S_{db} and S_{ww}) in separate test tubes. Subsequently, 1 ml of the final reagent was added to each tube, followed by an incubation of 5 min. The absorbance of each sample was then measured at 885 nm using a spectrophotometer.

7.5.4 Coagulant Test

The coagulant test aimed to evaluate the ability of *Xanthium strumarium* (Cocklebur) leaf powder to remove phosphate from water samples. In the laboratory setup, three beakers were used, each containing 500 ml of distilled water. To simulate phosphate contamination, potassium dihydrogen phosphate (KH_2PO_4) was added to each beaker. Varying amounts of *Xanthium strumarium* leaf powder were then introduced into the beakers: 0.1 g in beaker 1, 0.2 g in beaker 2, and 0.3 g in beaker 3. The mixtures were thoroughly stirred for 30 min to ensure proper dispersion of the leaf powder.

After the stirring period, the setups were allowed to sit undisturbed for 72 h. This duration was chosen to mimic real-world conditions where water treatment processes may take some time to complete. During this time, the leaf powder was expected to interact with the phosphate in the water, potentially forming coagulants that could precipitate out, carrying phosphate with them.

Following the 72 h incubation period, the phosphate-plant sample mixtures underwent filtration to separate any precipitates formed. The resulting filtrates were then subjected to spectrophotometric analysis using the Ascorbic Acid method (Strickland 1968; WPCF, Washington 1992). This method is commonly employed to determine phosphate levels in water samples, providing a quantitative assessment of phosphate concentration.

To calculate the concentration of phosphate present in the samples, a formula involving corrected absorbance and a standardization factor was utilized. This allowed for a precise determination of the efficacy of the *Xanthium strumarium* leaf powder in removing phosphate from the water samples.

The content of phosphate present was calculated using the following method:

$$\text{Concentration of orthophosphate or total phosphate } (\mu\text{m mol/L}) = F^{*} \text{ corrected absorbance}$$

where

Corrected absorbance = sample absorbance − reagent blank.

F = standardization factor A standardization factor F can be calculated as

$$F = 3.0\,\mu\text{mol/kg}/(\text{Es} - \text{Eb})$$

where

3.0 μmol/kg = concentration of the standard
Es = mean absorbance of the standards
Eb = mean absorbance of the blanks.

The procedure was replicated using water samples collected from two areas of Guwahati, Assam, i.e. Deepor Beel (S_{db}) and a residential area near Noonmati Oil Refinery (S_{ww}). This ensured a comprehensive assessment of the plant's coagulant properties across different water sources and potential contamination levels. Coagulant test was done in order to check the efficiency of the plant sample to remove phosphate from the water sample.

7.6 Results

7.6.1 Result for Qualitative Phytochemical Tests

Xanthium strumarium (Cocklebur)

In the qualitative phytochemical tests conducted on the phenolic extract of *Xanthium strumarium* (Cocklebur), several phytochemicals were identified. The results indicated the presence of Tannin, Alkaloid, Terpenoid, and Phenol in the extract, while Saponin, Flavonoid, Glycosides, and Quinonnes were not detected. These findings suggest that *Xanthium strumarium* contains a specific profile of bioactive compounds, including Tannin, Alkaloid, Terpenoid, and Phenol, which may contribute to its medicinal properties and potential applications. Further quantification of these phytochemicals was carried out using various procedures outlined in the methodology, allowing for a more comprehensive understanding of their concentrations and potential biological activities (Table 7.1).

Table 7.1 Phytochemicals in Phenolic extract of *Xanthium strumarium* Cocklebur

Phenolic extract	Phytochemicals	Result
1	Saponin	(−)
2	Tannin	(+)
3	Flavonoid	(−)
4	Glycosides	(−)
5	Alkaloid	(+)
6	Terpenoid	(+)
7	Phenol	(+)
8	Quinones	(−)

7.6.2 Result for Quantitative Phytochemical Tests

Quantitative phytochemical analyses yielded the following results

Alkaloids: The alkaloid content in *Xanthium strumarium* was quantified using the Harborne method. From 1.25 g of plant leaf sample, 0.09 g of total alkaloids were extracted, resulting in a percentage yield of alkaloid content in the plant sample of 7.2%.

Tannins: Tannin levels in *Xanthium strumarium* were determined through the Folin-Ciocalteu method, with tannic acid employed as the standard. The concentration of tannin in *Xanthium strumarium* was found to be 4.25 μg in a 25 μg/ml sample, corresponding to a 1:2000 dilution ratio.

Phenolics: Quantification of phenolic compounds in *Xanthium strumarium* was conducted using the Folin-Ciocalteu method with gallic acid as the reference standard. Upon dilution of the plant sample extract to a concentration of 5 mg/ml, the total phenolic content was measured to be 0.05875 mg. This translates to 0.01175 mg/mg of the 10 × diluted plant sample.

Terpenoids: The terpenoid content in Xanthium was assessed to be 13 mg per 100 mg of extract.

7.6.3 Results for Coagulant Tests

7.6.3.1 Results of Laboratory Setup of Phosphate Coagulant Test for *Xanthium Strumarium*

The results of the laboratory setup for the phosphate coagulant test using *Xanthium strumarium* leaf samples demonstrate a considerable decrease in the concentration of KH_2PO_4 (potassium dihydrogen phosphate) post treatment. Initially, the setup contained KH_2PO_4 at a concentration of 0.01 g/ml (equivalent to 10 mg/ml). After treatment with various concentrations of *Xanthium strumarium* leaf samples (0.5, 1, and 1.5 mg/ml), the concentration of KH_2PO_4 decreased notably. Across three replicates, the average concentration of KH_2PO_4 after treatment with 0.1 g of *Xanthium strumarium* leaf powder (0.5 mg/ml) was measured at 0.00323 mg/ml. Similarly, treatment with 0.2 g and 0.3 g of leaf powder yielded average post-treatment concentrations of 0.0030 mg/ml and 0.0029 mg/ml, respectively. These findings underscore the efficacy of *Xanthium strumarium* leaf powder in reducing phosphate levels in the setup, indicating its potential as a coagulant agent for phosphate removal in water treatment applications. Additionally, the percentage decrease in phosphate concentration was calculated for each dose of the plant sample, revealing significant reductions ranging from 99.967 to 99.971%. These results emphasize the effectiveness of *Xanthium strumarium* leaf powder in phosphate removal, warranting further investigation into its practical application in water treatment systems.

Table 7.2 Concentration of phosphate in water samples post treatment with *Xanthium strumarium*

Water samples (conc. of plant sample in 200 mL of sample water) (g)	SET 1 Conc. of phosphate post treatment (mg/L)	SET 2 Conc. of phosphate post treatment (mg/L)	SET 3 Conc. of phosphate post treatment (mg/L)	Average Conc. of phosphate post treatment (mg/L)	Average percentage decrease in phosphate concentration (%)
S_{db} 0.1	0.020	0.0308	0.023	0.0246	42.388
S_{db} 0.2	0.026	0.0364	0.0261	0.0295	30.91
S_{db} 0.3	0.0327	0.0361	0.0314	0.0334	21.77
S_{ww} 0.1	0.0146	0.0226	0.0128	0.0166	57.86
S_{ww} 0.2	0.0179	0.0314	0.020	0.0231	41.37
S_{ww} 0.3	0.0216	0.038	0.023	0.0275	30.2

7.6.3.2 Results of Phosphate Coagulant Tests of the Water Samples Post Treatment with *Xanthium Strumarium*

The phosphate coagulant tests conducted on water samples post treatment with *Xanthium strumarium* leaf powder revealed significant reductions in phosphate concentrations. In the initial water samples, the phosphate concentrations were measured at 0.0427 mg/L for Deepor Beel (S_{db}) and 0.0394 mg/L for well water from Noonmati (S_{ww}). Following treatment with varying concentrations of *Xanthium strumarium* leaf powder, the phosphate levels decreased noticeably across all sets of experiments. In Deepor Beel samples treated with 0.3 g of the leaf powder, for instance, the average post-treatment phosphate concentration was calculated at 0.0334 mg/L, marking a substantial reduction from the initial concentration. Similarly, in well water from Noonmati treated with the same dosage, the average post-treatment phosphate concentration was measured at 0.0275 mg/L, indicating effective phosphate removal. These results underscore the potential of *Xanthium strumarium* leaf powder as a viable coagulant for phosphate removal in water treatment applications, with varying efficacy observed across different concentrations and water sources (Table 7.2).

7.7 Discussion

Phosphates are a frequent source of water pollution and the main cause of eutrophication in lakes and other natural waters (Elser et al. 1990). River eutrophication and the growth of algae can result from high phosphate levels. This may result in lower oxygen levels, which would render aquatic life impossible in the river (Badamasi et al. 2019). Significant problems with wastewater management have arisen in urbanized civilizations due to significant industries and high human density. Wastewater from industries, agricultural fields, sewage, household wastes, etc. can cause significant accumulation of phosphate and other pollutants in the water bodies where the wastewater is usually dumped. Seeping of phosphate into the ground water also poses a serious threat of many kinds affecting the drinking water source for the majority of population. Once thought to be unimportant, wastewater is now a valuable source of clean water for both potable and non-potable uses. There have been a lot of studies carried out to find a sustainable solution to clean wastewater and to make it fit for use (Obaideen et al. 2022).

Our study here is focused on the coagulation and removal of phosphate from water using natural coagulants. The water samples selected for the tests were samples from Deepor Beel, a lake that is used to dispose of wastewater from many industrial and urban sewage sources, thus aiding in the accumulation of many heavy metals and inorganic ions like phosphate ions in different forms. The second sample was obtained from a well of a residential area near the Noonmati Oil Refinery. The well was in an area of 500 m around the oil refinery. The dumping of waste materials in the nearby area and river from the industry leads to contamination of the ground water as well. Thus phosphate ions can be found in the ground water of the area around the industry along with other pollutants.

The selection of plant for the coagulation test was based on previous literature and works. *Xanthium Strumarium* has shown the potential to be used as a natural adsorbent for textile wastewater treatment particularly as a dye remover (Khamparia and Jaspal 2017a). In our study, results obtained solidified the effectiveness of *Xanthium strumarium* as a natural coagulant for phosphates in the water samples. At different doses of the plant sample, there was seen significant decreases of more than 99% in the phosphate content in laboratory setup. When the plant sample was used to treat the collected water samples from different areas of polluted water sources, there was a decrease of around 42% in the phosphate levels of the water sample from Deepor Beel and around 57% decrease in the phosphate levels of the water sample from the ground water of the area from around the Noonmati Oil Refinery.

There is a difference in the results of the laboratory setup test conducted for the standardization and the tests performed on the water samples (S_{db} and S_{ww}). It was observed that there is a decrease in the coagulant activity of the plant sample when it was used to treat the sample water collected from Deepor Beel and well water from nearby Noonmati Oil Refinery. The detection of phosphate in water mainly depends on the detection of free orthophosphate in the sample (Burton 1973). In the laboratory setup of the jar test for standardization, these were no debris and other components involved in the test as KH_2PO_4 was dissolved in deionized water. But in the case of the tests performed with the water samples, there were a lot of factors that could have hindered the test. There are other forms in which phosphate can exist in nature such as phosphate which are organically combined. Under favorable conditions, these organophosphates can be oxidized to form orthophosphate (Obaideen et al. 2022). But due to the presence of other organic and inorganic components, the accuracy of detection of phosphate in the collected water samples was seen to be less than that of the prepared KH_2PO_4 solution.

Phytochemical tests performed on plant *Xanthium strumarium* showed the presence of tannins as a phytochemical constituent of the plant. Tannins has a phenolic structure similar to that of synthetic phenols and thus have many uses one of the most significant one being its antioxidant properties (Shirmohammadli et al. 2018). Available literature has also shown that tannins along with alum can be used for phosphate removal, and it has a wide-range effectiveness to even remove phosphate in trace amounts thus providing a base for the results obtained from the conducted tests for phosphate removal (Ozacar and Sengil 2003). Thus the plant can be used as a potential and sustainable alternative to the chemical coagulants and polymeric flocculants widely used which have shown to have toxic traits (Fouché et al. 2008). The plant *Xanthium strumarium* has also shown the presence of terpenoids and plant phenolics. Terpenoids have shown promising results as antimicrobial and thus the plant may also possess antimicrobial activity against commonly found harmful microbes in wastewaters (Sharma et al. 2020). Terpineol which is an isomeric form of mono-terpenoids has the ability to cause cell death through destruction of the cell membrane (Guimarães et al. 2019). Plant phenolics have shown promising results in suppressing biofilm production and toxin production of many strains of pathogenic microbes (Takó et al. 2020).

7.8 Advantages of *Xanthium Strumarium* as a Coagulant: Emphasizing Biodegradability and Environmental Impact

The plant known as *Xanthium strumarium* is becoming more and more well liked as a potential replacement for traditional chemical coagulants in water treatment processes. There are several advantages to this natural coagulant, particularly in terms of its biodegradability and effect on the environment. It is manufactured from cocklebur plant seeds. This essay will look at these advantages to show why *Xanthium strumarium* is important as a sustainable water treatment alternative (Baş et al. 2022).

Firstly, one of the main advantages of employing *Xanthium strumarium* as a coagulant is that it degrades naturally. Unlike artificial chemical coagulants that occasionally stay in the terrain and beget pollution, natural declination mechanisms limit the long-term environmental effect of *Xanthium strumarium. Xanthium strumarium* is regarded as biodegradable due to its organic composition, which allows it to break down into inoffensive derivations through microbial exertion and other natural processes. For the treatment of water, *Xanthium strumarium* is a more environmentally friendly option due to its natural capability to putrefy spontaneously (Baş et al. 2022; Rao et al. 2014; Mouhamad 2022).

Moreover, *Xanthium strumarium* can be used as a coagulant to considerably reduce the environmental impact of water treatment procedures. For their manufacture and use, synthetic chemical coagulants like ferric chloride and aluminum sulfate can require large energy inputs in addition to chemical additions. Naturally occurring plant resources provide an alternative, sustainable source of *Xanthium strumarium* that lowers carbon emissions. As a result, less energy-intensive production methods are required. Enhancing its environmental advantages, *Xanthium strumarium* cultivation may also aid in carbon sequestration and biodiversity preservation (Rao et al. 2014).

Not only is *Xanthium strumarium* biodegradable and has a low impact on the environment during production, but it also has a positive effect on water purification. Research has indicated that *Xanthium strumarium* demonstrates coagulation ability that is on par with or even better than chemical coagulants, especially when it comes to eliminating organic materials, suspended particles, and infectious agents from water sources. It works well with ecologically friendly water treatment techniques because of its capacity to coagulate contaminants without releasing hazardous compounds into the environment (Rao et al. 2014).

Apart from its ecological benefits, *Xanthium strumarium* presents economic advantages as well, since it has the ability to lower the total expenses related to water treatment. Moving to natural coagulants may come with some upfront costs, but in the long run, the savings from using fewer chemicals, using less energy, and not having to clean up the environment may exceed these costs. Furthermore, *Xanthium strumarium* is a cheap and easily available choice for communities looking for environmentally friendly water treatment solutions due to its availability in a variety of geographical zones.

7.9 Advantages of *Xanthium Strumarium* as a Coagulant: Cost-Effectiveness and Accessibility

Xanthium strumarium, sourced from cocklebur seeds, emerges as a promising cost-effective coagulant for water treatment. Unlike synthetic counterparts, its extraction process is straightforward, and its abundant availability makes it economically appealing, especially for financially constrained water treatment facilities. The cultivation of *Xanthium strumarium* demands minimal resources and can be seamlessly integrated into existing agricultural practices, thereby further reducing production costs (Baş et al. 2022).

In contrast to chemical coagulants prone to supply chain disruptions, *Xanthium strumarium* can be locally sourced, diminishing reliance on external suppliers and transportation and consequently lowering associated carbon emissions. This accessibility not only meets water treatment standards but also enhances public health outcomes, particularly in underserved regions (Mouhamad 2022).

Furthermore, owing to its natural origin, *Xanthium strumarium* may encounter fewer regulatory obstacles, facilitating swifter approval and integration into water treatment processes compared to synthetic alternatives. Its acceptance in traditional and natural treatment practices fosters collaboration and trust among stakeholders (Mouhamad 2022).

Moreover, *Xanthium strumarium's* versatility allows for its application across various water treatment settings, from large-scale facilities to decentralized community systems. This adaptability proves effective in combating waterborne illnesses and improving water quality without necessitating costly infrastructure upgrades (Baş et al. 2022).

7.10 Conclusion

After performing the tests in the laboratory setup to check the effect of coagulation properties of the plants *Xanthium strumarium* for phosphate dissolved in water with an initial concentration of 0.01 g/ml (10 mg/ml), it was observed that there was more than 99% decrease in the concentration of the phosphate content in the water after a period of 72 h. Promising results were also obtained during the treatment of collected water samples after 72 h. From the results of the jar tests, it can be observed that for both the water samples decrease in the phosphate content of the water (mg/L) is the highest for 0.1 g in 200 ml dose of *Xanthium strumarium.* In the case of water sample from Deepor Beel, the dose (0.1 g/200 ml) showed a 42.388% decrease from the initial 0.0427 mg/L phosphate concentration. In the case of the water sample from a well of a residential area around the Noonmati Oil Refinery, the dose (0.1 g/200 ml) showed a 57.86% decrease from the initial phosphate concentration of 0.0394 mg/L.

Phytochemical tests performed on the plant *Xanthium strumarium* showed the presence of Alkanoids, Tannins, Phenolic, and Terpenoids. Tannins in combination with many polymeric flocculants and chemical coagulants such as alum have shown great results in the coagulation effect of phosphate in water (Obaideen et al. 2022; Khamparia and Jaspal 2017b). Phytochemicals such as terpenoids and plant phenolics have antimicrobial qualities which can aid in the treatment of wastewater (Shirmohammadli et al. 2018; Ozacar and Sengil 2003).

Thus, in conclusion, the plant *Xanthium strumarium* shows promising results as a natural coagulant without association with any chemical or synthetic coagulants for phosphate pollutants and also has potential use as an antimicrobial compound.

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Chapter 8
Biological Methods for Removal of Pharmaceuticals and Personal Care Products (PPCPs) and Their Fate

Shivashis Bikram Banerjee, Tannishtha Das, and Satarupa Dey

Abstract The waste produced by Pharmaceuticals and personal care products (PPCPs) industries has hazardous impact on the environment and public health and are considered as a matter of emerging concern. These wastes if disposed untreated are found to be poisonous to aquatic flora and fauna as they contains products of drug and formulation development process. Lack of a profound treatment of wastewater may lead to discharge PPCPs residues making them the chief source of PPCP contamination of water bodies. However, for proper treatment of PPCP it is essential to have a knowledge on the chemical characteristics and components of the influent water. Several studies have been carried out on various treatment methods associated with PPCP. This chapter compares the physical, chemical and bioremoval methods. Biological treatment is considered to be most sustainable, economically viable and less energy-intensive option. Various microorganisms, including bacteria, algae, fungi and plant species have displayed promising bioremedial as well as phyoremedial potential in removing drug residues from pharmaceutical effluents. This chapter discusses the various types of biological treatment procedures, their usages and limitations in context of industrial wastewater treatment aimed at decreasing the ecotoxicological effects of pharmaceutical wastewater which will encourage the industry to reuse water.

Keywords Biodegradation · Pharmaceuticals · Personal care product · Wastewater treatment · Xenobiotics

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S. Dey and M. P. Shah (eds.), *Biotechnological Removal of Emerging Pollutants from Wastewater Systems*, Advances in Wastewater Research,
https://doi.org/10.1007/978-981-96-3945-8_8

8.1 Introduction

Pharmaceuticals and personal care products (PPCPs) are present everywhere and their disposal poses unique challenges. Rapid industrialization and urbanization had led to increase in pharmaceuticals and personal care products (PPCPs) production which are considered as microorganic contaminant and may led to carcinogenic, mutagenic, and reproductive toxicity risks (Wang and Wang 2016). These products are often disposed of in water bodies, leading to public health risks and is toxic to aquatic flora and fauna. Most PPCP possess deleterious effects and effects gastrointestinal, nervous, endocrine and reproductive systems. Compounds such as polychlorinated biphenyls possess carcinogenic risks. These compounds can enter and accumulate through food chain when untreated effluents and treated sewage and sludge is used in agricultural applications (Yang et al. 2017a). Pharmaceuticals products mainly consist of antibiotics, hormone and anti-inflammatory drugs, whereas personal care products include products mainly used for cosmetics, hygiene products, disinfectants, fragrances and insect repellents (Zhang et al. 2022). Few of these products are represented in Fig. 8.1. According to the list of micropollutants in 2007 several PPCP have enlisted as priority pollutant including ibuprofen, carbamazepine, clofibric acid, diclofenac, iopamidol, musks, triclosan, and phthalates.

Several studies of PPCP have already been published by several groups of researchers which can be grouped according to various geographical regions (Liu and Wong 2013; Balakrishna et al. 2017), types of drugs (Vieno and Sillanpää 2014; Kümmerer 2009) and toxic effects (Xin et al. 2021). Several reviews have discussed various processes of removal of PPCP products from contaminated waste water by adsorption (Neha et al. 2021; Zhang et al. 2021), ozonation (Sauter et al. 2021; Wang and Wang 2018), membrane filtration (Couto et al. 2018; Jamil et al. 2021), Fenton oxidation (Wang and Wang 2018; Lama et al. 2022), ozone-based processes (Derco et al. 2021; Rekhate and Srivastava 2020), UV oxidation (Wang and Wang 2018) and biological processes (Wang and Wang 2018; Roberts et al. 2016). However, as these PPCP vary in their chemical structure, molecular weight, charge, hydrophobicity, nature of chemical bonds and oxidising property any single removal process is not sufficient to treat all the compounds (Wang and Wang 2016). Combination of treatment are required to remove diverse types of PPCP. Biological methods for the removal of PPCPs are gaining attention due to their cost-effectiveness and environmental sustainability. Microorganisms can remove organic contaminants either individually or in consortium by metabolic activity. The produce diverse type of hydrolytic enzymes which can degrade the organic compounds. This essay explores various biological treatment methods, their effectiveness, and the fate of PPCPs post-treatment.

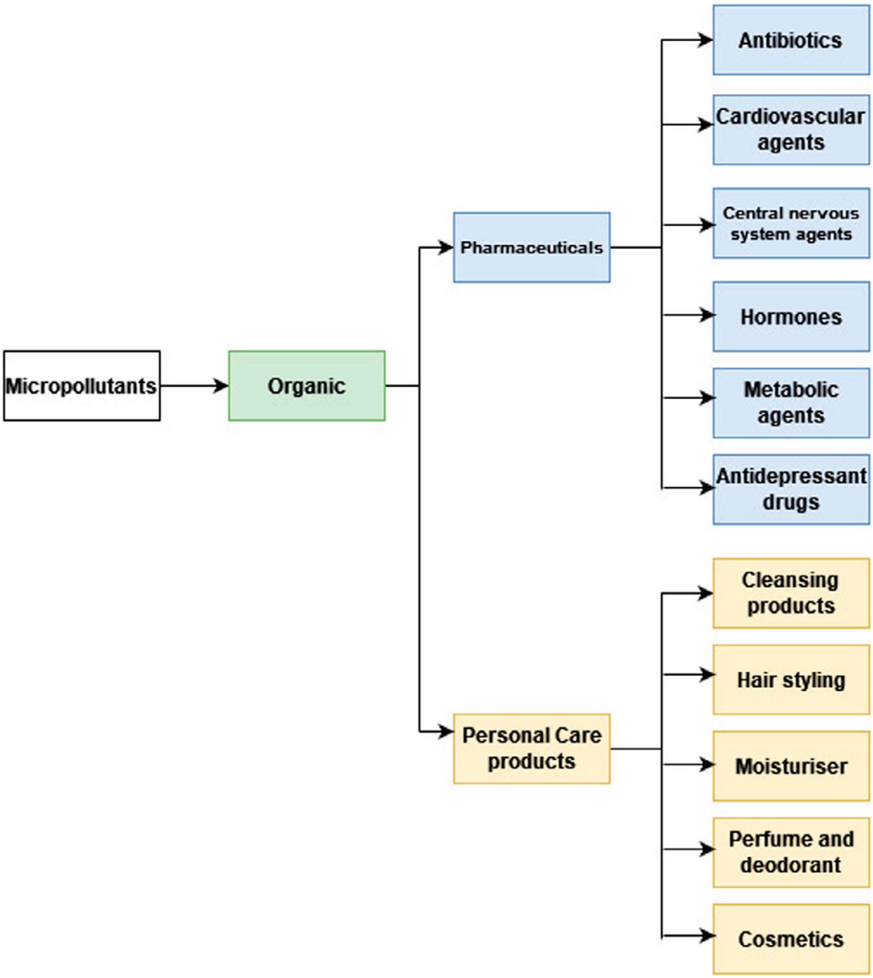

Fig. 8.1 Different categories of pharmaceuticals and personal care products

8.2 Types of Pharmaceuticals and Personal Care Products

PPCP consists of a diverse group of complex organic compound consisting of antibiotics, cardiovascular drugs, drugs used for treatment of nervous disorders, anti-inflammatory drugs, antiepileptic drugs, hormones, lipid regulators, β-blockers, antimicrobial agents, mosquito repellent, preservatives, hair styling products, moisturiser, sunscreen UV filters, perfumes and deodorant as stated in Fig. 8.1 (Daughton and Ternes 1999). Presence of antibiotics of subgroups belonging to macrolides, sulfonamides, fluoroquinolones and various antibiotic residues are very common in waste water systems due to over exploitation of antibiotics in treatment of livestock and human which results in the emergence of antibiotic resistance trait in different pathogenic microbes (Zhang et al. 2006). Hormonal supplements such as natural steroids estrogens, are excreted by humans and animals which is subsequently released in waste water. The most concerned hormones are estrone (E1), estradiol (E2), estriol (E3), and synthetic steroid estrogens which are used as oral contraceptives (Caldwell et al. 2010). Pharmaceutical groups such as analgesics, antiepileptic drugs, blood lipid regulators, anti-inflammatory drugs and β-blockers are also detected in waste water. Preservatives such as Parabens, 4-methyl-benzilidine-camphor (4MBC) and 2-ethyl-hexyl-4-trimethoxycinnamate (EHMC) are also considered as most available CCPC in waste water (Brausch and Rand 2011).

8.3 Mechanisms and Strategies in Removal of PPCP from Waste Water

Pharmaceuticals and personal care products (PPCPs) are emerging contaminants in aquatic environments due to their extensive use and incomplete removal during standard and conventional wastewater treatment processes. Addressing the environmental and health risks posed by these compounds requires a comprehensive understanding of the various mechanisms for their removal. Each mechanism targets specific properties or interactions of PPCPs, offering different levels of effectiveness and efficiency. PPCP can be treated in physical, chemical, biological as well as combined mechanisms for successful removal of PPCP (Fig. 8.2).

8.4 Physical Mechanisms in Removal of PPCP

8.4.1 Adsorption

Adsorption takes place when the PPCP binds to the surface of solid materials like activated carbon, biochar, or other adsorbents. The rate of removal of the PPCP depends on the surface area, porosity, and chemical functional groups of the adsorbent. This mechanism is widely used due to its simplicity and effectiveness for a broad range of PPCPs. Activated carbon, with its high surface area and porous structure, is particularly effective at adsorbing hydrophobic PPCPs (Nam et al. 2014). The hydrophobicity, molecular size, and charge of PPCPs influence their adsorption affinity, with hydrophobic compounds and larger molecules tending to adsorb more readily onto activated carbon and similar materials.

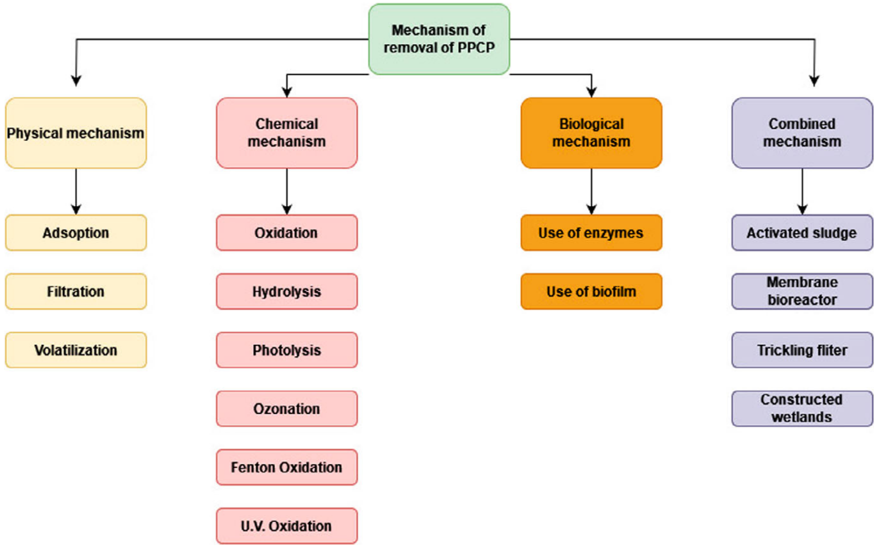

Fig. 8.2 Mechanism of removal of PPCP from waste water

8.4.2 Filtration

Filtration uses physical barriers like membranes or filters to remove PPCPs based on size or charge. In processes such as nanofiltration (NF) and reverse osmosis (RO), the pore size, charge, and hydrophilicity of membranes determine their ability to separate PPCPs. RO membranes, with their small pore size, can effectively remove a wide range of PPCPs, including both hydrophilic and hydrophobic compounds (Yangali-Quintanilla et al. 2010). Factors such as transmembrane pressure, flow rate, and fouling propensity affect filtration efficiency, making proper maintenance and periodic cleaning necessary to sustain membrane performance.

8.4.3 Volatilization

Volatilization refers to the evaporation of PPCPs into the air, particularly those with high vapor pressure. While this mechanism can remove PPCPs from water, it may transfer the contamination to the atmosphere. Compounds with high vapor pressure and low water solubility are more prone to volatilization; however, most PPCPs have low volatility, limiting the effectiveness of this mechanism. Volatilization can lead to the dispersion of PPCPs in the air, potentially causing air quality issues, making it a less favoured method for PPCP removal.

8.5 Chemical Mechanisms in Removal of PPCP

8.5.1 Oxidation

Oxidation involves the use of chemical oxidants like ozone, hydrogen peroxide, or chlorine to break down PPCPs into smaller molecules. Advanced oxidation processes (AOPs) enhance this mechanism by combining oxidants with catalysts or UV light. Different oxidants have varying reactivities and efficiencies; for instance, ozone is highly effective for oxidizing a wide range of PPCPs, while hydrogen peroxide is often used in combination with UV light in the UV/H_2O_2 process (Michael et al. 2014). The use of catalysts such as titanium dioxide (TiO_2) in photocatalytic oxidation can significantly enhance PPCP degradation rates by generating reactive radicals (e.g., hydroxyl radicals) that play a crucial role in breaking down complex PPCPs.

8.5.2 Ozonation

Ozonation is widely used to remove PPCP from waste water, in this process free hydroxyl radicals (OH^-) is generated and the efficiency of the process is entirely dependent on the concentration of the ions generated. This process is a post treatment process which is very efficient in degrading PPCP (Gomes et al. 2017). However, the removal of PPCP was mostly dependent on its chemical nature and extensive researches are required on the effectiveness of oxidation of PPCP in presence of other pollutants.

8.5.3 Fenton Oxidation

In this method, highly reactive free radicals, such as hydroxide radical, sulphate radical and superoxide radicals are used to oxidise PPCP. They form precursor oxidants such as hydrogen peroxide, persulfate/peroxodisulfate, peroxymonosulfate and sodium percarbonate (Lama et al. 2022), which utilizes metal-based catalysts, ultrasound, alkaline aqueous medium, UV radiation, visible light, and heat. The main drawback of Fenton oxidation is that it can be applied within narrow pH range. Moreover, precipitation of metals may lead to toxic sludge formation.

8.5.4 UV Oxidation Treatment

UV oxidation process is a very common treatment procedure used for tertiary treatment of waste water. UV oxidation method helps in photolysis of chemical bonds of

PPCP, which subsequently helps in removal of PPCP from waste water (Kim et al. 2009). For treatment of PPCPs, in the advanced oxidation process (AOP), hydrogen peroxide is coupled with UV to effectively remove PPCP (Yuan et al. 2011).

8.5.5 Hydrolysis

Hydrolysis is the reaction of PPCPs with water, leading to their breakdown into simpler compounds. This process is influenced by pH and temperature. Acidic or basic conditions can accelerate hydrolysis rates for certain PPCPs, while higher temperatures generally enhance hydrolysis (Boreen et al. 2003). The chemical structure of PPCPs determines their susceptibility to hydrolysis, with ester-containing PPCPs being more prone to hydrolysis compared to amide-containing compounds.

8.5.6 Photolysis

Photolysis involves the breakdown of PPCPs through photochemical reactions induced by UV light. This method is often used in combination with other treatment processes for enhanced effectiveness. Low-pressure and medium-pressure UV lamps are commonly used for photolysis, with the wavelength and intensity of UV light affecting the photodegradation rates of PPCPs (Kovacic et al. 2018). Combining photolysis with other processes, such as oxidation (e.g., UV/H_2O_2), can improve PPCP removal efficiency by generating reactive radicals that enhance degradation.

8.6 Biological Mechanisms in Removal of PPCP

Biological treatment processes used in removal of PPCP is mainly done by various enzymes produced by various microorganisms as well as biofilms.

8.6.1 Use of Enzymes

Enzymes can break down well known organic compounds. This process can be standardised, and trials are currently ongoing. PPCPs are transformed into less harmful byproducts. Enzyme treatments have shown promise in degrading PPCPs like oestrogens and non-steroidal anti-inflammatory drugs (NSAIDs), potentially reducing their environmental impact (Kim et al. 2007). Microorganisms, cyanobacteria, microalgae and fungus produces various enzymes which can biotransform complex PPCP products. A plethora of enzymes are usually required a PPCP vary widely in chemical structures, the biodegradability potentials. Microbial laccase is an extracellular oxidative enzyme which can degrade broad range of aromatic compounds, phenols and amines (Yang et al. 2017b). This enzyme is characterised by low substrate specificity, requires oxygen as the final electron acceptor and depending on its source has diverse ranges of redox potentials (Janusz et al. 2020). Several fungal species such as *Pleurous ostreatus*, *Phlebia ochraceofulva*, *Trametes versicolor* and *Trames hirsuta* have been seen to produce laccase (Olic´on-Hern´andez et al. 2017; Yang et al. 2017b). Among which *Trametes versicolor* is regarded as a model organism which is responsible for the production of laccase with high redox potential, having long-term stability (Mate and Alcalde 2015) and has been employed for PPCPs removal (Margot et al. 2013). Immobilized enzymes are extensively used to treat PPCP compounds. Laccase enzyme immobilised in Grafted ceramic membrane, Magnetic alginate beads, Fumed silica nanoparticles, Polyamide 6/chitosan Nanofibers have been used to treat antibiotics, Triclosan and BPA respectively (Becker et al. 2016; Le et al. 2016; Arca-Ramos et al. 2016; Maryšková et al. 2016).

8.6.2 Use of Biofilms

Biofilms, which are microbial communities attached to surfaces, can degrade PPCPs. This process can be enhanced by optimizing conditions for biofilm growth or by using specific biofilm-forming microorganisms. Similar to other biodegradation processes, PPCPs are transformed into byproducts. Enhanced biofilm reactors have demonstrated effective degradation of various PPCPs, including antibiotics and hormones (Noguera and Picioreanu 2004). Algal biofilm has been used to remove PPCP products from waste water. A Revolving Algal Biofilm (RAB) reactor can be effectively used to remove PPCP from waste water. As most algal biofilms contains Extracellular Polymeric substances which are amphiphilic biopolymer with hydrophobic patches which serves as binding spot for organic compounds and adsorbs PPCPs (Peng et al. 2019). In most cases the microbial species occurring in biofilm consists of bacteria such as Nitrosomonas and Nitrobacter, along with filamentous fungi which plays vital role in oxidative degradation of organic matters (Chen et al. 2006). However, higher concentration of PPCP can be detrimental for biofilm growth.

8.7 Various Mechanisms Involved in Biological Treatment

8.7.1 Biodegradation

Biodegradation is the process by which microorganisms such as bacteria and fungi metabolize PPCPs, breaking them down into simpler, less harmful substances. However, biodegradation efficiency depends on several factors, mainly on capabilities of the microbial community. They vary in enzymatic capabilities, influencing the ability to degrade specific PPCPs. For instance, *Pseudomonas putida* bacteria can degrade ibuprofen, while certain fungi are more effective at degrading triclosan (Vasiliadou et al. 2019). Optimal environmental conditions, such as appropriate temperature, pH, and nutrient availability, enhance microbial activity and biodegradation rates. Some PPCPs may be more effectively degraded under anaerobic conditions, while others require aerobic conditions. The chemicals structure also influences breakdown, because simpler smaller structures are degraded easily, but more complex structures take longer to be broken down like carbamazepine.

8.7.2 Biotransformation

Biotransformation involves the modification of PPCP chemical structures by microorganisms, potentially reducing their toxicity or making them more amenable to further degradation. Microorganisms produce enzymes that catalyze the transformation of PPCPs. For instance, cytochrome P450 enzymes in bacteria can hydroxylate certain pharmaceuticals, altering their structure and reactivity (Bessegato et al. 2019). This process can result in the formation of metabolites that are less harmful than the parent compounds, though some transformation products may still pose environmental risks. Biotransformation does not always result in complete mineralization, and some PPCPs are converted into intermediate products that require further treatment for complete removal.

8.7.3 Biosorption

Biosorption involves adherence of the PPCP to the bacterial extracellular matrix, produced by self-produced polymers. These biofilms can chelate the PCPs and effectively remove them from the source of contamination. The complexity and density of biofilms can influence their biosorptive capacity (Guo et al. 2019). The efficiency of biosorption depends on the properties of the biofilm or microbial surface, such as surface charge, hydrophobicity, and functional groups. Biofilms enriched with specific microorganisms can be tailored to target particular PPCPs, enhancing the retention and removal of these compounds.

8.8 Combined Mechanisms

Many wastewater treatment processes combine multiple mechanisms to achieve effective PPCP removal. These hybrid approaches leverage the strengths of individual mechanisms to enhance overall treatment efficiency. The different types of biological treatment are represented in Fig. 8.3.

8.8.1 Activated Sludge

This method makes use of microorganisms, or consortia of such microbes that have the ability to remove the existence of organic substances. Since PCP falls in this category, it is a preferred method of removal of PCP. The effectiveness of this method varies based on the chemical composition of PPCP and the operational conditions, such as sludge retention time and oxygen levels. Some PPCPs such as ibuprofen and diclofenac are partially degraded during the process of activated sludge treatment, while others such as carbamazepine may become incorporated into the sludge (Carballa et al. 2004). Researches done by Kapelewska et al. (2018) reports around >90% removal of triclosan in conventional activated sludge process. This study reported that the removal of PPCP is largely dependent on the type of PPCP present, seasonality and treatment process (Mohapatra et al. 2016). The removal rate was reported to be 90.1% and 38.9% for triclosan and DEET respectively. On the other hand, removal of metoprolol was 80% during the summer, which was reduced to be 30% during winter (Mohapatra et al. 2016).

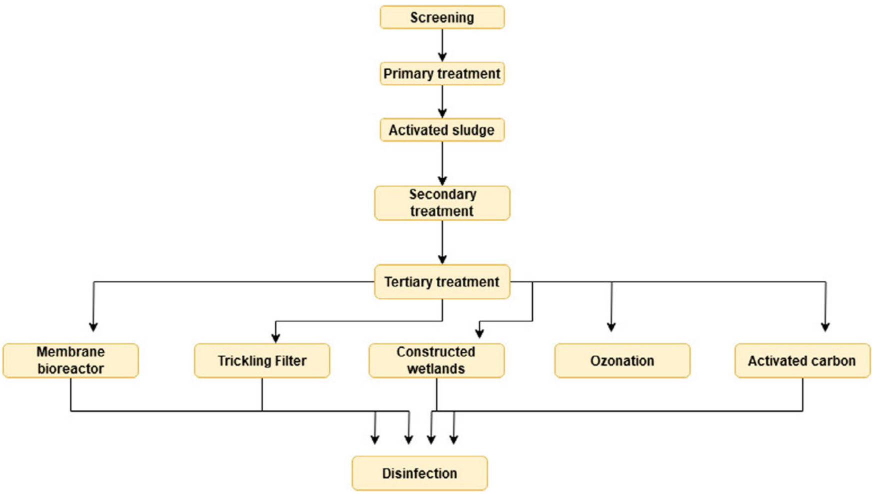

Fig. 8.3 Flow chart of various treatment process of waste water

8.8.2 Membrane Bioreactors (MBRs)

In this process the activated sludge process is combined with membrane filtration, by enhancing the efficiency of the process by retaining higher biomass concentrations and providing greater operational control. It is similar in basic mechanism to the activated sludge process, but this has expected higher efficiency and removal rates. Research has previously demonstrated that MBRs can achieve higher removal efficiencies for PPCPs like sulfamethoxazole and atenolol compared to conventional activated sludge systems (Radjenović et al. 2009).

8.8.3 Advanced Treatment Systems

Advanced treatment systems may integrate AOPs with biological or physical processes for optimal PPCP removal. These systems aim to achieve synergistic effects by combining different mechanisms. Combining UV/H_2O_2 oxidation with biological treatment can enhance the degradation of PPCPs that are resistant to single-process treatments. The sequential or simultaneous application of multiple mechanisms maximizes removal efficiency (Gerrity et al. 2011).

8.8.4 Trickling Filters

A bed of non-degradable medium is used, such as rocks or sand, which holds biofilms of microorganisms that can successfully degrade PCP. Some PCPs characteristically are retained, some degraded while some pass through untreated. The untreated portion could possibly lead to loss in efficiency of the process. Studies indicate that trickling filters can effectively remove biodegradable PPCPs like ibuprofen, though more recalcitrant compounds may escape treatment (Matamoros and Bayona 2006).

8.8.5 Constructed Wetlands

These structures are constructed using plant, soil and the natural environment of natural wetlands, such that the microbial flora can be recreated. This flora in turn possesses the capability to degrade PCPs through adsorption and related processes. For example, wetlands have been shown to reduce concentrations of PPCPs such as caffeine and triclosan through various removal mechanisms (Matamoros et al. 2009).

8.9 Factors Influencing Removal Mechanisms

A solid strategy based on thorough planning is needed to plan the removal of PCPS from wastewater. Conventional wastewater removal strategies do not have sufficient efficiency to be able to remove PCPs from wastewater. One key factor is the properties of the PPCPs themselves, including their hydrophobicity, charge, molecular size, and chemical structure. Hydrophobic PPCPs are more likely to adsorb onto solids or biofilms, making adsorption and biosorption more effective for these compounds. Conversely, hydrophilic compounds tend to remain in the aqueous phase and may require different treatment approaches such as advanced oxidation processes or membrane filtration. Positively charged PCPs can be removed from the environment using negatively charged adsorbents. The converse is also true. Esters and amides are functional groups that influence the susceptibility of PPCPs to hydrolysis and oxidation.

Environmental conditions, including pH, temperature, and the presence of other substances, significantly impact the efficiency of PPCP removal mechanisms. The pH of the treatment environment affects the ionization state and reactivity of PPCPs, thereby influencing processes like hydrolysis, adsorption, and microbial activity. Optimal pH conditions lead to the correct ionisation state further enhancing these processes, improving overall removal efficiency. Temperature is another critical factor; higher temperatures generally increase the rates of chemical and biological reactions, enhancing the degradation and removal of PPCPs. It is important to mitigate excessive stressors on the microbes performing the process. Hence, excessive heat can reduce their enzyme activity. So, proper protocols need to be maintained such that the optimum enzyme activity is reached by the microbial enzymes during degradation or chelation and adsorption. The presence of co-contaminants and organic matter in wastewater can further complicate treatment efforts. Co-contaminants may compete for adsorption sites, reducing the effectiveness of adsorptive removal mechanisms. They can also inhibit microbial activity, complicating biodegradation efforts.

The choice of treatment technology and operational parameters also plays a pivotal role in determining the dominant removal mechanisms and their effectiveness. Advanced technologies like membrane bioreactors (MBRs) and advanced oxidation processes (AOPs) offer enhanced removal capabilities but may involve higher operational costs and complexity. A single method is not as efficient as a combination of methods. For instance, combining biological treatment with membrane filtration can enhance the overall removal efficiency by addressing both soluble and particulate forms of PPCPs. Optimizing operational parameters, such as contact time, flow rates, and dosages, is essential for maximizing the performance of PPCP removal mechanisms. It is important to maintain sanitation and operational hygiene to reduce mishaps and reduce fouling o system apparatus. By understanding and addressing these factors, wastewater treatment facilities can develop more effective strategies to mitigate the environmental impact of PPCPs and protect public health.

8.10 Fate of PPCPs After Biological Treatment

The fate of PPCPs after biological treatment is influenced by the treatment method, the properties of the PPCPs, and environmental conditions involved. The main pathways include.

The main pathways of degradation of PPCP includes biodegradation, where PPCPs are broken down into smaller, less harmful compounds. Compounds like ibuprofen can be metabolized into carboxy-ibuprofen and hydroxy-ibuprofen (Ternes et al. 2002). The PPCP products such as triclosan can also be adsorbed by binding to sludge or soil. Plants in constructed wetlands can absorb PPCPs, effectively removing them from the wastewater. Studies have shown that plants like *Typha latifolia* can uptake PPCPs like naproxen (Dordio et al. 2010). PPCPs may be converted into other compounds with different properties. For example, certain antibiotics can transform into less active metabolites. Some PPCPs may volatilized into the air, though this is less common for most PPCPs due to their low volatility.

The efficiency of PPCP removal from biologicals processes tends to vary depending on the method and on various other factors such as hydrophobicity, charge, and biodegradability. Hydrophobic compounds tend to adsorb to sludge, while hydrophilic compounds may remain in the water phase. The treatment process has a crucial role to play in the mechanism and efficiency of removal. Membrane bioreactors (MBRs) have higher removal efficiencies than activated sludge systems when it comes to removing hydrophilic PPCPs. The temperature, pH, and nutrient availability affect microbial activity and thus PPCP removal. Optimal conditions lead to efficient biofilm formation, and can lead to higher removal efficiency.

Despite advancements, several challenges remain in the removal of PPCPs from wastewater. Developing standardized methods for identifying and quantifying PPCPs is crucial for accurate assessment of treatment efficiency and environmental impact. Research is needed to understand the toxicity and environmental impact of PPCP transformation products, as some byproducts may be more harmful than the parent compounds. Optimizing treatment processes to find the most effective and efficient combinations of biological methods is essential, including the integration of advanced technologies to enhance removal rates. Implementing new technologies like enzyme-based treatments and genetically engineered microorganisms shows promise for targeting specific PPCPs resistant to conventional treatments.

Biological methods offer a promising approach to the removal of PPCPs from wastewater, balancing cost-effectiveness and environmental sustainability. By understanding the fate of PPCPs and continuously developing new and improved biological treatment methods, we can work towards minimizing their environmental impact and protecting water resources. Continued research and innovation are essential to address the challenges and enhance the efficiency of PPCP removal in wastewater treatment processes.

8.11 Conclusion

Understanding the different mechanisms involved in PPCP removal is crucial for designing effective wastewater treatment strategies and minimizing the environmental impact of these emerging contaminants. Biological, physical, chemical, and combined mechanisms each offer unique advantages and face specific challenges. By developing and collating different mechanisms, and optimizing treatment conditions, it is possible to achieve efficient and comprehensive removal of PPCPs from wastewater, thereby protecting aquatic environments and public health.

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Chapter 9
Bioremediation of Pharmaceutically Active Compounds (PhACs): Strategies, Mechanisms, and Future Prospects

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Abstract In recent years, pharmaceutically active compounds (PhACs) have emerged as ubiquitous contaminants in various environmental matrices, posing potential risks to the ecosystem. As reported in different studies, the indirect ingestion of these compounds can cause adverse effects on human health. Traditional water treatment techniques are not fully efficient to remove these compounds from wastewater and other contaminated environments. The bioremediation by utilization of microorganisms e.g., bacteria, fungi, and algae in various treatment processes like activated sludge process (ASP), membrane bioreactors (MBRs), moving bed biofilm reactors (MBBRs) have drawn interest as a sustainable and efficient technique to degrade PhACs. The performance of these processes is influenced by different environmental factors such as pH, temperature, and co-contaminants. The highest efficiency for the removal of different PhACs was achieved through microbe based remediation processes as reported in some studies. The sorption process using biochar has also shown higher efficiency for removing a number of PhACs like diclofenac, ibuprofen, sulfamethoxazole etc. This chapter comprehensively explores the diverse microbial mechanisms involved in bioremediation of PhACs, elucidating the interplay between microbial consortia and genetically modified microorganisms, with special emphasis on their synergistic effects in enhancing degradation efficiency and substrate specificity. The prospect, potential challenges, limitations and possible solutions related to bioremediation techniques such as reactor design, microbial adaptability, and substrate toxicity are also explored. This review may be an invaluable

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S. Dey and M. P. Shah (eds.), *Biotechnological Removal of Emerging Pollutants from Wastewater Systems*, Advances in Wastewater Research,
https://doi.org/10.1007/978-981-96-3945-8_9

resource for academics, practitioners, and policymakers involved in environmental remediation projects.

Keywords Pharmaceutical active compounds (PhACs) · Bioremediation · Biochar · Membrane bioreactors (MBRs) · Genetically modified microorganisms · Activated sludge process (ASP) · Environmental factors

9.1 Introduction

In the age of modern medicine, the benefits of pharmaceuticals have transformed healthcare, alleviating suffering, and prolonging lives. As the reliance on these compounds has grown, the unintentional environmental impacts are also evident now. The pharmaceutically active compounds (PhACs), represent a new category of pollutants also known as contaminants of emerging concerns (CECs). PhAcs include analgesics, antipsychotics, diuretics, tranquilisers, and psychiatric drugs, as well as antioxidants, blood products, hormones, interleukins, monoclonal antibodies, and vaccines, the primary ingredients in human and veterinary medications (Amobonye et al. 2023).

PhACs are consumed or applied topically for therapeutic purposes. These compounds may enter into different environmental compartments like soil, water, and sediments primarily through discharged wastewater from households, municipalities, industries, healthcare facilities, research institutions; agricultural runoff and incorrect disposal. The concentration level of pharmaceutical compounds depends on the climate and socio-economic condition of that region. In the present situation, the human population uses both legal and illegal pharmaceutical compounds that ultimately find their way to our environment, which also pose a greater negative impact in small amounts of exposure. Even though PhACs may only be present in minute amounts (ng/L to μg/L), have been recorded in effluents, sediments, surface water, groundwater, and sometimes in drinking water supplies. The ability of PhACs to develop antibiotic resistance, alter the endocrine systems, and persist in the environment, poses alarming ecological and human health issues as they have the bioaccumulative capacity (Papagiannaki et al. 2022). In drinking water sources in a Chinese city in the middle reaches of the Yangtze River, varying concentrations (<LOQ–118.60 ng/L) of antibiotics, such as ciprofloxacin, erythromycin, ciprofloxacin, roxithromycin, sulfadiazine, sulfamethoxazole, tetracycline, and oxytetracycline, along with analgesics, ibuprofen, and naproxen, were found (He et al. 2022). Ramaswamy et al. (2011) reported the occurrence of pharmaceutical compounds like carbamazepine (CBZ) an antiepileptic drug in several water samples from the river Kaveri, Vellar, Tamiraparani and Pichavaram mangrove forest area in Tamil Nadu (TN). Mutiyar and Mittal (2014) reported the presence of antibiotics in influent and effluent STPs in Delhi. They have also traced the presence of antibiotics in the Yamuna river. According to this report, the concentration of ampicillin in untreated and treated wastewater was 104.2 μg/L and 12.7 μg/L respectively.

As reported in different studies, approximately 8–9 million kg of antibiotics were used during the year 2013 and consequently, much higher amounts of antibiotic residual were released to the environment, especially in the aquatic environment. It seems to be a very challenging task for researchers to remove these emerging contaminants from the environment (Amobonye et al. 2023; Papagiannaki et al. 2022; Pennington et al. 2017). Due to the complex nature of contamination by PhACs, there is a need for novel composite strategies for the remediation of these compounds, based on biological processes. The biological remediation processes go beyond the limits of conventional remedial techniques. One important viable solution to the contamination by PhACs is to use living organisms or their metabolic activities to detoxify or remove contaminants. At its core, the bioremediation process capitalizes on the inherent biochemical capabilities of microorganisms and plants to metabolize, degrade, or sequestrate PhACs and transform them into less harmful forms or incorporate them into biological structures (Amobonye et al. 2023; Barooah et al. 2023). As we navigate to the frontiers of PhAC bioremediation, we confront a spectrum of challenges and opportunities. From microbial community dynamics to substrate specificity, the efficacy of bioremediation hinges upon a myriad of factors that dictate its success in diverse environmental contexts. Moreover, the ethical, regulatory, and socio-economic dimensions of the bioremediation process for PhACs, need a multidisciplinary approach, encompassing scientific inquiry, policy formulation, and public engagement. In visualizing the future of bioremediation for PhACs, we glimpse an outlook, defined by innovation, collaboration, and adaptive resilience. In this regard, organisms from all classes ranging from bacteria to microalgae, and fungi have been highlighted to facilitate the bioremediation of PhACs as individuals or in consortia. Emerging technologies such as nano-bioremediation and synthetic biology hold the promise of enhancing remediation efficiency while raising novel ethical considerations and risk assessment paradigms also. All the spectrums of bioremediation are tried to be highlighted as follows.

9.2 Understanding Pharmaceutically Active Compounds (PhACs)

Pharmaceutically Active Compounds (PhACs) constitute a heterogeneous group of chemical entities that are derived from pharmaceuticals, and used as human and veterinary medicine to treat or prevent different diseases. It has various bioactive properties that influence biological systems upon exposure (Amobonye et al. 2023; Barooah et al. 2023). Globally pharmaceutical industries produce more than 10,000 distinct medicines with 3,000 and 4,000 distinct active components to treat twenty-four (24) therapeutic groups (Ramawat et al. 2009). These compounds encompass a broad spectrum of substances, including but not limited to analgesics, antibiotics, hormones, antiepileptics, lipid-lowering drugs, β-blockers, antiulcer drugs and antipsychotics, among others (Hawash et al. 2023; Nguyen et al. 2024). Along with these substances, veterinary drugs, and active ingredients found in cosmetics and hygiene products are also included under this category. The entry of PhACs into the environment is multifaceted, originating from various anthropogenic activities. Primary sources include the excretion of unmetabolized or metabolized drug residues by humans and animals, which can subsequently contaminate wastewater treatment plants and enter surface water and groundwater systems (He et al. 2022; Papagiannaki et al. 2022). Additionally, improper disposal of discarded medicines, effluents from pharmaceutical industries, and runoff from agricultural areas where veterinary drugs are used contribute to the environmental burden of PhACs. Effluents from wastewater treatment plants (WWTPs), which may incompletely remove PhACs, serve as significant contributors to environmental contamination. PhACs go through complex fate and transit processes when they enter the environment, which are impacted by both environmental factors and their physicochemical characteristics. These substances may transform abiotic activities like hydrolysis and photolysis, biotic processes mediated by microbes, and sorption to sediment and soil particles (Nguyen et al. 2021). The extent of transformation and persistence varies greatly among PhACs, with some exhibiting resistance to degradation and others undergoing rapid transformation or mineralisation. Contamination by PhACs has a wide range of ecological effects on different trophic levels within ecosystems. Because of their direct intake from water and sediment, aquatic organisms i.e., fish, invertebrates, and aquatic plants are more vulnerable to the negative consequences of PhAC exposure. Several pieces of evidence show that pharmaceuticals may disturb hormone balance, alter the composition and essential roles of natural microbial communities, harm fish and invertebrates, and, in the case of antibiotics, lead to antibiotic resistance genes (ARGs) and bacteria through horizontal gene transfer mechanisms (Alvarino et al. 2014; Ding and He 2010; Marti et al. 2014). The physiological and metabolic characteristics of *Danio rerio* larvae (zebrafish) were altered by a sublethal dose of mianserin, a tetracyclic antidepressant and 0.6 μg/L of bupropion resulting in a considerable decrease of their growth (Moreira et al. 2022; Yang et al. 2014). In another study, paracetamol exposure was found to cause oxidative stress, inhibition of liver enzymes, genotoxicity, and alterations in steroid hormones in *Rhamdia quelen* (catfish), similarly, ibuprofen (1.0 μg/L for 14 days) also showed nephrotoxicity (Mathias et al. 2018). Reproductive impairment, immunological issues, developmental abnormalities, and behavioural alterations are examples of a few of the negative outcomes linked to long-term exposure to sublethal amounts of PhACs. The development of antibiotic resistance genes caused by sublethal concentrations of antibiotics in aquatic ecosystems poses a significant public health concern, as environmental reservoirs of antibiotic resistant genes (ARGs) may serve as reservoirs for transmission to human pathogens, compromising the efficacy of antibiotic therapies (Amarasiri et al. 2020). This phenomenon of antimicrobial resistance (AMR) represents a significant concern associated with PhAC contamination. Subinhibitory concentrations of antibiotics in environmental compartments can be selected for antibiotic-resistant bacteria, potentially leading to the dissemination of resistance genes, and compromising the effectiveness of antibiotic therapies in clinical settings. Environmental, human, and animal health interconnectedness underscores the importance of addressing PhAC contamination through holistic and interdisciplinary approaches. Different types of pharmaceutical compounds with some basic details are mentioned in Table 9.1.

9.2.1 Sources and Pathways of Contamination

Understanding the sources of Pharmaceutically Active Compounds is essential for developing targeted mitigation strategies and implementing measures to reduce their release into the environment. Diverse sources of PhACs in the environment are discussed below.

9.2.1.1 Human and Animal Excretion

The excretion of pharmaceutical chemicals by humans and animals is one of the main sources of PhACs in the environment. When individuals consume medications, whether prescribed drugs or over-the-counter remedies, a portion of the active pharmaceutical ingredients (APIs) may be metabolized and excreted from the body unchanged or as metabolites. Excretion pathways involve active transporters, such as ATP-binding cassette (ABC) transporters and solute carrier (SLC) transporters, which facilitate the movement of pharmaceutical compounds and their metabolites across cellular membranes in organs such as the kidneys and liver (Taft 2009; Veiga-Matos et al. 2020). Pharmaceutical excretion is influenced by a variety of factors, including the characteristics of each patient, dosage schedules, and drug properties. Excretion of both parent chemicals and metabolites may contribute to the total load of PhACs in wastewater systems through sewage and contaminate groundwater and surface water (Couto et al. 2019).

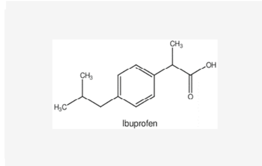
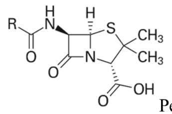
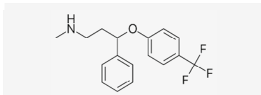
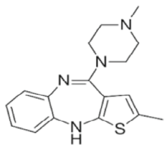
9.2.1.2 Pharmaceutical Manufacturing

The production techniques employed in pharmaceutical manufacturing facilities can make them substantial sources of contamination. Raw materials, intermediates, and finished products may be discharged into wastewater streams during the synthesis and formulation of pharmaceutical products (Nguyen et al. 2024). Wastewater from pharmaceutical production industries may not be properly treated, which can lead to the release of pharmaceutically active compounds into the environment, threatening nearby ecosystems and communities.

9.2.1.3 Agricultural Activities

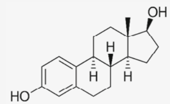
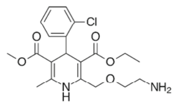
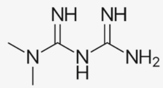
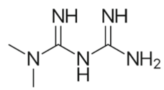
The use of pharmaceuticals in agriculture, particularly in livestock farming, is another important source of PhAC contamination. Veterinary medications given to livestock

Table 9.1 List of pharmaceutical compounds and their likely environmental impacts

Nature of the pharmaceutical compounds	Examples	Environmental impacts	Chemical structure
Analgesics/nonsteroidal anti-Inflammatory drugs (NSAIDs)	Ibuprofen, naproxen, acetaminophen (Paracetamol)	Disrupt physiological processes and behavior, leading to reduced reproductive success and altered community dynamics in aquatic ecosystems	
Antibiotics	Penicillin, ciprofloxacin, tetracycline	Antimicrobial resistance (AMR) in environmental bacteria, potentially compromises the effectiveness of antibiotic therapies in clinical settings Disrupt surface water microbial communities and ecosystem processes	 Penicillin
Antidepressants	Sertraline, fluoxetine, amitriptyline	Disrupt neuroendocrine function in fish, alter behaviour, and impair reproductive success	 Fluoxetine
Antipsychotics	Risperidone, olanzapine, quetiapine	Lead to behavioral changes, altered neurotransmitter levels, and reproductive impairment in exposed species	 Olanzapine

(continued)

Table 9.1 (continued)

Nature of the pharmaceutical compounds	Examples	Environmental impacts	Chemical structure
Hormones	Estradiol, testosterone, thyroxine	Disrupt endocrine function in aquatic organisms, leading to low fertility and decreased egg production in females, or lead to reduction gonad size or feminization of male fish	 Estradiol
Beta-blockers	Amlodipine, lisinopril, metoprolol	Impact the growth, reproduction, cardiac development, impaired ion regulation, and oxidative stress of aquatic organisms	 Amlodipine
Antidiabetics	Insulin, metformin, glipizide	Disrupt endocrine system	 Metformin
Antihistamines	Diphenhydramine, cetirizine, loratadine	Disrupt neurological function, alter feeding behavior, and impair reproduction in aquatic organisms	 Diphenhydramine

for therapeutic or preventive purposes can be excreted by animals and enter the environment through manure and runoff. It has been recorded that about 3,000–27,000 tons of drug chemicals are discharged via livestock manure into the environment (Song and Guo 2014). Additionally, the application of biosolids (treated sewage sludge) as fertilizer on agricultural lands can introduce PhACs into soil, where they may persist and impact soil quality and biota. According to a study by (Gros Calvo et al. 2019), swine slurry contains polycyclic aromatic hydrocarbons (PAHs) which are also included in PhACs at concentrations of up to 20 mg/L and 7500 µg/kg dw in the liquid and solid fractions. In contrast, cattle manure was found to contain fewer PhACs, specifically tetracyclines, lincosamides, pleuromutilins, and ionophores. As a result, soils amended with manure were enriched with average concentrations ranging from 0.078 to 150 µg/kg dw in surface layers. Sometimes the residual part of medicine remains in the animal's body after death this residual part affects the environment, for examples diclofenac, a nonsteroidal anti-inflammatory drug (NSAID) used for cattle joint pain but after the death of livestock it becomes causes kidney failure in vultures (Moreno-Opo et al. 2021) which was considered as prime cause for drastic declination of vulture (*Gyps bengalensis*) population in Southern Asia.

9.2.1.4 Disposal of Unused Medications

The environment becomes contaminated with PhACs when medicines that are unused or expired are disposed of improperly. Common disposal practices, such as flushing medications down the toilet or pouring them down the drain, can lead to the direct release of pharmaceutical compounds into wastewater systems. Landfill disposal of pharmaceutical waste also poses risks of leaching and contamination of soil, surface water and groundwater. In landfill leachates antibiotics were not as predominant as PhAC, for evidence globally, tetracycline and trimethoprim were detected up to 19 µg/L and 8.08 µg/L respectively in landfill leachates (Sui et al. 2017). Sulfamethazine was also found to be 16.17 µg/L in landfill leachates (Cheng et al. 2018; Yu et al. 2020).

9.2.1.5 Hospital and Healthcare Facilities

Healthcare facilities e.g., Hospitals, clinics, and nursing homes are important sources of PhAC contamination due to the widespread use of pharmaceuticals in patient care. Pharmaceutical compounds may enter wastewater systems through patient excretion, drug administration, and improper disposal practices within healthcare settings. Effluents from healthcare facilities can contain several hundreds of µg/L concentrations of antibiotics, analgesics, and hormones, contributing to environmental contamination (Khan et al. 2021). Solid waste disposal practices also encountered with PhACs cause soil and water contamination (Majumder et al. 2019).

9.2.1.6 Wastewater Treatment Plants (WWTPs)

While wastewater treatment plants play a crucial role in removing pollutants from sewage and wastewater, they are also potential sources of PhAC contamination. Despite treatment processes such as activated sludge, filtration, and disinfection, some PhACs may persist or remain in effluent discharged from WWTPs due to lack of advanced removal techniques of PhACs. PhACs, which range in concentration from 0.001 to 57 μg/L and include analgesics, antidiabetics, anti-inflammatory drugs, and psychiatric medications, were found in high amounts in WWTP effluents of Costa Rica (Ramírez Morales et al. 2020). Antibiotics including ofloxacin, erythromycin, ciprofloxacin, and roxithromycin were also found in WWTP at amounts as high as 6.7 μg/L in another investigation (Amobonye et al. 2023). Effluent from wastewater treatment plants can release PhACs into receiving water bodies, perpetuating environmental contamination.

By addressing the above mentioned sources through pollution prevention, improved treatment technologies, and responsible use and disposal practices, we can work towards minimizing PhAC contamination and safeguarding environmental and human health. Different sources and pathways of pharmaceutically active compounds (PhACs) in the ecological matrix are mentioned in Fig. 9.1.

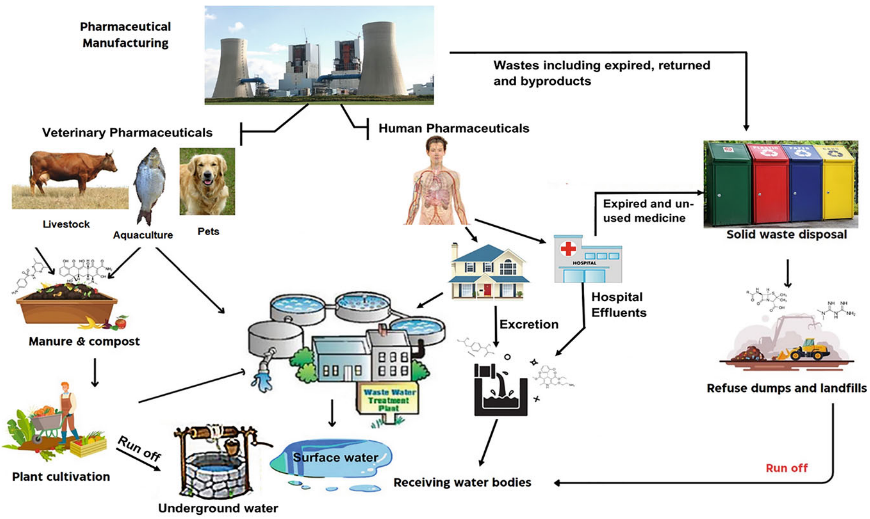


Fig. 9.1 Sources and pathways of pharmaceutically active compounds (PhACs) in the environmental matrix

9.2.2 Environmental Impact of PhACs

Pharmaceutically Active Compounds (PhACs) pose significant environmental challenges due to their persistence, bioaccumulation potential, and diverse modes of action. The presence of PhACs in environmental compartments can lead to a range of ecological disruptions and human health concerns, highlighting the need for comprehensive risk assessment and management strategies.

i. ***Ecological Disruption***:

- *Bioaccumulation*: Compounds like carbamazepine, an antiepileptic drug, have the potential to bioaccumulate in organisms due to their lipophilic nature and resistance to metabolic breakdown. Bioaccumulation occurs when organisms absorb and retain PhACs from the environment at concentrations higher than those in their surroundings. Studies have shown that carbamazepine (CBZ) can accumulate in fish tissues, which can lead to biomagnification along the food chain, with predators accumulating higher concentrations of PhACs than their prey (Vernouillet et al. 2010). *Jenynsia multidentata* exposed to CBZ and two of its metabolites (carbamazepine-10,11-epoxide—CBZ-EP and 2-hydroxy carbamazepine—2-OH-CBZ) were monitored under laboratory exposure as a result presence of CBZ in gill and muscle was observed (Valdés et al. 2016). Diclofenac was the medicinal compound with the highest concentration found in these edible fish species (range: 551.8–1812 ng/g) from samples taken from Kalk Bay Harbour in South Africa (Ojemaye and Petrik 2019).
- *Toxicological Effects*: PhACs can exert toxic effects on aquatic and terrestrial organisms, including fish, invertebrates, and plants. Chronic exposure to sublethal concentrations of PhACs may impair growth, reproduction, and behavior, leading to population declines and altered community dynamics. The cultivation of phytoplanktons, namely *Chlorella vulgaris*, *Scenedesmus obliquus*, and *Ulothrix sp.,* in a solution containing less than 21 mg/L of streptomycin, inhibited the development of *Chlamydomonas reinhardtii* at a concentration of 0.66 mg/L (Singh et al. 2021). Endocrine-disrupting compounds, such as synthetic hormones and estrogenic compounds, can interfere with hormonal signalling pathways in wildlife, resulting in reproductive abnormalities and developmental disorders (Ojemaye and Petrik 2019). Fluoxetine and venlafaxine, an antidepressant, have been found to induce behavioral changes and alter neurotransmitter levels causing neurotoxicity in a wide range of fish (Salahinejad et al. 2022). Chronic exposure to fluoxetine can disrupt mating behavior, feeding habits, and predator-prey interactions, impacting ecosystem dynamics.

ii. ***Antimicrobial Resistance (AMR) Emergence***:

- *Selective Pressure*: The presence of antibiotics and other antimicrobial agents in the environment can exert selective pressure on microbial communities, favouring the survival and proliferation of antibiotic-resistant bacteria. Subinhibitory concentrations of antibiotics in environmental compartments can promote the acquisition and spread of antibiotic resistance genes through horizontal gene transfer mechanisms. Tetracycline antibiotics, used extensively in livestock farming, exert selective pressure on environmental bacteria. Studies have demonstrated the enrichment of tetracycline-resistant bacteria in agricultural soils treated with manure from antibiotic-treated animals (Zalewska et al. 2021).
- *Public Health Risks*: The emergence and spread of antimicrobial resistance (AMR) in environmental bacteria pose risks to human and animal health. Resistant bacteria may transfer resistance genes to human pathogens, diminishing the effectiveness of antibiotic therapies and increasing the prevalence of treatment-resistant infections. It is thought that the gene pool of environmental microorganisms is still unexplored. Several of the genes they carry might be able to function as ARGs if they manage to enter a pathogenic bacterium. revealed that additional antibiotic resistance mechanisms, including synthetic ones, can already be present in the microbial pangenome and spread quickly after the medications were introduced into clinical use (Saima et al. 2020). AMR is recognized as a global health crisis, requiring coordinated efforts to mitigate its spread. Escherichia coli strains resistant to multiple antibiotics have been isolated from recreational waters, raising concerns about the transmission of resistant pathogens through recreational activities (Nappier et al. 2020).

iii. ***Endocrine Disruption***:

- *Hormonal Imbalance*: Certain PhACs, such as estrogenic chemicals and synthetic hormones, can interfere with a species' or human's ability to regulate their hormones. Through attaching to hormone receptors and changing hormonal signalling pathways, these substances imitate or interfere with natural hormones. In species exposed to endocrine disruption, problems in reproduction, developmental diseases, and compromised immunological function can result. Some plastic items and pharmaceutical formulations contain the chemical bisphenol A (BPA), which has estrogenic action and can interfere with wildlife's endocrine system. Research has connected BPA exposure to fish and amphibians' reduced fertility, changing hormone levels, and anomalies in their reproductive systems. For example, several reproductive anomalies, such as the ova-testis syndrome in male fish, have been linked to elevated amounts of circulating vitellogenin, as shown in Japanese medaka (*Oryzias latipes*) exposed to BPA (Horie et al. 2020). BPA also alters the gene expression profile responsible for steroid hormone production (Faheem and Bhandari 2021).

- *Population-Level Effects*: Endocrine-disrupting compounds can have population-level effects on wildlife, including changes in sex ratios, feminization of male organisms, and reproductive failure. Ethinylestradiol from contraceptive medications has been associated with the feminization of male fish in rivers impacted by wastewater effluents. Male fish exposed to estrogenic compounds may develop intersex characteristics, including the presence of oocytes in testicular tissue (Faheem and Bhandari 2021). These effects can cascade through ecosystems, leading to biodiversity and ecosystem resilience declines. Gestagens also cause disruptions to the hypothalamic-pituitary-gonadal (HPG) axis, which in turn causes changes in fish hormone levels. Furthermore, gestagen exposure can negatively impact fish reproduction even at low concentrations, leading to worries about their impact on the fish population. These consequences include decreased egg production, masculinization, feminization in males, and altered sex ratios (Jenila et al. 2023).

iv. ***Human Health Concerns***:

- *Drinking Water Contamination*: The presence of PhACs in drinking water sources raises concerns about potential human health effects. While concentrations of PhACs in drinking water are typically low, chronic exposure to mixtures of pharmaceutical compounds may pose risks to vulnerable populations, including pregnant women, infants, and individuals with compromised immune systems. Such as sulfamethoxazole, an antibiotic, has been detected in drinking water sources worldwide. Chronic exposure to low doses contributes to the selection and dissemination of antibiotic-resistant bacteria in the human gut microbiota (Zainab et al. 2020).

9.3 Bioremediation as a Strategy for Removal and Remediation

Removal and remediation of PhACs from the environmental matrix can done through different methods including Advanced Oxidation Processes, adsorption (Activated Carbon Adsorption); Abiotic degradation (Photolysis, Hydrolysis, Volatilization, Chemical Precipitation etc.) and Biotic degradation or Bioremediation. Among them, bioremediation processes offer environmentally sustainable approaches for the removal or degradation of Pharmaceutically Active Compounds (PhACs) from contaminated sewers and environments.

Bioremediation of PhACs refers to the process of using biological organisms or their byproducts to break down, metabolize, or otherwise mitigate the environmental impact of these compounds. Bioremediation approaches for PhACs typically involve the use of microorganisms such as bacteria, fungi, or algae, as well as plants, enzymes, or microbial consortia. These organisms possess the enzymatic machinery necessary to break down complex organic molecules into simpler, less harmful substances through processes such as biodegradation, biotransformation, or bioaccumulation to immobilize them for subsequent removal.

Bioremediation of PhACs can be done through the following mechanisms-

i. ***Biodegradation***: Indigenous microbial communities play a crucial role in biodegradation processes, with diverse microbial taxa contributing to the degradation of different PhACs (Pérez and Barceló 2007). Microorganisms utilize pharmaceutical ingredients as carbon and energy sources, initiating metabolic pathways that may involve oxidation, reduction, hydrolysis, or conjugation reactions. This process often involves the sequential breakdown of complex organic molecules into simpler compounds through enzymatic reactions. Aerobic degradation pathways typically involve the activation of PhACs by oxygenizing, leading to the formation of reactive intermediates that undergo subsequent transformations. Anaerobic degradation processes occur in oxygen-depleted environments and may involve fermentative, methanogenic, or sulfate-reducing microorganisms. For instance, *Pseudomonas stutzeri* and *Shewanella putrefaciens* have been found to effectively degrade common antibiotic sulfamethoxazole at 61.79% and 68.67% respectively, and also degrade chloramphenicol with about 85.75 and 85.70% efficiency, under aerobic conditions (Yang et al. 2021). This bacterium utilizes enzymes such as monooxygenases and dioxygenases to break down sulfamethoxazole into simpler compounds like 4-amino antipyrine and N4-acetyl sulfamethoxazole (Pérez and Barceló 2007).

ii. ***Biotransformation***: Microorganisms enzymatically modify PhACs, converting them into less toxic or more readily degradable forms. Biotransformation may involve processes such as hydroxylation, oxidation, reduction, or conjugation. For instance, *Phanerochaete chrysosporium* has been demonstrated to degrade the antibiotic tetracycline by oxidizing its aromatic rings, leading to the formation of less toxic metabolites (Pérez and Barceló 2007; Wen et al. 2010). These fungi produce ligninolytic enzymes such as lignin peroxidase, manganese peroxidase, and laccase, which can oxidize a variety of PhACs. Manganese peroxidase (MnP) prepared from the *P. chrysosporium*, 72.5% of 50 mg/L of tetracycline was degraded under treatment 40 U/L of MnP, while 84.3% of 50 mg/L of oxytetracycline was degraded with the same amount of the catalyst added, within 4 h (Wen et al. 2010).

iii. ***Sorption and Accumulation***: Some plants and microbes have the ability to absorb or deposit contaminants on their surfaces or in their tissues, which effectively isolates the chemicals from their surroundings environment and lowers their concentration. According to studies, *Phragmites australis* can efficiently remove pharmaceutical compounds like ibuprofen from wastewater effluents by metabolizing them into hydroxy ibuprofen, carboxy ibuprofen, 1,2-dihydroxy ibuprofen, and glucopyranosyloxy-hydroxy ibuprofen (He et al. 2017). This lowers the concentration of PACs in the aquatic environment.

iv. ***Synergistic Interactions***: Microbial consortia or engineered microbial communities may exhibit synergistic interactions that enhance the bioremediation of

PhACs through complementary metabolic pathways or cooperative behaviors. A different study demonstrated that a consortium consisting of *Pseudomonas aeruginosa*, *Bacillus subtilis*, and *Acinetobacter calcoaceticus* exhibited synergistic interactions and significantly enhanced the degradation of a mixture of PhACs including ibuprofen, diclofenac, and naproxen compared to individual bacterial strains. This consortium was able to degrade these PhACs through a combination of enzymatic pathways, including hydroxylation, oxidation, and conjugation.

v. ***Phytoremediation***: It is an emerging cost-effective, environment-friendly mechanism involving plants' and associated rhizospheric microorganisms' uptake, translocation, and metabolism of organic and inorganic pollutants. Plants absorb PhACs through their roots, where they may undergo metabolic transformations or translocate to above ground tissues, where they may undergo metabolic transformations or accumulate in plant biomass. Rhizospheric microorganisms contribute to degradation and detoxification. Rhizospheric microorganisms, including bacteria, fungi, and mycorrhizae, contribute to PhAC degradation and detoxification through enzymatic activities and metabolic interactions with plant roots. Root exudates, such as organic acids and sugars, serve as carbon and energy sources for rhizospheric microorganisms, enhancing PhAC degradation and mineralization. Many researchers have discovered that plants, including *Phragmites karka* and *Typha latifolia*, can help remove pharmaceuticals, in addition, *Juncus effusus*, *T. latifolia*, *Phragmites australis*, and *Iris pseudocorus* were able to extract iohexol and ibuprofen from culture solutions (Carvalho 2021). It has been discovered that duckweed, or *Lemna minor*, is effective at absorbing and degrading fluorinated and chlorinated phenols. Few studies have recently documented the efficient removal and absorption of veterinary medications from manure and reinforced soil media (Singh et al. 2021).

vi. ***Bioaugmentation***: Bioaugmentation involves the introduction of exogenous microbial strains or consortia with specific metabolic capabilities to enhance the biodegradation process in contaminated environments. Three types of microorganisms can be used that are autochthonous, allochthonous and genetically modified organisms (GMOs). Autochthonous microorganisms were isolated and reinjected from the same contaminated media. Allochthonous, exogenous microorganisms isolated from another medium. GMOs, engineered microbial inoculants supplement indigenous microbial communities, providing additional degradative pathways or enzymatic activities to accelerate PhAC removal (Aboudalle et al. 2021).

vii. ***Biostimulation***: Biostimulation aims to enhance the metabolic activity of indigenous microorganisms in contaminated environments by providing nutrients, electron acceptors, or other growth-promoting substances. Nutrient amendments stimulate microbial growth and activity, proportionally promoting the degradation of PhACs through natural attenuation processes (Muter et al. 2017). Nutrient availability, particularly carbon, nitrogen, and phosphorus, is a key limiting factor for microbial activity and PhAC degradation. The addition of carbon substrates, electron acceptors (e.g., oxygen, nitrate), and micronutrients can alleviate nutrient limitations and enhance biodegradation rates.

viii. ***Enzymatic Degradation***: Enzymatic degradation employs purified or immobilized enzymes to catalyze specific reactions that degrade or transform complex pharmaceutical compounds into less toxic compounds. Enzymes interact with PhAC molecules, facilitating chemical transformations such as hydrolysis, oxidation, or conjugation, leading to their breakdown or detoxification (Wen et al. 2010). Oxidoreductase enzymes from white-rot fungi (WRF) have been proposed as a low-cost and environmentally friendly solution for water treatment. Fungal cultures are more successful in degrading pharmaceutical substances that are more hydrophobic and include electron-donating groups, such as amine and hydroxyl, in their chemical structure (Naghdi et al. 2018).

ix. ***Constructed Wetlands***: Constructed wetlands (CWs) utilize natural or engineered wetland ecosystems that contain floating or emergent rooted wetland vegetation to treat the subsurface-horizontal flow of wastewater containing PhACs and other contaminants. Microbial communities inhabiting wetland sediments and plant species degrade, transform, or sequester PhACs through biological, physical, and chemical processes, some associated cofactors also influence the removal efficiency such as physical configuration and hydraulic mode (Li et al. 2017). Earlier studies suggested that using this technique azithromycin, clarithromycin, diclofenac, and erythromycin are successfully removed from the desired environment (Singh et al. 2021).

Bioremediation offers several advantages over traditional remediation methods for PhACs, including cost-effectiveness, environmental compatibility, and the potential for sustainable long-term solutions. However, the effectiveness of bioremediation can be influenced by various factors such as the chemical structure of the PhACs, environmental conditions (e.g., temperature, pH, oxygen availability), microbial community composition, and the presence of competing contaminants.

9.3.1 Categories of Bioremediation for Removal of PhACs

It is imperative to make sure that the biologically treated effluent's byproduct is not more harmful than the influent while implementing the biological treatment. The compound's complexity, toxicity, concentration in the effluent, and, ultimately, the microbial strain's effectiveness are all important variables that affect the degradation process. Three main categories can be used to categorize the microbial degradation strategies that are now in use or developing: Bacterial, algal, and fungal bioremediation, methods of bioremediation, and phyto-bioremediation. Each of these categories is covered in more detail below.

9.3.1.1 Bacterial Bioremediation

Bacterial remediation has been used extensively to treat both industrial and municipal wastewater treatment plants. Different types of bacteria such as endophytes, pseudomonas (*Pseudomonas putida* to degrade ibuprofen, naproxen, and sulfamethoxazole), Acinetobacter (*Acinetobacter baylyi* to degrade trimethoprim and carbamazepine) and other strains of bacteria as well as species such as *B. subtilis* have been employed in the treatment process. Even though using bacteria to remove pharmaceuticals is generally less effective than other methods and there is a chance that bacteria will become resistant to antibiotics, bioremediation is still a great alternative to many chemical and physical treatment methods because microbes can naturally degrade pollutants (Yang et al. 2021; Zainab et al. 2020). Bioaugmentation or the use of a biostimulator can also improve this process. A diverse bacterial community was reported in several studies estimating the dynamics of the bacteria in the elimination of pharmaceutical traces in an aerobic granular sludge membrane reactor (Sui et al. 2017). The pharmaceuticals included salbutamol, venlafaxine, bisoprolol, metoprolol, propranolol, fluoxetine, and norfluoxetine. Proteobacteria, Bacteroidetes, and Actinobacteria are the most prevalent taxa in Latvian sewage water, followed by Firmicutes, Gemmatimonadetes, Tenericutes, Chloroflexi, Chlamydiae, Cyanobacteria, and Epsilonproteobacteria (Aboudalle et al. 2021). Researchers have employed activated sludge in lab-scale treatment to assess the removal of pharmaceuticals such as ciprofloxacin, atorvastatin, and atenolol. Biostimulation, adding nutrients to sludges, can enhance the rate of biodegradation by increasing the activity of phylum Verrucomicrobia, Gemmatimonadetes, Nitrospirae, Chlorobi, Acidobacteria, Chloroflexi, Actinobacteria, Firmicutes, Bacteroidetes, and proteobacteria (Muter et al. 2017; Singh et al. 2021). The efficiency of different bacterial genera in getting rid of a few pharmaceutical contaminants is shown in Table 9.2.

9.3.1.2 Algal Bioremediation

Algae that are chlorophyll-containing and photosynthesis-producing, such as cyanobacteria, prokaryotic organisms, and all other algae species, eukaryotic beings. Algae are extremely adaptable microorganisms that can thrive in a variety of extreme environments, including low nutrient levels, extreme pH and temperature, and can grow autotrophically, heterotrophic or mixotrophic. After being acclimated to the altered environmental conditions, algae, particularly microalgae, showed improved biodegradation capacity and tolerance. When *Chlorella vulgaris* was exposed to levofloxacin many times and its salinity increased, its biodegradation capacity to break down the antibiotic was much enhanced (Xiong et al. 2017). The processes of biodegradation, biomineralization (bioprecipitation), biosorption (cell adsorption and/or bioaccumulation), stripping (volatilization), and photodegradation appear to be involved in algal biodegradation. Pharmaceutical bioaccumulation in algal cells can lead to the production of free radicals (such as $O_2^{\cdot}$–superoxide radicals

Table 9.2 Enumeration of several effective bacterial remediation for eliminating pharmaceutical-based contaminants

Name of the pharmaceutical contaminants	Source of contaminants	Bacterial species	Removal efficiency
Ibuprofen	Wastewater	*Pseudomonas putida*	95%
	Sewage treatment plant	*Sphingopyxis sp.*	
Acetaminophen	Industrial effluents	*Bacillus subtilis*	80%
Ciprofloxacin	Hospital waste	*Arthrobacter oxydans*	70%
Cefalexin	Activated sludge	*Pseudomonas sp. CE21*	46.7%
		Pseudomonas sp. CE22	<90%
Trimethoprim	Agricultural runoff	*Rhodococcus erythropolis*	85%
Sulfamethoxazole	Urban sewage	*Mycobacterium sp.*	90%
	Activated sludge	*Pseudomonas sp. CE21*	88.1–100%
		Pseudomonas sp. CE22	87.5–95%
Carbamazepine	Pharmaceutical manufacturing	*Rhodococcus jostii*	75%
Fluoxetine	Domestic sewage	*Pseudomonas fluorescens*	88%
Salicylic acid	In vitro	*Pseudomonas fluorescens*	80–90%
	Activated sludge	*Pseudomonas sp. CE21*	36.5–100%
		Pseudomonas sp. CE22	64.5–96.9%
Oxytetracycline	Aquaculture effluents	*Bacillus cereus*	82%
Metformin	Surface water	*Cupriavidus metallidurans*	93%
Diclofenac	Landfill leachate	*Sphingomonas sp.*	78%
Erythromycin	Livestock farming waste	*Streptomyces albus*	87%
Bisphenol A	Industrial discharges	*Alcaligenes eutrophus*	91%
		Sphingomonas sp.	

(continued)

Table 9.2 (continued)

Name of the pharmaceutical contaminants	Source of contaminants	Bacterial species	Removal efficiency
Triclosan	Household products	*Bacillus thuringiensis*	84%
Atorvastatin	Pharmaceutical waste	*Pseudomonas stutzeri*	79%
Gemfibrozil	Urban runoff	*Bacillus megaterium*	86%
Naproxen	Agricultural drainage	*Escherichia coli*	68%
Sildenafil	Domestic sewage	*Rhodococcus ruber*	94%
Chloramphenicol	Veterinary pharmaceutical	*Streptomyces rimosus*	81%
Tetracycline	Poultry farm waste	*Lysinibacillus sphaericus*	77%
Quinalphos	Aquaculture effluents	*Bacillus spp. Pseudomonas spp.*	>88%
17α-Ethynylestradiol	Bioreactor	*Nitrosomonas europaea*	96%

and $OH^{\cdot}$–hydroxyl radicals) and non-radical forms (such as H_2O_2). Pharmaceuticals are broken down inside cells by two types of enzymes: phase I (cytochrome P_{450}) and phase II (which includes glutathione-S-transferases (Chen et al. 2020; Kumar et al. 2016; Matamoros et al. 2016; Xiong et al. 2016, 2017). The microalgae *Scenedesmus obliquus* and *Chlorella pyrenoidosa* were found to remove progesterone and norgestrel primarily through biotransformation, as per the research conducted by Peng et al. (2014). The algal transformation of the target chemicals by *Chlorella pyrenoidosa* was suggested to involve hydroxylation, oxidation/reduction, and side-chain breakage. In contrast, carbamazepine is eliminated by the microalgae *Scenedesmus obliquus* and *Chlamydomonas mexicana* through the processes of biodegradation, adsorption, and bioaccumulation (Xiong et al. 2016). On the other hand, it was discovered that the photodegradation and biosorption processes were prevalent and crucial in *Chlorella vulgaris*' removal of tetracycline from synthetic wastewater (de Godos et al. 2012). The efficiency of different algal species in getting rid of a few pharmaceutical contaminants is shown in Table 9.3.

9.3.1.3 Fungal Bioremediation

The fungi kingdom is a broadly distributed group well-known for its phylogenetic diversity. They are particularly noteworthy for their adaptability in the cycling of nutrients and their ability to break down organic matter in the environment (Hurdeal

Table 9.3 Enumeration of several effective algal remediations for eliminating pharmaceutical-based contaminants

Name of the pharmaceutical contaminants	Source of contaminants	Algal species	Removal efficiency (%)
Ibuprofen	Wastewater	*Chlorella vulgaris*	60–80
Atenolol	Hospital wastewater	*Chlorella vulgaris*	50–70
Enrofloxacin	Domestic wastewater	*Chlorella vulgaris*	52
		Scenedesmus obliquus	43.3
Sulfamethazine	Agricultural runoff	*Chlorella vulgaris*	24
		Scenedesmus obliquus	11
Acetaminophen	Wastewater	*Scenedesmus sp.*	70–90
Tetracycline	Aquaculture runoff	*Spirulina platensis*	50–70
Carbamazepine	Sewage effluent	*Microcystis aeruginosa*	40–60
		Chlamydomonas mexicana	35
		Scenedesmus obliquus	28
Ciprofloxacin	Hospital wastewater	*Chlamydomonas reinhardtii*	50–75
Bisphenol A (BPA)	Industrial wastewater	*Chlorella pyrenoidosa*	60–80
		Monoraphidium braunii	35–48
Sulfamethoxazole	Urban wastewater	*Desmodesmus communis*	50–70
Diclofenac	Pharmaceutical industry effluent	*Anabaena variabilis*	40–60
Naproxen	Urban wastewater	*Scenedesmus quadricauda*	60–80

et al. 2021). It makes them an effective tool for removing pollutants from homes and industries, but their ongoing growth period creates barriers to remediation technologies (Amobonye et al. 2023). Filamentous fungi in particular are being used to break down complicated and newly discovered environmental contaminants like PhACs (Ferreira et al. 2020). The breakdown of pollutants is mostly linked to three groups of filamentous fungi: ascomycetes, basidiomycetes, and zygomycetes. They are also employed as a scrubber to remove pharmaceuticals from the contaminated environment (Ferreira et al. 2020). The degradation capacity of Ascomycetes is thought to be mediated significantly by the expression of intracellular cytochrome oxidases and/

or non-specific peroxygenase, which play an important role in extracellular hydroxylation (Badia-Fabregat et al. 2017). Through hydroxylation, *Pestalotiopsis sp.* and *Epicoccum nigrum* can bioconvert diclofenac to the 4-hydroxy diclofenac metabolite (Gonda et al. 2016). The broader use of basidiomycete lignin-solubilizing enzymes for the degradation of PhACs and other emerging contaminants is made possible by their non-specificity (Roccuzzo et al. 2021; Rodarte-Morales et al. 2011). It has been established that several Basidiomycetes, such as *Bjerkandera adjusta, Ceriporiopsis subvermispora*, and *Ganoderma lucidum*, are capable efficiently of bioremediate PhACs (Naghdi et al. 2018; Saibi et al. 2022). the synergistic impact of *Bjerkandera adjusta* and *Phanerochaete chrysosporium* effectively broke down the antidepressant citalopram and fluoxetine in wastewater effluents (Rodarte-Morales et al. 2011). From the group of Zygomycetes *Mucor rammanianus* and *Umbelopsis ramanniana* are reported to Transform fluoroquinolones and carbamazepine (Kang et al. 2008; Singh et al. 2019). *Mucor hiemalis* was also capable of degrading significant levels of acetaminophen (Esterhuizen-Londt et al. 2016). The efficiency of different fungal species in getting rid of a few pharmaceutical contaminants is shown in Table 9.4.

Box 9.1 Microbial Fuel Cells: Cost-Effective Way for PhACs Removal

Microbial fuel cells (MFCs) are bio-electrochemical systems that leverage the metabolic activities of microorganisms to generate electricity from organic compounds. Recently, MFCs have gained attention for their potential in environmental applications, including the remediation of pharmaceutically active compounds (PhACs) in wastewater. MFCs consist of two main compartments:

Table 9.4 Details of several effective fungal remediations for eliminating pharmaceutical-based contaminants

Name of the pharmaceutical contaminants	Source of contaminants	Fungal species	Removal efficiency (%)
Diclofenac	Pharmaceutical industry effluent	*Phanerochaete chrysosporium*	>90
Carbamazepine	Sewage effluent	*Trametes versicolor*	>80
Fluoxetine	White-rot fungus	*Pleurotus ostreatus*	~75
Ibuprofen	Sewage effluent	*Aspergillus niger*	~65
Tetracycline	Aquaculture runoff	*Penicillium chrysogenum*	~70
Naproxen	Urban wastewater	*Trichoderma harzianum*	~60
Sulfamethoxazole	Urban wastewater	*Ganoderma lucidum*	~85
Paracetamol	Wastewater/hospital wastewater	*Rhizopus arrhizus*	~70
Ciprofloxacin	Hospital wastewater	*Aspergillus flavus*	~68

an anode and a cathode, separated by a proton exchange membrane (PEM). Microorganisms colonize the anode, where they oxidize organic matter and release electrons and protons. The electrons travel through an external circuit to the cathode, generating an electric current, while protons migrate through the PEM to the cathode. At the cathode, electrons, protons, and an electron acceptor (usually oxygen) combine to form water (Prathiba et al. 2022). Unlike costly conventional treatment methods, this low-cost energy-generating device can degrade a wide range of compounds due to its dual oxidative/reductive environment. The degradability of actual pharmaceutical wastewater in MFCs can be further improved by adjusting operating parameters or electrode materials such as anolyte composition, anode catalyst, pre-acclimation of biocatalysts, physicochemical pretreatment, and electric stimulation (Bagchi and Behera 2020; Mahmoud et al. 2022). Using an electrical system and a selective proton exchange membrane, MFCs collect free electrons and protons created by the oxidation of organic molecules from a cathode under anaerobic conditions. MFCs can treat a wide range of contaminants, such as wastewater from cities, farms, and industries (Mahmoud et al. 2022). An MFC fed with steroidal drug manufacturing wastewater (SPW) and PhACs demonstrated improved COD, an efficiency of 82%, and high-power production of 23 W/m^3, which was comparable to an MFC fed with acetate. A further instance of enhanced performance is the addition of penicillin to synthetic pharmaceutical effluent. Compared to MFCs fed wastewater containing penicillin and glucose alone, an MFC given synthetic wastewater containing both glucose and penicillin performed comparatively better (Wen et al. 2011). The MFC comprising 1 g/L glucose and 50 g/L penicillin exhibited the highest power generation of 101.2 W/m^3, which was six times greater than the total power production by MFC fed with glucose and penicillin as the only fuel. For MFC given penicillin, the current density was found to be 3.5 times higher. In addition, 98% of penicillin was also removed from the penicillin and glucose mixture within 24 h (Zhou et al. 2018).

9.3.1.4 Plant-Based Remediation Techniques

Phytoremediation is a green and sustainable technology that employs plants and their associated microorganisms to clean up contaminated environments, including those polluted with Pharmaceutically Active Compounds (PhACs). This method leverages the natural processes of plants to absorb, accumulate, transform, or stabilize contaminants, offering an environmentally friendly alternative to conventional remediation techniques. A few processes are performed in the phytoremediation process which is, Phytoextraction: Plants absorb contaminants through their roots and translocate them to above ground tissues (stems, leaves). The contaminants can be harvested along with the plant biomass. *Phragmites australis* (common reed) have been observed to uptake antibiotics from water (Zhang et al. 2022). In phytodegradation (Phytotransformation), plants take up contaminants and enzymatically (such as peroxidases, laccases, and cytochrome P450s) break them down into less toxic metabolites within plant tissues. *Populus spp.* (poplar trees) can degrade trichloroethylene (TCE) and some PhACs like carbamazepine (Limmer et al. 2018). Typha spp. (Cattails) used in constructed wetlands to treat wastewater containing PhACs such as ibuprofen, naproxen, and diclofenac. The plants take up and degrade these compounds, significantly reducing their concentrations in the treated water (Dordio et al. 2018; Zhang et al. 2023). Water hyacinth (*Eichornia crassipes*) is also capable of removing dyes that are used in pharmaceutical industries, for instance, Methylene blue, Congo red, Crystal violet, etc. with an efficiency of 88–92% within 5 contact days (Sharma et al. 2021; Wang et al. 2021). This also infers that they are also capable of Phytoremediation of removal of drugs and phenol.

9.3.2 Emerging Technologies in Bioremediation

The field of bioremediation is always changing as a result of the incorporation of novel techniques and cutting-edge technology to improve the effectiveness and efficiency of the degradation of pharmaceutically active compounds (PhACs). Some of them are mentioned below.

i. **Genetically Engineered Microorganisms (GEMs)**: Genetic engineering enables the modification of microorganisms to enhance their ability to degrade specific contaminants. This involves introducing or overexpressing genes encoding for enzymes that can break down pharmaceutical compounds. For example, *Pseudomonas putida* is genetically modified to express enhanced levels of monooxygenases and dioxygenases, which can degrade a variety of PhACs, including ibuprofen and naproxen. *Escherichia coli* is also engineered to express cytochrome P450 enzymes capable of metabolizing PhACs such as carbamazepine and diclofenac (Sahota and Sharma 2022).

ii. **Nano-bioremediation**: Nanoparticles can be used to deliver enzymes, adsorbents, or even microorganisms to contaminated sites, improving the degradation of PhACs. Nanomaterials also can be used to induce microbial degradation activity. Modified multiwall carbon nanotubes (M-MWCNTs) with immobilized laccase (L@M-MWCNTs) are capable of removing PAH and PhACs from the aquatic environment efficiently and sustainably (Grmasha et al. 2024).

iii. **Bioelectrochemical Systems (BES)**: Bioelectrochemical systems leverage the interaction between microbial metabolism and electrochemical processes to degrade contaminants. BES includes technologies like microbial fuel cells (MFCs) and microbial electrolysis cells (MECs). PhACs are efficient producers in microbial fuel cell systems during the degradation of the compounds (Bagchi and Behera 2020).

iv. **Phytomicrobiome**: This approach involves manipulating the plant-associated microbial communities (Phyto microbiomes) to enhance the degradation of PhACs. It combines phytoremediation and microbial remediation strategies. For example, modifying plant root exudates to promote the growth of specific degrading microbes and facilitate them in degrading organic pollutants (Chojnacka et al. 2023).

9.4 Future Perspectives

Pharmaceutically Active Compounds (PhACs) are of serious environmental concerns, so the remedial measures should be addressed by innovative methods and substantial breakthroughs may be obtained in the field of bioremediation. The future perspective of bioremediation for pharmaceutically active compounds (PhACs) includes the development and application of different sustainable technologies. However, by applying and/or enriching the following spectra, it will be feasible to enhance the effectiveness of removal and efficiency of degradation for PhACs from environmental matrices like water, soil:

i. **Advancement in Genetic Engineering**: Advancement of genetic engineering, can develop engineered microbes, which are specialized species to remediate newly emerging contaminants like PhACs. Genetically engineered microorganisms have more potential than naturally occurring species and may degrade contaminants more faster as they can be adapted quickly to new pollutants they encounter or co-metabolize.
ii. **Integration of Omics Technologies**: The principles of genomics, transcriptomics, metabolomics, and proteomics can be used in bioremediation technology as important future perspective bioremediation of PhACs. Omics technologies can be able to correlate DNA sequences with the abundance of metabolites, proteins, and mRNA (Sar and Islam 2012; Villegas-Plazas et al. 2019).
iii. **Nanotechnology Innovations**: Many potential toxic contaminants e.g., PhACs can be removed with the help of various nanomaterials. Water treatment has been given a new dimension by nanotechnology.
iv. **Use of machine learning tool**: The application of Machine Learning (ML) tools can significantly in modeling bioremediation mechanisms more accurately and non-limited applicability.

9.5 Conclusion

The long term persistence of Pharmaceutically Active Compounds (PhACs) in the environment poses a significant challenge due to their potential adverse effects on ecosystems and human health. Conventional treatment methods often fall short in effective removal of these contaminants. So, there is a necessity for the exploration of

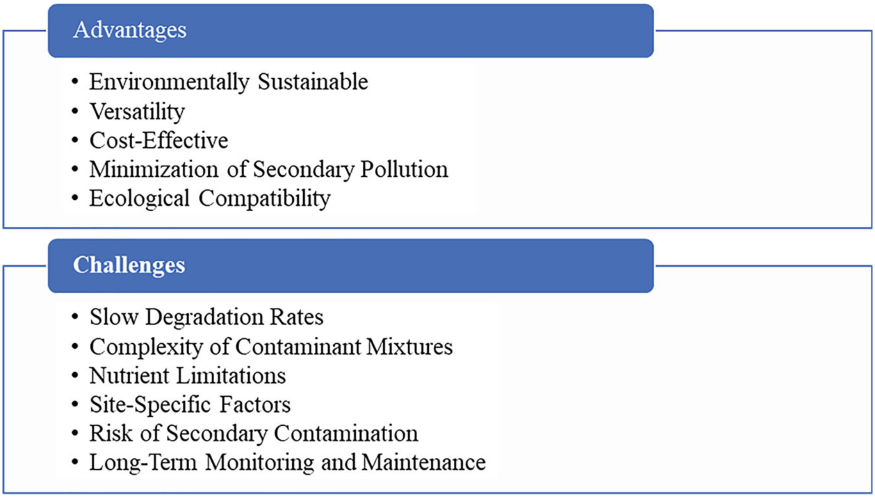


Fig. 9.2 Advantages and challenges of bioremediation practice of PhACs

bioremediation as a sustainable and efficient alternative. The advantages and challenges of bioremediation of PhACs are summarized in Fig. 9.2. This comprehensive study of bioremediation strategies, mechanisms, and prospects underscores the potential of biological processes to mitigate the environmental impact of PhACs. Bioremediation is a promising approach to address the growing concern of PhAC contamination in the environment. By harnessing the natural capabilities of microorganisms and plants, and integrating emerging technologies, effective strategies can be developed to mitigate the impact of these contaminants. However, significant challenges persist, such as environmental variability, the complexity of PhAC mixtures, and the risk of secondary pollution or bioaccumulation. Genetically Engineered Microorganisms (GEMs) can optimize the breakdown of recalcitrant PhACs through genetic engineering, while phytoremediation, such as phytoextraction and phytodegradation, utilizes plants to uptake and metabolize PhACs. Another important factor in the biodegradation of PhACs is rhizodegradation, which occurs when plant root exudates increase microbial activity in the rhizosphere. Nanotechnology, bioelectrochemical systems (BES), and synthetic biology offer novel solutions for targeted and efficient breakdown of PhACs. However, technical, and economic barriers need to be overcome. Future prospects include advanced omics technologies, interdisciplinary collaboration, and scalable solutions. Genomics, and proteomics, will provide deeper insights into microbial and plant processes involved in PhAC degradation, enabling the optimization of bioremediation strategies. To sum up, bioremediation is a viable and long-term solution to the expanding problem of PhAC pollution in the environment. A cleaner and healthier future depends on balancing technological advancements with ecological integrity, economic viability, and public acceptance.

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Chapter 10
Bioremediation of Antibiotics and Their Metabolites from Waste Water

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Abstract The last century's discovery of Antibiotics (AB) became the game changer and has turned into a big revolution in Medical and human therapeutics. Additionally, AB has several other biotechnology applications, specifically recombinant DNA technology, agriculture, animal husbandry, etc. AB are the most reliable drugs for preventing bacterial infections worldwide and are released either partially degraded in the form of some metabolites or undegraded into the environment leading to antibiotic pollution, and its remediation has been a great challenge in the present scenario. There are various antibiotic sources like laboratories, hospitals, dairy industry, and agriculture croplands generating Ab pollution and their contamination in wastewater has severe environmental repercussions. Easy availability, increased prescription and consumption rates led to an upsurge in AB concentration in the wastewater and environment. Most of the conventional wastewater treatment methods have been found ineffective for antibiotic removal and have posed serious environmental risks of AB and associated antibiotic-resistant genes (ARGs) in the microorganism channelizing the development of multiple drug-resistant microorganisms. Thus, it's important to understand the strategies for antibiotic resistance development by bacteria and also the techniques to identify AB and AGR. WHO (World Health Organization) and National policies have been implemented to prevent antibiotic resistance development in the environment, where bioremediation techniques like phytoremediation, bacterial remediation, and other living entities can play immense roles in antibiotic removal. Therefore, the present work aims to address various sources of AB,

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S. Dey and M. P. Shah (eds.), *Biotechnological Removal of Emerging Pollutants from Wastewater Systems*, Advances in Wastewater Research,
https://doi.org/10.1007/978-981-96-3945-8_10

possible decomposition mechanisms, their adverse outcomes, antibiotic resistance mechanisms, bioremediation strategies, and future challenges in mitigating AB from the environment.

Keywords Antibiotic · Antibiotic resistance genes (AGR) · Bioremediation · Biodegradation

10.1 Introduction

AB is a class of medicines that have revolutionized the eradication of bacteria in humans, animals, and plants. Since its discovery by Alexander Fleming (1928), AB has been extremely exploited to combat various diseases, saving countless lives. It has become a boon to modern medicine and enables vital therapies and procedures with a wide array of applications in broad fields. However, the immense success and their immense potential have made their continuous use is jeopardized by several threats and challenges in recent century (Gaynes 2017).

The AB research and its development are getting costlier using traditional procedures. Therefore, mushroom-like growing companies and laboratories are delivering new Ab, threatening infection control. It also requires substantial changes in the societal understanding of these drugs, policy, and investment in alternate strategies of traditional AB production. However, the microbes removed by these AB evolve resistance over time in an individual using it regularly. The unjudicial use and misuse have raised an uninvited situation of the development of antibiotic-resistant bacteria, rendering them less effective (Cook and Wright 2022).

Further, the use of AB has been extended beyond medical treatment, i.e., in research, animal farming, etc., listed below. Various types of Ab are represented in Table 10.1. They have been used in animal farming as animal growth promoters, a practice banned in the European Union since 2006 but still occurs in some countries. Statistical studies have revealed that in animal husbandry antibiotic consumption is more used than in human medicine. The first global map (mentioning 228 countries) for antibiotics used in livestock mentioned a gross estimation that 63,151 tons of total antibiotic consumption has occurred till 2010 and assumed the antibiotic consumption will get enhanced by 67% by 2030 and approximately will double in some countries (Polianciuc et al. 2020).

In livestock farming, around 24.6 million pounds of Ab are being used annually. The large amounts of Ab in animal farming may contaminate the agro-based ecosystem by the application of contaminated manure on the farmlands as fertilizer and the use of wastewater for irrigation of crops can further worsen the situation. However, there are limited studies related to the toxic levels of antibiotics present in vegetables and on resistance selection (Zhou et al. 2014). Most of the risk assessment work has pointed out the insignificant toxicity, although the link between Ab present in crops and the development of gut microbiome resistance selection has been overlooked. So, the adverse effect of Ab in irrigated water, its uptake, and persistence

Table 10.1 Antibiotics and their general characteristics

Antibiotic class	Example	Application	Type	Target
Beta-lactams	Penicillin G Cefazolin Ceftiofur	Animal, human, Veterinary (Vet.) Human Vet	Bactericidal	Targets cell wall
Aminoglycosides	Neomycin Kanamycin A	Vet Human	Bactericidal	Inhibit protein synthesis
Macrolides	Azithromycin Erythromycin	Human Human, Vet	Bacteriostatic	Abolish protein synthesis
Quinolones and fluoroquinolones	Ciprofloxacin Oxolinic acid	Human Vet	Bactericidal	Inhibit DNA replication
Glycopeptides	Vancomycin Bleomycin Polymyxin B	Vet Human Vet., human	Bactericidal	Target cell wall
Lincosamides	Clindamycin Lincomycin	Human Vet	Bacteriostatic	Abolish protein synthesis
Nitrofurans	Furaltadone Nitrofuranation nitrofurazone	Human and Vet	Bactericidal	Inhibit nucleic acid synthesis
Amphenicols	Chloramphenicol thiamphenicol	Vet Vet	Bacteriostatic	Inhibit protein synthesis
Phosphonates	Fosfomycin	Human	Bacteriostatic	Target cell wall synthesis
Tetracyclines	Chlortetracycline tetracycline	Vet Human, vet	Bacteriostatic	Inhibit protein synthesis
Rifamycin	Rifampicin Rifapentine	Human Human	Bactericidal	Inhibit nucleic acid synthesis
Sulfonamides	Sulfachloropyridazine Sulphanilamide Sulfamethazine Sulfadimethoxine Sulfamethoxazole Sulfapyridine Sulfadiazine	Human, vet Human Vet Vet Vet Human vet	Bacteriostatic	Inhibit folic acid synthesis

in edible parts of plants should be focused and more research is required on these aspects.

The bacterial resistance selection may take place even at very lower concentrations than lethal doses of susceptible cells and such mutants selected at low dosages are found to be extremely resistant in comparison to those selected at higher dosages.

Thus, the minimum acceptable antibiotic concentration permissible in irrigation water has to be declared apart from the dosage causing toxicity which will improve food security (Gudda et al. 2020).

The AB utilized in human and animal therapy through urine and excreta is causing severe contamination in the environment, thus requiring sincere optimization and/or control in the usage of Ab might play an immense role in the reduction of environmental contamination. Approximately 40–90% of the antibiotic dose gets released via excreta as a parent compound, finally reaching the surroundings and leading to contaminated soils, waters, plants, etc. (Penakalapati et al. 2017).

The other major concern arises from the unjudicial disposal of medicinal products by discharging them into the sewage systems. Pharmaceutical wastewater containing higher concentrations of Ab and resistance genes poses a severe health impact and risk due to unjustified and irresponsible disposal without proper treatment adversely harms water sources and ecosystems (Samrot et al. 2023). Therefore, it requires great collaborative efforts of policymakers, companies, scientists, regulators, society, and communities, to adopt a systematic scheme to stop AMR's spread. The global standards for assessing pharmaceutical effluents should be developed like antibiotic treatment methods and diagnostics are mandatory for assessing the impact on the environment to protect the environment and ensure better public health. Further National action plans involving comprehensive approaches should be built for combating Ab drug resistance (Rayan 2023). AB-contaminated wastewaters are treated in WWTP (wastewater treatment plants), but it is impossible to ensure 100% removal of Ab through conventional WWTP. Therefore, the sludge and final effluent from WWTP may contain Ab, and if the sludge is being used as manure fertilizer and effluent gets discharged may cause significant contamination of AB into the surrounding via wastewater, agriculture practices, sewage, contaminating soil, water, and air (Manyi-Loh et al. 2018).

The environmental impact of AB is a growing concern. They can harm non-target organisms, disrupt ecosystems, and affect the balance of microbial communities. It is not unexpected that antibiotic resistance has an intricate ecological role in affecting microbial ecosystems (Koch et al. 2021). A recent research work has tried to determine the existence of antibiotic resistance independent of human involvement. The results suggested that multiple AB resistance is a normal environmental phenomenon, which is not much affected by high anthropogenic antibiotic pressures (Perry et al. 2016).

The high AB concentrations in water sources make it challenging to assess water quality, posing many serious consequences for plant, human, and animal health. Moreover, the accelerated use of AB has led to the development of ARGs (ARGs) and antibiotic-resistant bacteria (ARB), further reducing the effectiveness of these medicines (Haenni et al. 2022). The dissemination of ARGs and ARB through horizontal gene transfer (HGT) represents a serious health risk. Various ARG subtypes like bacitracin, macrolide-lincosamide-streptogramin, quinolone, and sulfonamide resistance genes have been reported in sediments of urban rivers with various metal/biocide resistance genes and MGEs (mobile genetic elements) (Han et al. 2022; Reddy et al. 2022) and studies suggest the occurrence of HGT of ARGs in urban river ecosystems. The unjustified and unconscious release of anthropogenic and industrial waste into the water bodies will cause adverse impacts on the environment and public health (Reddy et al. 2022).

The researchers are struggling to articulate innovative multifarious approaches to remove AB from the environment. These include enzymatic remediation, bioelectrochemical methods, hydrolysis, redox reactions, and phytolysis (Prathiba et al. 2022). Biological techniques are considered better than chemical treatments to minimize contamination after the treatment process. It's essential to develop sustainable solutions to reduce their effects on the environment and human health (Huang et al. 2021). The foremost aim of this chapter is to anticipate the knowledge regarding the sources of Ab, the effects of their contamination on the environment, detection and analysis techniques, and mitigation strategies for Ab.

10.2 Possible Sources of AB in Wastewater

The rampant usage of AB in various sectors has led to traumatic consequences in antibiotic pollution in the surroundings (Kafaei et al. 2018). This pollution comes from multiple sources, including (Fig. 10.1):

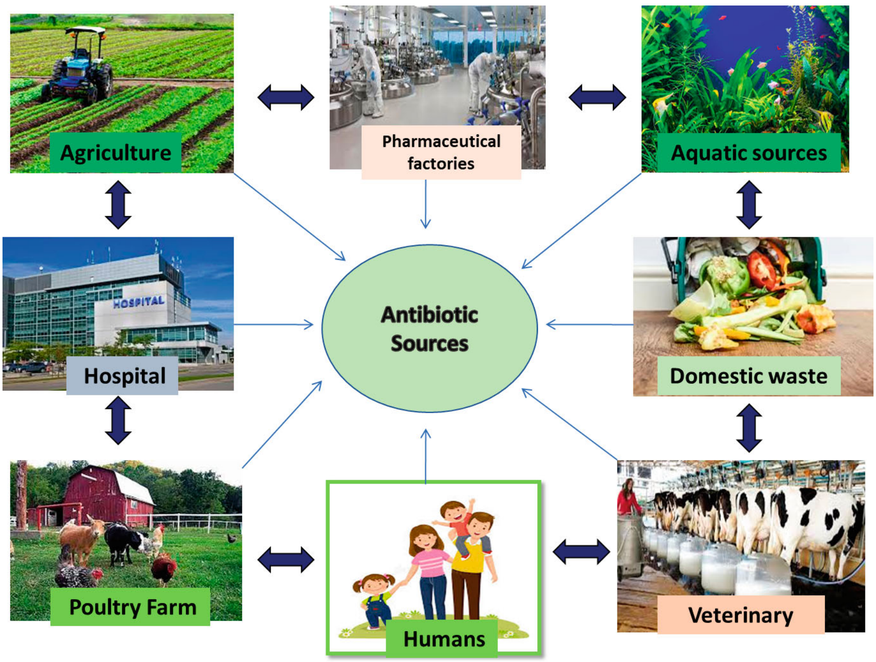

Fig. 10.1 Sources of Antibiotics causing contamination in the environment

- Hospital waste, which often contains unused AB and metabolites
- Veterinary clinics, where AB is used to treat animals
- Pharmaceutical factories, which produce AB on a large scale
- Dairy farms, where AB like monensin (increases milk production)
- Animal excreta may contain AB and their byproducts
- Domestic waste, which may include expired or unused AB
- Animal husbandry (promote growth and prevent disease)
- Municipal waste
- Poultry farms (promote growth and prevent infection).

The use of Ab have several pros and cons in the agriculture industry. It promotes growth and increases efficiency in livestock, beekeeping, and fish farming. However, it may contribute significantly to causing environmental contamination by the release of unused AB and their metabolites via animal waste. This can contaminate land and water bodies posing a risk to human health. Although plants use fewer AB than animals, they can still be present in waterways near agricultural land. It points out the upsurge of AB on a large scale in farming, contributing to environmental pollution (Kumar et al. 2019).

Pharmaceutical industries also make a major contribution to antibiotic pollution. Their wastewater, which contains AB and other pollutants, enters sewage treatment systems including domestic and industrial effluents. This can lead to the release of AB in the surroundings, getting persistent and accumulate for longer durations. Generally, AB are small molecules getting easily dissolved in water, making them quite difficult to clear from the environment (Samal et al. 2022). Examples of these AB include:

- Beta-lactams, mostly used to treat bacterial infections
- Aminoglycosides, to treat serious bacterial infections
- Lincosamides, to treat skin infections, etc.
- Macrolides, to treat respiration system related infections
- Nitrofurans, to treat urinary tract infections
- Amphenicols, to reduce bacterial disease in animals
- Phosphonates, treat bacterial infections in animals
- Quinolones, to eliminate bacteria
- Fluoroquinolones, to treat serious bacterial infections
- Rifamycins, to treat tuberculosis and other bacterial infections
- Sulfonamides, to eliminate bacteria
- Tetracyclines, to eliminate bacteria.

These AB and their variants can contaminate the environment, posing a risk to human health and the ecosystem. It's essential to address antibiotic pollution through sustainable practices and innovative solutions. Wastewater treatment plants (WWTPs) have less efficiency in AB and other micropollutants removal from water. As a result, these pollutants continue to enter our environment through wastewater (Zieliński et al. 2021). This is a global problem, and it's a significant contributor to the spread of AB in our environment. When AB is given to livestock, they can spread into fields through manure and contaminate soil and groundwater. Similarly, AB treated crops and used in aquaculture may get accumulated in the environment led to upsurge its concentration in surroundings (Gržinić et al. 2023).

AB used in animal feed get released in excreta and contaminate soil when manure is used as fertilizer. They can also enter waterways through runoff and drain flow, and even seep into groundwater. This means they can end up causing biomagnification (Kivits et al. 2018). Improper release of expiry drugs, such as flushing them down the toilet or throwing them away in landfills, can also lead to contamination. Additionally, waste from manufacturing facilities or accidental spills during production and distribution can release AB into the environment (Insani et al. 2020). These AB compounds persist and cause antibiotic-resistant bacteria development, making them less effective against infections (Prestinaci et al. 2015).

In summary, AB are not being effectively removed from wastewater, and their use in agro and animal farming industry is leading to environmental contamination. This can have serious consequences for human health and the environment, and we need to take action to address this issue (Mishra et al. 2006).

10.3 Contamination of AB in Biological Systems and Its Toxic Effects on Environment

The AB can be detected in various environmental samples, including water and soil. This contamination occurs through multiple pathways, such as wastewater effluent, agricultural runoff, and disposal of unused or expired AB. The two categories of Ab, i.e., narrow and broad-spectrum are detected in various environmental sample worldwide (Samal et al. 2022). These are discharged into different drains, followed by river and seas depending on its consumption like in sea, Hailing island, and wastewater treatment plants. Hospital effluents, municipal wastewater, aquaculture samples, veterinary and its hospitals, dairy wastes, and poultry waste are the various biological waste systems, where the antibiotic might be a challenging contaminant (Kumar et al. 2019). The accumulation of AB in the environment is a growing concern, as some can remain for extended periods, leading to antibiotic-resistant bacteria development. Fluoroquinolones, macrolides, and tetracyclines are examples of AB that can persist in the environment, while others like penicillins may break down more quickly. The impact of AB on microbial communities and biogeochemical cycles is not yet fully understood but is an area of growing concern. Research suggests that AB can alter the balance of microbial populations, leading to unintended consequences, such as the proliferation of Ab-resistant bacteria (Polianciuc et al. 2020).

Europian countries have made regulations for Ab concentration and related compounds in various medical formulations which are strictly followed in west countries. However, India lacks any legal norms for Ab usage, no strictness, less expertise and lack of regular monitoring might create an alarming situation for superbugs development with multidrug resistance (Kumar et al. 2019).

The problem of ARB is quite complicated and has multifarious factors, including geography, temperature, and antibiotic prescription rates. Studies have shown that antibiotic resistance patterns vary across regions, with higher temperatures and latitudes correlated with increased resistance. Addressing the issue of antibiotic contamination and resistance requires a comprehensive approach that involves reducing antibiotic use, improving wastewater treatment, and promoting sustainable agricultural practices. This includes implementing stricter regulations on antibiotic use, investing in wastewater treatment infrastructure, and encouraging the use of alternative treatments in agriculture (Larsson and Flach 2022).

10.4 AB and Antibiotic Resistance Gene Correlations

The use of AB in medicine and agriculture field has led to their presence in the environment, posing a serious consequences to human health and the ecosystem. In China, the estimated amount of AB entering the environment is staggering, with over 53,000 tons per year. However, conventional sewage treatment processes only remove a fraction of these AB, leaving high levels to contaminate surface water, sediment, soil, and feces (Rathinavelu et al. 2024).

The long-term presence of AB in surroundings can have devastating aftereffects, including the release of ARGs (ARGs). These genes can spread through the biomagnification, leading to resistance development in humans and making infections harder to treat. The World Health Organization has identified ARGs as a major threat to environment (Almansour et al. 2023).

There might be several methods to reveal the correlation between the antibiotic and AGRs, i.e., culture-based methods, molecular techniques like variants of polymerase chain reaction, molecular cloning, and microarray, and high-throughput sequencing-based metagenomic analysis (Zhao et al. 2023). Further ARGs are evolved by various resistant mechanisms in bacteria, which are affected by certain factors like antibiotic remnants, heavy metals, and environmental factors (Zhao et al. 2018). For example, previous reports suggest that ARGs are widespread in China's waterways, including the Yangtze River in China, used for drinking and irrigation purposes. The Yangtze River basin is home to over 400 million people and is a significant industrial and agricultural hub, making it a critical area for studying antibiotic contamination. However, there is little research on the correlations between Ab and ARG abundance (Jiang et al. 2024). By exploring the relationships between Ab concentrations and ARG abundance, these studies may provide valuable insights into the impact of AB. The findings will be crucial for developing effective strategies to mitigate the spread of ARGs (Samreen et al. 2021).

10.5 Techniques Used for Detection and Analysis of AB

Antimicrobial substances that are active against bacteria are known as AB. Antibiotic drugs have a major role in both treating and preventing bacterial infections, as they are the most effective type of antibacterial agent against infection. They might eliminate microorganisms or stop them from growing (Pauter et al. 2020). A variety of methods are used in the detection and analysis of AB in order to ensure their existence, potency, and concentration. Here are a few popular techniques (Fig. 10.2).

1. **Microbiological Methods**
   - **Disk Diffusion (Kirby–Bauer Test)**: This involves inoculating an agar plate with a bacterial strain by putting disks impregnated with AB. The zone of inhibition surrounding each disk is measured to ascertain the antibiotic's efficacy (Schiller et al. 2022).
   - **Minimum Inhibitory Concentration (MIC) Testing**: This determines the minimum antibiotic concentration necessary to stop bacterial development. Agar and broth dilution are two techniques (Kowalska-Krochmal and Dudek-Wicher 2021).
2. **Chromatographic Techniques**
   - **High-Performance Liquid Chromatography (HPLC)**: It uses the interactions between a stationary phase and a mobile phase to separate the AB in a sample. It is very accurate for quantitative analysis (Joshi 2002).
   - **Gas Chromatography (GC)**: It analyzes AB by converting them into volatile derivatives. The process involves sample extraction, derivatization, and separation on a GC column. Detection is usually done with Flame Ionization Detector (FID) or Mass Spectrometry (MS). For non-volatile AB, liquid chromatography (LC) or LC-MS might be more suitable (Bobbitt and Ng 1992).
3. **Spectrometric Techniques**
   - **Mass Spectrometry (MS)**: It identifies AB based on their mass-to-charge ratio. It is often coupled with chromatography (LC-MS or GC-MS) for enhanced specificity (Zhang et al. 2019).
   - **UV–visible Spectroscopy**: UV–visible spectroscopy detects AB by measuring their light absorption at specific wavelengths. The resulting absorption spectra help identify and quantify the AB based on their unique absorbance patterns (Luo et al. 2024).
4. **Immunoassays**
   - **Enzyme-Linked Immunosorbent Assay (ELISA)**: ELISA detects AB by using antibodies specific to the AB. The sample is added to a plate coated with these antibodies, and any AB present bind to them. A secondary antibody,

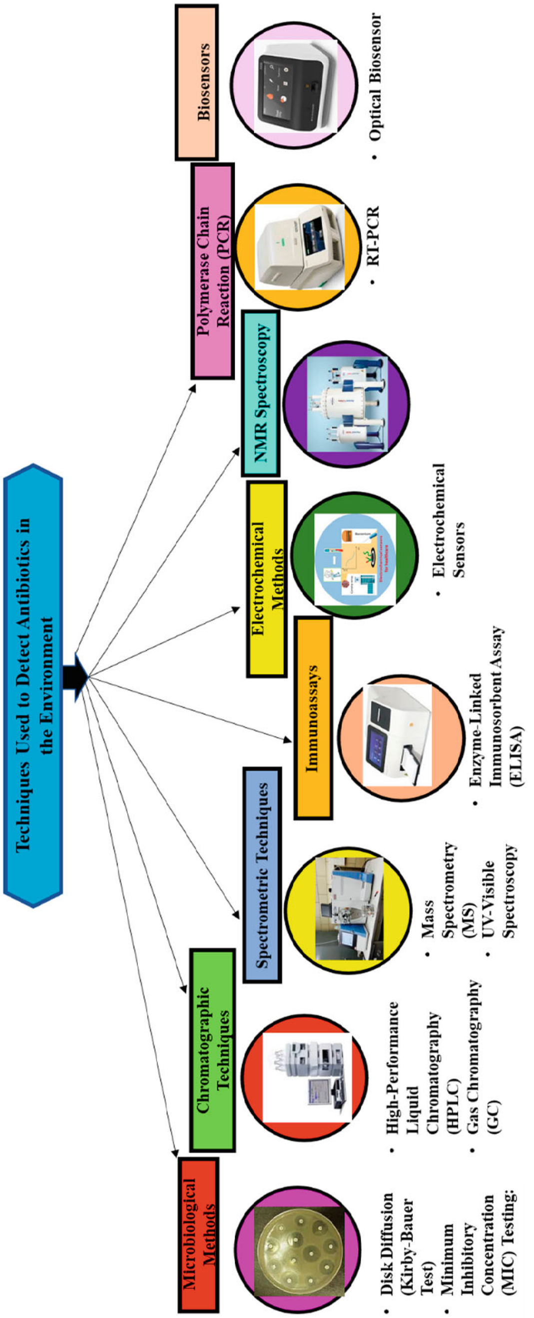

Fig. 10.2 Techniques to detect the Ab present in environment

linked to an enzyme, binds to the antibiotic, and a colorimetric reaction reveals the presence of AB based on the color change (Ahmed et al. 2020).

5. **Electrochemical Methods**

   - **Electrochemical Sensors**: Electrochemical sensors detect AB by measuring alteration of electrical properties, like current or potential, when the AB interacts with an electrode. The presence of AB causes specific electrochemical responses, which are correlated with their concentration, enabling sensitive and rapid detection (Wang et al. 2021).

6. **Nuclear Magnetic Resonance (NMR) Spectroscopy**

   - Provides detailed structural information about AB by analyzing their nuclear magnetic properties. It's useful for structural elucidation and identification (Hoerr et al. 2016).

7. **Polymerase Chain Reaction (PCR)**

   - **Real-Time PCR (qPCR)**: Detects AB by amplifying specific DNA sequences related to antibiotic resistance genes or microbial targets. The process involves measuring fluorescence in real-time as DNA amplifies, providing sensitive and quantitative detection of AB or resistance markers with high specificity (Vandeweyer et al. 2019).

8. **Biosensors**

   - **Optical Biosensors**: Optical biosensors detect AB using light-based methods, such as SPR or fluorescence, to measure binding interactions with high sensitivity and specificity. They are used in clinical diagnostics, pharmaceutical quality control, environmental monitoring, and food safety, offering real-time results with minimal sample preparation (Lu et al. 2023).

10.6 Biodegradability of AB and Bioremediation Strategies

There could be several methods for the mitigation of Ab from the environment, which are listed below:

Biological Treatment: There can be two main biological treatment methods for AB removal: sludge adsorption and biodegradation. It can be categorized on the basis of oxygen requirements like anaerobic methods (anaerobic digestion (AD), upflow anaerobic sludge blanket (UASB), anaerobic filter (AF), and anaerobic baffled reactor (ABR) processes), aerobic (biological aerated filter system (BAF)), combined aerobic and anaerobic methods (sequencing batch reactor (SBR) and membrane bioreactor (MBR) processes) (Huang et al. 2021). Some of the anaerobic methods are:

Anaerobic Digestion: It is multiple-step procedure: hydrolysis, acidification, hydrogen production, acetic acid, and methane production. Several advantages of this method are the lack of additional aeration equipment, energy investment, and less sludge production, but still treated sludge and wastewater can be harmful to the environment. However, the treated wastewater and sludge residues could still cause harm to the surrounding environment (Zubair et al. 2023).

MBR Process: It is a combinatorial approach using modern membrane separation technology and biological technology. It has certain advantages like high nitrification performance, long sludge retention time, flexible operation, and low sludge output, still suffers from certain disadvantages like high energy consumption and operating costs (Li et al. 2019).

SBR Process: It has one or more aeration reaction tanks, whereas the sewage gets inside the tank in batches. The SBR reactor also has multiple-step procedures like influent feeding, anoxic phase, aerobic phase, sludge settling, and effluent discharge. It has certain advantages like flexibility, saves land and energy, although its operation and management procedure is quite complex (Karim and Shriwastav 2023).

Biological Aerated Filter (BAF) Process: Biological Aerated Filters (BAFs) have been used in wastewater treatment plants in case of high organic loading, are cost-effective, and require lesser energy consumption. Its filter media supports microorganism's growth and its setup has three phases: one is a stable segment playing the role of guide media for improving the growth of microorganisms, second liquid segment having a stable fabric submerged, and the third is the gas segment formed by injecting the air into the reactor. It has high biofilm attachment capacity and a wide specific area involved in enhancing the sludge adsorption and ultimately showed extensive antibiotic removal efficiency. It has several advantages including compactness and taking very less space than conventional activated sludge systems, can handle high biomass concentration, resistant to organic and hydraulic load shocks, and require no special treatment for operation. Previous studies have reported the removal of Ab such as sulfamonomethoxine, sulfachloropyridazine, sulfamethazine, trimethoprim, and fluoroquinolones including norfloxacin, ofloxacin, lincosamides, macrolides, sulfonamides, fluoroquinolones, and ciprofloxacin (Zhu et al. 2021).

Advanced Oxidation Processes (AOPs): These are oxidation-based technologies based on strong oxidizing hydroxyl radicals (·OH) for decomposing and mineralizing organic pollutants (OP) in water. The ·OH oxidizes OP by breaking chemical bonds or reactions (electron transfer, addition, and substitution, degrading to small molecules. It includes processes like electrochemical oxidation, ozonation process, and the Fenton process (Khan et al. 2023).

Electrochemical Oxidation: It produces strong oxidants like $^{\cdot}OH$, $HO_2^{\cdot}$, and O_2^- to degrade pollutants through electrode reactions. Sulfadimidine and norfloxacin, as well as NH^{4+}–N and COD, showed complete removal by flow-through electro-oxidation process (Yuan et al. 2023).

Ozonation: There might be two processes involving the direct oxidation of ozone and indirect oxidation via free radicals generation. Ozone acting as an electrophilic reactant may degrade aromatic rings, and unsaturated double bonds of TC, SM, and QN Ab for their removal. This can be combined with ultraviolet light (UV), hydrogen peroxide (H_2O_2), or catalysts for generating large amounts of ·OH for attacking organic pollutants (Gorito et al. 2022).

Fenton Process: It uses reagents like H_2O_2 and Fe^{2+} for generating ·OH radicals for oxidizing and decomposing Ab. Microwave irradiation can be associated with the Fenton process, i.e., microwave-assisted Fenton oxidation for the removal of Ab. This process is affected by H_2O_2 and Fe^{2+} dosage, pH affects reaction rate, etc. (Paiva et al. 2023).

UV/H_2O_2 Method: In this, H_2O_2 is decomposed to produce ·OH with UV irradiation. It is a relatively stable process in operation and may remove OP. Certain things about this technology are less solid waste production than other methods and used to treat organic wastewater treatment. It has been affected by pH, H_2O_2 concentration, and reaction time changes antibiotic removal efficiency (Keen and Linden 2013).

Membrane Technology: It is a technology in which wastewater passes through small membrane pores. The methods mainly depend on microfiltration, ultrafiltration, nanofiltration, and reverse osmosis. It has certain advantages like high work efficiency, simple operation, and low cost (Nasrollahi et al. 2022).

1. **Ultrafiltration**

It is dependent on various parameters such as particle load and size. It cannot be used for separating organic streams but can hold the contaminated species of a wide range of molecular weights (300 and 500,000 Da) and pore sizes (10–1000 Å). Its membranes can be utilized for water filtration, for the removal of harmful bacteria, macromolecules, and suspended matter consuming the least energy. Although it's unable to remove dissolved inorganic pollutants from water and requires high pressure for efficient cleaning. It can be best used for oxytetracycline and can attain 99.79% efficiency in the removal of ARGs and bacteria. Ultrafiltration shows high turbidity rate, and filtration accuracy, and maintains the effluent water quality remains stable and reliable (Bourgeous et al. 2001).

2. **Microfiltration**

It is a filtration method involving pores of a diameter of 1–10 μ, which cannot be crossed by microorganisms. It is an initial step used before nanofiltration and reverse osmosis. It is used to separate colloidal particles via a screening mechanism and can have a membrane filter either organic (polyvinylidine fluoride, polysulfone, cellulose acetate, and polyamide) or inorganic (porous alumina and metals). It can be used for suspensions, emulsions, and for removal of sediment, algae, protozoa, bacteria, monovalent ions, dissolved organic materials, tiny colloid viruses, etc. It can be used for increased oxidizable material removal, but cannot remove impurities (dissolved particles) less than 1 mm in size (Qiu et al. 2021).

3. **Nanofiltration**

It uses nanoparticles for the removal of large organic materials and average-sized minerals. The nanofiltration membranes are made of cellulose acetate blends or polyamide composites, sulfonated polysulfone. In this, wastewater is fed into the inlet, and the incoming stream is separated: the permeate (filtered component) and concentrate (non-filtered fraction). It can be used for the removal of organic matter and based on hydrostatic pressure application passing solvents, low-molecular weight solutes, while others get trapped inside the membrane. However soluble fractions cannot be treated by this method and highly contaminated fluids need a pretreatment process (Ren et al. 2022).

4. **Reverse Osmosis (RO)**

In this method, large ions and molecules are removed from liquid effluents through diffusion, and also require pressure application in one side of a semipermeable membrane. The effluent impurities remain confined toward the pressured side of the membrane and clean effluent flows against a concentration gradient. Further, it can also be used to remove bacteria, viruses, solid particles, and other microbial agents inhabiting in wastewater. The RO membrane has several benefits, but it does not guarantee the complete removal of organic micropollutants (Labella et al. 2021).

5. **Membranous Biological Reactor**

MBR is a combinatorial approach using membrane separation technology with biological technology. In this, a chamber contains biological matter and is separated by a membrane, containing a micro-filter of approximately size 1–10 μm. It includes biological processes such as activated sludge along with membrane filtration processes such as ultrafiltration, nanofiltration, and microfiltration. It comprises many advantages such as a long sludge holding period, easy operation, excellent nitrification performance, and low sludge output (Wang et al. 2023).

6. **Biodegradability of Ab and Bioremediation Strategies**

The ability of AB to be broken down by living entities into less toxic, simpler compounds is known as their biodegradability. The chemical complexity of the antibiotic, the pH and temperature of the surrounding environment, and the existence of particular microorganisms that can break down the antibiotic are some of the factors influencing this process. Although certain ABs break down quite quickly, others could linger in the environment and pose a threat to the ecosystem as well as the possibility of antibiotic resistance (Reis et al. 2020). Antibiotic bioremediation techniques seek to lessen the impact of AB on the environment by using biological processes (Hong et al. 2020). Bioremediation strategies includes:

- **Bioaugmentation**: Introducing specific microorganisms that can effectively degrade AB.
- **Biostimulation**: Enhancing the activity of native microbes by adding nutrients or adjusting environmental conditions.
- **Phytoremediation**: Using plants to absorb and degrade AB from soil and water.

- **Enzyme-Based Remediation**: Applying enzymes that specifically break down AB.

It is an eco-friendly practice of exploiting living organisms to extract and/or detoxify chemicals and involves both in situ and ex situ approaches. The in situ bioremediation approach works for the removal of Ab on the site, whereas ex situ involves contamination removal to be treated elsewhere (Ezzariai et al. 2018). The bioremediation technology uses living organisms like bacteria, fungi, algae, biochar, and plants. In the degradation of Ab, both biotic and abiotic processes are used to degrade Ab. The biotic methods involve microorganisms, plants, biochars, and abiotic factors including hydrolysis, sorption, oxidation, photolysis, and reduction (Bala et al. 2022). The abiotic degradation gets changed according to chemical structure.

Generally, bacteria-mediated procedure is highly precious, ecosensitive to reduce Ab from the surroundings. Such antibiotic-degrading bacteria should be able to bear adverse conditions. Certain bacteria like *Proteobacteria* and Acidobacteria, Firmicutes, and Bacteroidetes have the inherent capacity to degrade antibiotic compounds like sulfamethaz (Liao et al. 2016). Some other bacterial species involved in sulfanilamide (SAD) biodegradation are *Firmicutes,* and Chryseobacterium, *Rhodopirellula baltica, Pseudomonas* sp., *Micrococcus luteus, Methylibium petroleiphilum, Oligotropha carboxidovoran, Delftia acidvorans,* and *Acinetobacter* (Islas-Espinoza et al. 2012). Few microorganisms have a quite high biodegradation rate showing 100% degradation for sulfamethoxazole. Microbes in surface water, soil, and sewage treatment systems, degrade Ab. The sediments containing ampicillin, oxytetracycline, doxycycline, and thiamphenicol get efficiently degraded, but josamycin mostly remains undegraded (Koch et al. 2021).

Certain studies indicate that josamycin-resistant bacteria cannot destroy drugs or inhibit other Ab in josamycin-resistant sediments. Likewise, penicillin (β-lactam Ab) gets biodegraded by bacterial β-lactamases, but fluoroquinolone Ab in aquatic systems and sediments shows lesser degradation (Lai and Lin 2009). Previously the treatment of β-lactamase effluent and wastewater (containing cephalexin, ceftaroline, ampicillin, and amoxicillin) has been conducted successfully using *B. subtilis* 1556WTNC (Al-Gheethi and Ismail 2014).

Similarly, algae can also be used being cost-effective, safe, and non-intrusive. There are various Ab like Cephalosporins (alga-activated sludge system), ceftazidime, cephalexin, cefradine, and cefixime (*Chlorella pyrenoidosa*), 7-amino cephalosporin acid (*Mychonastes* sp. YL-02, *Chlamydomonas* sp. Tai-03, *Chlorella* sp. Cha-01), ceftazidime (*C. pyrenoidosa*) have been removed using algae (Koch et al. 2021; Ndlela et al. 2023).

Phytoremediation technology has been implemented for the removal of Ab by exploiting the potential of hyper-accumulators and revealing the mechanism of various plants and the chemical composition of Ab influencing the potential for accumulation. It comprises of various physical, chemical, and biological processes including mechanisms, like (1) accumulation (phytoextraction, rhizofiltration); (2) immobilization (phytostabilization); (3) degradation (rhizodegradation, phytodegradation; (4) dissipation (phytovolatilization) to remove, degrade, or immobilize Ab.

There are various plants like water lettuce or *Pistia stratiotes* (tetracycline, oxytetracycline), *Myriophyllum aquaticum* (norfloxacin, sulfamethazine, and tetracycline), *L. minor* and *A. filiculoides* (sulfadimethoxine and flumequine), erythromycin removal between free-floating (*Salvinia molesta* and L. minor) and submerged macrophyte species (*M. aquaticum* and *Rotala rotundufolia*) has also been studied. (Rocha et al. 2020), erythromycin (free-floating and submerged plants), Eichhornia crassipes, (ciprofloxacin), etc. (Chowdhury et al. 2023).

Similarly, Ab like Cefdinir which is a β-lactam antibiotic and cephalosporin derivates can be degraded using *Ustilago* sp. SMN03 for used as a carbon and energy source and convert it into simpler products like carboxyl, hydroxyl, lactam, and carbonyl groups. *Aspergillus terreus* FZC3, has shown 95% removal efficiency for gentamicin degradation. Likewise, some mushroom species like *Pleurotus ostreatus* (oxytetracycline), *Imleria badia,* and *Lentinula edodes* (cefuroxime axetil, a cephalosporin derivate) suggest the importance of fungus and mushroom in the antibiotic degradation (Warsito 2022).

Biochar engineering may further pave a novel and efficient way for the removal of Ab by providing several new interactions and bonding with antibiotics for enhancing bioremediation efficiency. Previously combinatorial approaches combing phytoremediation, microbe-mediated remediation, etc., along with biochar have been employed such as waste-fungus-chaff-biochar (WFCB) and *Herbaspirillum huttiense* (enrofloxacin (ENR) and oxytetracycline (OTC)), abundance of Proteobacteria, Rhodanobacter, and Brevundimonas as in biochar may enhance the remediation efficiency (Katiyar et al. 2022).

Enzymatic degradation is mainly involved in the formation and breakdown of AB and has an immense role in the antibacterial resistance mechanism. Previous research analysis shows that ARG expression, antibiotic-degrading enzymes production, and antibiotic-resistant bacteria (ARB) all are interrelated to each other. ARGs involve the expression of aminoglycoside modification and β-lactamase enzymes have been present before the production of manmade Ab and used for various applications. There are several possible pathways for biodegradation by the microcosm containing *Gamma-proteobacteria, Bacteroidia* , and *Beta-proteobacteria* can be used. Ciprofloxacin biodegradation gets degraded by deamination (C–N bond cleavage), hydroxylation, defluorination (C–F bond cleavage), and dealkylation (C–C-bond cleavage) detected (Liao et al. 2016). In the case of sulphonamides biodegradation takes place at aniline or amino heteroaromatic sulfonamide structure via hydroxylation and acetylation reactions. Whereas other chemical changes occur by cleavage of C–N, C–S, and C–C-bond along with oxidation (Koch et al. 2021).

10.7 Conclusion and Future Perspectives

Antibiotic contamination has become a serious threat worldwide, which may raise the risk of the development of antibiotic resistance in microbiota. There are various AB that are banned, but some countries are still using it at the mass level and are creating a great challenge for public health and the environment. Recent studies suggested that WWTP cannot be a one-go or complete solution for the elimination of Ab remnants from the environment, thus it requires further initiatives for searching for effective solutions as per the present conditions worldwide. Microorganisms having ARB, MDRS (multiple drug-resistant strains), and ARGs are a big matter of concern for the environment nowadays, even though they have short life spans, hydrophobicity and lipophilic nature make them persistent in the environment. The current situation requires inventive measures to be adopted for the justified usage of AB, antibiotics should be sold with proper prescription and excreta should be disposed of properly to avoid contamination. The entire removal of remnant AB is not possible, still, eco-friendly bioremediation techniques can be the best approach for cleaning the environment and a safer future for the next generations.

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Chapter 11
Microbial-Based Systems for Emerging Pollutant Removal from Sewage Waste: A Comprehensive Overview

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Abstract The removal of emerging pollutants from sewage waste has emerged as a pressing global challenge due to their adverse effects on both human health and the environment. Microbial-based systems have garnered significant attention as sustainable and effective approaches for mitigating emerging pollutant contamination. This chapter provides a comprehensive overview of microbial-based systems for the removal of emerging pollutants from sewage waste, addressing the pressing global challenge of mitigating their adverse impacts on human health and the environment. It examines the key emerging pollutants present in sewage waste, their sources, and the mechanisms through which microbial communities can degrade, transform, or immobilize these contaminants. Various microbial-based treatment technologies, including activated sludge processes, biofilm reactors, constructed wetlands, and microbial fuel cells, are critically evaluated for their efficacy in pollutant removal. Factors influencing system performance, such as microbial community composition, environmental conditions, and operational parameters, are discussed alongside recent advances in microbial ecology and biotechnology that enhance treatment efficiency. Challenges and limitations are addressed, with strategies for optimization and overcoming obstacles presented, including bioaugmentation and integration with physicochemical processes. The chapter concludes by highlighting prospects and emerging trends, emphasizing the need for interdisciplinary collaboration to advance microbial-based technologies toward sustainable wastewater treatment and environmental protection.

Keywords Microbes · Sewage · Pollution · Waste · Environment

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S. Dey and M. P. Shah (eds.), *Biotechnological Removal of Emerging Pollutants from Wastewater Systems*, Advances in Wastewater Research,
https://doi.org/10.1007/978-981-96-3945-8_11

11.1 Introduction

Emerging pollutants are substances that are increasingly recognized as potential threats to human health and ecosystem but are not currently regulated by existing water quality standards (Krishnakumar et al. 2022). These pollutants include a wide range of compounds such as pharmaceuticals, antibiotics, endocrine disruptors, steroids, industrial chemicals, hormones, microbeads, and microplastics (Sauvé and Desrosiers 2014). Due to their widespread toxicity, distribution, and bioaccumulative nature, these pollutants pose significant risks to both the public health and environment (Santos-Beneit 2024). These contaminants originate from various sources, including hospitals, industries, agricultural practices, and households (Selim et al. 2024). The persistent presence of these pollutants in the environment, particularly in aquatic systems, raises concerns about their long-term impacts on both aquatic life and human health due to their toxicity.

The widespread potential risk and distribution associated with emerging pollutants underscore the urgent need for effective wastewater treatment techniques designed to mitigate their presence on a global scale (Arman et al. 2021). Addressing this issue has become a significant challenge for researchers, driven by growing awareness of their prevalence and the associated risks (Bracamontes-Ruelas et al. 2022; Fijan et al. 2024).

11.1.1 Addressing the Pollutants in Sewage Water

Addressing emerging pollutants in sewage waste is crucial for several reasons, primarily due to their potential impacts on human health, environmental integrity, antibiotic resistance, and water quality.

11.1.1.1 Human Health

Emerging pollutants, such as pharmaceuticals, personal care products, and microplastics, pose significant risks to human health. These substances can enter drinking water systems and bioaccumulate in the food chain, leading to various health conditions. For instance, exposure to pharmaceutical residues can disrupt endocrine function and promote the development of antimicrobial resistance in humans (Krishnakumar et al. 2022).

11.1.1.2 Environmental Impact

Pollutants can significantly disrupt ecosystems by harming wildlife and altering biogeochemical cycles. Discharges from medical, domestic facilities, and industry, introduce a wide range of contaminants into water bodies, where they can concentrate in aquatic organisms which is also called biomagnification. This can lead to a range of health issues within these organisms, including reproductive, developmental, and behavioral changes. For example, microplastics ingested by marine life can cause physical blockages and chemical exposure, negatively affecting their health and, consequently, the entire food web (Verstraete et al. 2022; Arman et al. 2021; Sauvé and Desrosiers 2014).

11.1.1.3 Antibiotic Resistance

The presence of antibiotics in sewage, particularly from hospital waste, can promote the development of antibiotic-resistant bacteria. These bacteria can spread in aquatic environments, posing a threat to both aquatic life as well as human health. The rise of antibiotic-resistant pathogens reduces the effectiveness of antibiotics, making it more difficult to treat infections and increasing disease outbreaks (Agriopoulou et al. 2020).

11.1.1.4 Water Quality

The contamination of water bodies with pollutants can significantly degrade the quality of water, posing a risk to environmental health. Exposure to chemicals, such as endocrine disruptors and persistent organic pollutants, can lead to waterborne diseases and negatively affect aquatic life. Additionally, the presence of microplastics and other persistent pollutants in water can impair natural filtration processes and reduce the overall availability of clean water for ecological purposes and human consumption (Ptaszek et al. 2023).

Traditional chemical treatments for the management of wastewater often rely on the use of several chemicals to neutralize or remove contaminants. While these methods can be effective for certain types of pollutants, they have many drawbacks. Chemical treatments can be costly, requiring continuous input of reagents and energy, and they often produce secondary pollutants or toxic by-products that require additional treatment. Moreover, these processes may not be effective against a broad range of emerging pollutants, such as pharmaceuticals, personal care products, and microplastics, due to the diversity and complexity of these contaminants. In contrast, microbial-based systems offer a more sustainable and versatile approach to wastewater treatment, leveraging the natural ability of microorganisms to degrade and detoxify a wide variety of contaminants.

Microbial-based systems are an innovative solution that utilizes systems biology to understand and harness the metabolic capabilities of microbes and their interactions with the ecosystem (Kakkar and Kumar 2024). These systems employ microorganisms, such as fungi, bacteria, and algae, to break down complex pollutants into simpler harmful compounds. This method effectively targets a wide spectrum of contaminants, including those classified as emerging pollutants, which are not easily treated by conventional methods.

11.1.2 Working Mechanisms of Microbial-Based Systems

11.1.2.1 Biodegradation

Biodegradation is a process within microbial-based systems where microbes such as bacteria, fungi, and algae metabolize complex pollutants into less toxic compounds. These microorganisms utilize various enzymes to break down pollutants, transforming them into harmless substances like water, carbon dioxide, and biomass. This natural process is effective against a wide range of contaminants, including organic chemicals, heavy metals, and various other pollutants, making it a versatile tool for wastewater treatment. Biodegradation not only reduces the toxicity of pollutants but also minimizes their impact on the environment, contributing to the restoration of ecosystems.

11.1.2.2 Bioaugmentation

Bioaugmentation involves the deliberate introduction of specific strains of microorganisms into wastewater to enhance the degradation process of pollutants. These microorganisms are selected based on their ability to metabolize specific contaminants that may be present in the wastewater. By adding these specialized microbial strains, the efficiency of the biodegradation process is improved significantly, especially for contaminants that are otherwise resistant to degradation. This targeted approach allows for the effective treatment of pollutants such as pharmaceuticals, hormones, and other complex organic compounds that are difficult to remove using traditional methods (Van Stempvoort et al. 2024).

11.1.2.3 Enzyme Production

Microbes naturally produce enzymes that can specifically target and degrade the pollutants. These enzymes facilitate the breakdown of complex molecules into simpler forms, which can then be further degraded by other microorganisms or dispersed in the environment. Enzyme production is a critical component of microbial-based systems because it allows for the breakdown of a wide variety of chemical structures, including those of persistent organic pollutants and synthetic chemicals that are not biodegradable (Bracamontes-Ruelas et al. 2022; Fijan et al. 2024).

11.2 Types of Emerging Pollutants in Sewage Waste

Emerging pollutants in sewage waste encompass an array of chemical compounds and elements that are increasingly detected but are not typically regulated by conventional water quality standards. These pollutants pose significant risks to the environment and human health and originate from various sources, including pharmaceuticals, personal care products, microplastics, microplastics, antibiotics, and pesticides. The primary categories of emerging pollutants in sewage discharge are outlined below.

11.2.1 Pharmaceuticals and Personal Care Products (PPCPs)

Pharmaceuticals and personal care products (PPCPs) are classified as emerging contaminants because they have been detected at low concentrations in water bodies and can have adverse effects on both the environment and human health (Mariano et al. 2023). PPCPs include a wide range of substances such as medications, skincare products toothpaste, fragrances, antibiotics, and other items used for cosmetics and personal hygiene (Dey et al. 2019). These substances can enter the environment through several pathways such as leaching from agricultural areas, and the discharge of treated wastewater (Mishra et al. 2023).

PPCPs found in sewage sludge have the potential to pose health risks and ecological harm when released into the environment. While some PPCPs are subject to microbial degradation, their persistence depends on their physicochemical properties. Hydrophilic PPCPs, such as sulfonamide antibiotics, tend to remain in the aqueous phase due to their water solubility, while hydrophobic PPCPs are more likely to adsorb onto particulate matter and sediments, influencing their environmental mobility and bioavailability (Bayabil et al. 2022). This differential behavior underscores the complexity of PPCP pollution in aquatic environments and the need for management strategies and advanced treatments to mitigate their ecological and health impacts (Dey et al. 2019; Mishra et al. 2023).

11.2.1.1 Specific Examples of PPCPs

Non-steroidal anti-inflammatory Drugs (NSAIDs): These include drugs with analgesic, antipyretic, and anti-inflammatory properties, such as aspirin, paracetamol, diclofenac, and mefenamic acid, which are frequently detected in water bodies (Mishra et al. 2023).

Triclosan: A widely used bactericide found in lotions, skincare products, shower gel, and toothpaste often present in low concentrations (Dey et al. 2019).

11.2.2 Endocrine-Disrupting Compounds (EDCs)

EDCs are exogenous agents that can interfere with the normal functioning of hormones responsible for homeostasis, development, and reproduction. EDCs are emerging pollutants in sewage waste due to their potential to cause ecological and health impacts, even at low concentrations (Mishra et al. 2023). High concentrations of estrogens and alkyl phenols have been detected in coastal areas near sewage discharge sites, highlighting the environmental risks posed by these substances. Natural estrogens that are released from animal and human waste also pose significant threats to the environment by disrupting hormonal pathways (Wang et al. 2024).

11.2.2.1 Examples of EDCs

Bisphenol A (BPA): Known to increase the risk of breast cancer in humans due to its estrogenic effects. BPA also has anti-androgenic properties, leading to feminizing effects in men (Helland 2006).

(a) Dioxins: By-products of industrial processes and waste treatment, which can accumulate in the environment and exhibit toxic effects.
(b) Phthalates: Commonly found in cosmetics, plastics, and fragrances, known for their ability to disrupt endocrine functions.
(c) Perfluorinated Compounds (PFCs): Found in non-stick cookware and water-resistant fabrics, these compounds can bioaccumulate and be persistent in the environment (Zahmatkesh et al. 2022).
(d) Cadmium: A heavy metal that poses chronic or acute toxic effects if ingested, commonly found in industrial waste and sewage (Wang et al. 2024).

11.2.3 Nanoparticles

Nanoparticles are emerging environmental contaminants characterized by their unique chemical properties and small size (1–100 nm in diameter). These particles, which can be composed of natural or artificial polymers, are often released into waterbodies through solid waste and wastewater discharges (Mariano et al. 2023). Nanoparticles are considered emerging pollutants due to their potential toxicity and persistence and ability to bioaccumulate (Nzilu et al. 2023).

Challenges in Wastewater Treatment of Nanoparticles: Conventional wastewater treatment methods are often inadequate for removing nanoparticles due to their small size (Bayabil et al. 2022). Advanced methods, such as nanocomposites and nanomembranes, are being explored to enhance the absorption and degradation of nanoparticles in sewage.

11.2.3.1 Categories of Nanoparticles

(a) Carbon-Based Nanoparticles: Include graphene, carbon nanotubes, and nanodiamonds.
(b) Inorganic-Based Nanoparticles: Comprise metal nanoparticles (e.g., gold, silver) and metal oxide nanoparticles (e.g., zinc oxide, and titanium dioxide).
(c) Organic-Based Nanoparticles: Include micelles, liposomes, and dendrimers, primarily made of organic materials (Yaqoob et al. 2020).

11.2.4 Microplastics

Microplastics are plastic particles less than 5 mm in size, widely recognized as pollutants in sewage water significantly. They are synthesized from the breakdown of larger plastic debris and are persistent in the environment, contributing to widespread plastic pollution (Bhardwaj et al. 2024). Microplastics in sewage sludge pose serious concerns, especially in circular economy practices, as they can contaminate agricultural soils when sewage sludge is used as fertilizer, subsequently entering the food chain (Yu et al. 2022).

Sources and Pathways of Microplastics: Microplastics enter aquatic environments through several pathways, including runoff from urban areas, fragmentation of larger plastic items, shipping and fishing activities, and effluents from wastewater treatment plants (Stapleton and Hai 2023; Hassan et al. 2023).

11.2.5 Other Emerging Pollutants (e.g., Antibiotics, Pesticides)

11.2.5.1 Antibiotics

Antibiotics are chemical compounds, either natural or synthetic, used to treat bacterial infections. Amounts of antibiotics consumed by humans and animals are excreted and enter sewage systems, eventually reaching wastewater treatment plants (Baralla et al. 2021). Commonly detected antibiotics in wastewater include macrolides and quinolones, which pose risks of developing antibiotic-resistant bacteria. The accumulation of these compounds in sewage sludge sediments poses environmental and human health risks (Milić et al. 2013).

11.2.5.2 Pesticides

Pesticides, used extensively in agriculture to increase crop yields and protect against pests, are another group of emerging pollutants in sewage waste. Many pesticides

Table 11.1 Types of emerging pollutants and the diseases that can be caused due to these pollutants

Pollution source	Contamination type	Compounds	Source of diseases
Domestic sewage	Pathogens	Bacteria (e.g., *Salmonella, E. coli*), viruses (e.g., *hepatitis A*), protozoa (e.g., *Giardia lamblia*)	Gastroenteritis, cholera, hepatitis A, dysentery, and other waterborne diseases
Industrial waste	Toxic chemicals	Heavy metals (e.g., mercury, lead), PCBs, dioxins, phenols	Various cancers, neurological disorders, and reproductive issues due to exposure to heavy metals and toxins
Agricultural runoff	Nutrients and pathogens	Nitrogen and phosphorus (from fertilizers), pathogens from animal waste	Eutrophication leading to harmful algal blooms, which can produce toxins affecting human health
Stormwater runoff	Debris and pathogens	Oils, greases, heavy metals, pathogens from urban areas	Respiratory issues, skin infections, and gastrointestinal diseases from contaminated water
Combined sewers	Mixed contaminants	Fecal matter, industrial pollutants, nutrients	Waterborne diseases, especially during overflow events when untreated sewage is released into water bodies

contain synthetic chemicals that can persist in the environment and pose risks to ecosystems, plants, and animal life (Rad et al. 2022). Studies have shown that pesticides such as prochloraz, clofenvinphos, and DDT reduce the activity of soil and can contaminate water systems through agricultural runoff and improper disposal (Rousis et al. 2021).

Household Products and Industrial Waste: Many household products, such as bleach, liquid soaps, and antifreeze, contain chemicals that, when disposed of improperly, enter wastewater systems and subsequently contaminate water bodies, impacting aquatic life (Cybulski et al. 2021). Wastewater-based epidemiology (WBE) is a developing tool to assess population exposure to these pollutants by analyzing human urinary metabolites found in sewage (Bayabil et al. 2022) (Table 11.1).

11.3 Microbial Communities in Sewage Treatment

Sewage treatment plants are home to a diverse array of microorganisms vital for water purification. These microbial communities are a mix of human-derived microbes from fecal matter and indigenous microbes that flourish within the sewer system, contributing to the breakdown and removal of contaminants (McLellan et al. 2010). In wastewater treatment systems, the breakdown of contaminants is largely dependent on microbial populations.

The functioning and variety of these microbial communities play a major role in determining the effectiveness of these systems. In wastewater treatment systems, the breakdown of contaminants is largely dependent on microbial populations. The functioning and variety of these microbial communities play a major role in determining the effectiveness of these systems. Before wastewater is discharged into the environment, it must first be purified through their interactions and metabolic processes, which make it easier to break down and remove a variety of pollutants (Begmatov et al. 2022).

11.3.1 Bacteria

The predominant microbial groups in traditional activated sludge systems are frequently *Bacteroidota, Actinobacteriota*, and *Proteobacteria.* These groups are essential for many biological activities, including the removal of phosphorus and the processes of nitrification and denitrification. For example, systems intended for nitrification often contain Nitrosomonas species, whereas increased biological phosphorus removal involves *Candidatus Accumulibacter* (Abudaqqa et al. 2024). Different microbial communities are present at different phases of wastewater treatment. *Bacteroidales* and *Desulforvibrionales* are among the anaerobic genera that flourish, whereas *Burkholderiales* and *Thermomicrobiales* predominate in aerobic phases. This variety suggests that certain microbial populations that have evolved to their distinct habitats support the metabolic activities that take place at each stage (Agriopoulou et al. 2020).

11.3.2 Protozoa

In wastewater treatment systems, protozoa are crucial for preserving the efficiency and stability of microbial populations. They help in the regulation of bacterial populations and prevent the expansion of filamentous bacteria, which may lead to sludge thickening, by feeding on bacteria and minute particulate debris. Common protozoa found in activated sludge include flagellates, ciliates, and amoebae, which aid in the reduction of suspended particles and the clearing of wastewater (Pauli et al. 2001).

11.3.3 Fungi

Fungi play a vital role in the breakdown of complex organic molecules, especially those that are resistant to bacterial decomposition, despite their relative lack of dominance over bacteria. By breaking down cellulose, lignin, and other resistant organic compounds, filamentous fungus can improve the treatment procedure as a whole. In activated sludge, fungi like *Aspergillus* and *Penicillium* are frequently present and aid in the breakdown of persistent organic contaminants (More et al. 2010).

11.3.4 Algae

Algae and bacteria work together to remove nutrients from wastewater, including phosphate and nitrogen. Oxygen is produced by algae through photosynthesis, which helps aerobic microorganisms and sustains the aerobic conditions required for efficient wastewater treatment. Algae may also absorb and digest inorganic nutrients, which lowers the amount of nutrients in treated effluent (Bhatt et al. 2022).

11.3.5 Archaea

The processes of anaerobic digestion require archaea, especially methanogens. They produce methane and carbon dioxide from the intermediate by-products of anaerobic digestion, such as hydrogen and acetate. It produces biogas, which can later be recovered and utilized as a sustainable energy source, along with lowering the amount of sludge. Anaerobic decomposition culminates in the involvement of methanogenic archaea, namely those belonging to the genera *Methanobacterium* and *Methanosarcina* (Płaza et al. 2021).

11.3.6 Nematodes and Rotifers

The quality of wastewater can be determined by the presence of nematodes. Since certain species are sensitive to changes in their surroundings, they can be used as bioindicators to gauge pollution levels and the general health of the treatment system. Nematodes' availability generally indicates an effective treatment method, but their absence may point to low water quality or inefficiencies in the system (Santos et al. 2014).

In wastewater treatment systems, rotifers are yet another kind of organism. They aid in decomposing organic molecules and contribute to the microbial food chain.

Rotifers are essential for maintaining microbial populations under control and optimizing the treatment process since they consume bacteria, algae, and organic debris as food. Rotifer population fluctuations may indicate changes in the effectiveness of the treatment method or water quality (Table 11.2).

11.4 Factors Influencing Microbial Activity During Sewage Treatment

Several factors influence microbial activity during wastewater treatment, impacting the efficiency and effectiveness of the treatment processes. Understanding these factors is essential for optimizing wastewater treatment systems.

11.4.1 Temperature

The metabolism of microorganisms is significantly influenced by temperature. Anaerobic bacteria, such as methanogens, prefer temperatures between 35 and 55 °C, whereas aerobic microbes normally flourish in the range of 15–30 °C. Temperature variations can impact metabolic activity, microbial growth rates, and the overall stability of the treatment process. Overall, prolonged exposure to low temperatures reduces the diversity and activity of microbial communities, resulting in decreased process performance. Previous studies have indicated that *Methanosarcina mazei*-like microbes and *Methanocorpusculum*-like methane bacteria may play a more significant role under low-temperature conditions (O'Reilly et al. 2009). *Pelotomaculum schinkii*, *Methanospirillum*, and *Methanosaeta* exhibited high activity at moderate temperatures (Ban et al. 2015), whereas *Methanosarcin*a thermophile was more likely to dominate at elevated temperatures (Zielińska et al. 2013).

11.4.2 pH Levels

Microorganisms in wastewater treatment systems can thrive within a broad pH range of 6–9 (Van der Gast and Thompson 2005); however, variations in pH significantly impact the composition of the microbial community (Gao et al. 2016). The efficacy of microbial communities in treating wastewater can be negatively impacted by deviations from these ideal pH levels.

Table 11.2 Other microorganism and their role in sewage water treatment

Microorganism type	Microorganism	Mechanism of action	Role in sewage degradation	Reference
Bacteria	Aerobic bacteria	Utilize oxygen to metabolize organic matter through aerobic respiration, producing CO_2 and water	Efficiently decompose organic pollutants, reducing biochemical oxygen demand (BOD)	Metcalf & Eddy et al. (2014)
	Pseudomonas aeruginosa	Degrades complex organic compounds using various metabolic pathways, including plastic degradation	Important in breaking down pollutants and aiding in bioremediation	Menon et al. (2021)
	Escherichia coli	Ferments organic matter and can indicate fecal contamination	Plays a role in organic matter breakdown and serves as an indicator of water quality	Khan and Gupta (2020)
	Bacillus subtilis	Produces enzymes that degrade proteins and polysaccharides	Contributes to the breakdown of organic waste in sewage	Xia et al. (2022)
	Anaerobic bacteria	Operate in the absence of oxygen, fermenting organic matter to produce methane and hydrogen sulfide	Reduce sludge volume and produce biogas, which can be used for energy	Metcalf & Eddy et al. (2014)
	Desulfovibrio spp.	Reduce sulfate to sulfide, playing a key role in the sulfur cycle	Important for organic matter degradation and sulfur removal	Muyzer and Stams, (2008)
	Clostridium spp.	Ferments organic matter to produce methane and other by-products	Key in anaerobic digestion processes, reducing waste volume	Demirel and Scherer (2008)
	Facultative bacteria	Can switch between aerobic and anaerobic metabolism depending on oxygen availability	Adapt to changing conditions, enhancing organic matter breakdown	Metcalf & Eddy et al. (2014)

(continued)

Table 11.2 (continued)

Microorganism type	Microorganism	Mechanism of action	Role in sewage degradation	Reference
Fungi	*Aspergillus niger*	Decomposes complex organic materials, including lignin and cellulose, through enzymatic action	Plays a role in the breakdown of organic waste, enhancing nutrient cycling	Wang et al. (2019)
Algae	*Chlorella* spp.	Photosynthetic, utilizing sunlight to convert CO_2 and nutrients into biomass	Assists in nutrient removal and oxygenation of wastewater	Kumari et al. (2021)
	Scenedesmus spp.	Helps in biocapture of environmental CO_2	Helps in nutrient cycling and improves water quality	López-Pacheco et al. (2021)

11.4.3 Dissolved Oxygen (DO)

Oxygen availability is vital for aerobic microbial processes, as a sufficient dissolved oxygen (DO) level is essential for the growth of aerobic bacteria. These bacteria play a key role in breaking down organic matter and reducing biological oxygen demand (BOD). For example, when the system operates at a low dissolved oxygen (DO) level for an extended period, the stable accumulation rate of nitrous acid can be disrupted, leading to the inhibition of NOB proliferation (Almstrand et al. 2011; Shen et al. 2014). In anaerobic systems, maintaining low dissolved oxygen (DO) levels is essential to stimulate the activity of methanogenic bacteria, which decompose organic matter without oxygen.

11.4.4 Nutrient Availability

Nutrients like nitrogen and phosphorus are crucial for microbial growth and activity. An imbalance in nutrient levels can impair microbial performance. For example, a lack of nitrogen can restrict the growth of nitrifying bacteria, which are essential for ammonia oxidation in wastewater treatment. Moreover, an overabundance of nutrients can cause issues like algal blooms in wastewater treatment systems, which can further disrupt microbial balance and system efficiency. Thus, achieving the proper nutrient balance is crucial for enhancing microbial activity and ensuring effective sewage water treatment (Maqbool et al. 2019).

11.5 Mechanisms of Pollutant Removal by Microorganisms

Microbial processes play a crucial role in the removal of pollutants from the environment. They can use various mechanisms to degrade pollutants. Three major ways are biodegradation pathways, sorption and biosorption processes, and metabolic transformations and enzymatic activities.

11.5.1 Biodegradation Pathways for Different Classes of Pollutants

Biodegradation is a crucial microbial process that transforms organic pollutants into less harmful substances. Microorganisms such as bacteria, fungi, and algae have diverse metabolic capabilities to perform biodegradation. This natural process is essential for mitigating environmental contamination and restoring ecosystem health. Different classes of pollutants such as hydrocarbons, heavy metals and other emerging pollutants can be biodegraded.

Hydrocarbons, particularly those released during oil spills, are major environmental pollutants with significant impacts on both aquatic and terrestrial ecosystems. These compounds are typically composed of carbon and hydrogen, and their persistence in the environment can lead to long-term ecological damage. Microbial degradation is a vital process in the remediation of hydrocarbon-contaminated sites, where microorganisms break down these complex compounds into simpler, less toxic substances (Abdel-Shafy and Mansour 2018).

Microbial remediation of oil spills primarily involves the action of bacteria and fungi that utilize specialized enzymes to degrade hydrocarbons. Bacteria from the genera *Pseudomonas* and *Mycobacterium* are particularly effective in this regard. For instance, *Pseudomonas aeruginosa* and *Pseudomonas putida* are well-known for their ability to degrade aliphatic and aromatic hydrocarbons through the action of oxygenases (Wasi et al. 2013). These enzymes initiate the oxidation of hydrocarbon molecules, breaking them down into intermediate compounds that are further degraded through various metabolic pathways.

Microbial communities enhance the efficiency of hydrocarbon degradation. The combination of different bacterial species can synergistically improve the breakdown of complex hydrocarbon mixtures (Olajire and Essien 2014). This synergistic effect is often achieved by optimizing environmental conditions, such as nutrient availability and temperature, to support the activity of these microbial communities. Advanced environmental manipulation techniques, such as bio-stimulation and bioaugmentation, have been explored to enhance the effectiveness of microbial remediation efforts. Bio-stimulation involves adding nutrients or other substances to the environment to stimulate the growth and activity of Indigenous hydrocarbon-degrading microorganisms, while bioaugmentation refers to introducing specialized microbial strains to the contaminated site to improve degradation rates (Tyagi et al. 2011).

Emerging pollutants have become a growing concern due to their persistence and potential toxicity. Unlike conventional pollutants, these substances often have complex chemical structures and are resistant to conventional wastewater treatment processes. As a result, there is an increasing need to develop effective bioremediation strategies to address these contaminants.

Microbial degradation of this class of pollutants involves intricate metabolic pathways that vary depending on the chemical nature of the contaminants. For example, *Pseudomonas putida* has been shown to effectively degrade a range of pharmaceuticals through oxidative and hydrolytic processes. This bacterium employs a variety of enzymes, including oxidases and hydrolases, to break down complex pharmaceutical compounds into simpler, less toxic products.

Recent advancements in genetic engineering have significantly enhanced the degradation capabilities of microorganisms. Genetically modified strains of *Pseudomonas* and *Bacillus* have been developed to degrade specific pollutants more efficiently. These engineered microorganisms can possess tailored metabolic pathways or enhanced enzymatic activities that allow them to break down contaminants that are otherwise resistant to natural degradation processes. Microbial consortia are also effective in degrading complex mixtures of emerging contaminants. By combining different microbial species with complementary metabolic capabilities, it is possible to achieve more comprehensive and efficient pollutant degradation (Bala et al. 2022).

The application of these advanced microbial strategies in real-world scenarios requires careful optimization of environmental conditions. Factors such as pH, temperature, and the presence of co-contaminants can influence the efficiency of microbial degradation. Optimization of operational parameters for microbial treatment systems to improve their performance in degrading emerging pollutants can be carried out. Growth conditions of genetically engineered strains and microbial consortia can be optimized to maximize their pollutant-degrading capabilities.

Heavy metals, though not organic pollutants, pose significant environmental and health risks due to their toxicity and persistence in the environment. Contamination with heavy metals such as lead, cadmium, and chromium can result from industrial activities, mining, and improper waste disposal. Unlike organic pollutants, heavy metals do not degrade biologically but can be transformed or immobilized by microbial processes (Hemmat-Jou et al. 2018).

Microorganisms can mitigate heavy metal contamination through processes such as biosorption and biotransformation. Biosorption involves the uptake and immobilization of metal ions by microbial biomass, which can bind heavy metals through ion exchange, complexation, or precipitation mechanisms. In addition to biosorption, microorganisms can also transform heavy metals through biotransformation processes. This involves the reduction of metal ions to less toxic states. For instance, *Desulfovibrio* spp. is capable of reducing toxic hexavalent chromium (Cr(VI)) to less toxic trivalent chromium (Cr(III)) through enzymatic activities (Pande et al. 2022). These processes are often integrated with other bioremediation strategies to enhance overall effectiveness.

To improve the efficiency of heavy metal remediation, researchers are exploring integrated approaches that combine microbial processes with other treatment technologies. Recent studies have demonstrated that integrating biosorption with techniques such as chemical precipitation or electrochemical methods can improve the overall effectiveness of heavy metal remediation. New microbial strains with enhanced capabilities can also be developed for heavy metal detoxification. Advances in biotechnology, such as genetic engineering and synthetic biology, hold promise for creating microorganisms with tailored metal-binding properties and enhanced tolerance to environmental stressors.

11.5.2 Sorption and Biosorption Processes

Sorption processes consist of both adsorption and absorption. These are essential for the removal of pollutants from contaminated environments. These mechanisms are pivotal in environmental remediation, where biological and non-biological materials interact with pollutants to either sequester or remove them from aqueous solutions. Among these, biosorption stands out as a particularly effective method, used for substrates such as microbial biomass and plant matter to address a variety of pollutants, including heavy metals and organic compounds.

Biosorption refers to the process by which biological materials, including microbial biomass and plant tissues, bind and concentrate heavy metals from aqueous solutions. This process involves multiple mechanisms such as ion exchange, complexation, adsorption, and precipitation. Microorganisms like fungi, bacteria, and algae, as well as plant materials, have been identified as effective biosorbents due to their high surface area and functional groups that facilitate metal ion binding (Filote et al. 2021).

Many microbial species such as fungi and algae, exhibit significant potential for biosorption. *Saccharomyces cerevisiae*, a common yeast, is employed to remove heavy metals like lead, cadmium, and chromium from contaminated solutions. The biosorption process by *S. cerevisiae* primarily involves ion exchange and chemical bonding, where metal ions replace hydrogen ions or interact with functional groups on the cell wall (Hadiani et al. 2018). Similarly, *Chlorella vulgaris*, a green microalga, has demonstrated high efficacy in adsorbing metals such as copper and zinc through mechanisms involving cell wall binding and metal ion exchange (Ayilara and Babalola 2023).

The efficiency of biosorption is influenced by several parameters, including pH, temperature, and metal ion concentration. pH plays a critical role, as it affects the ionization state of functional groups on the biosorbent and the metal ion speciation. For example, an acidic pH often enhances the biosorption of metal cations by providing more hydrogen ions that compete with metal ions for binding sites. Temperature also impacts the biosorption process, with higher temperatures generally increasing the rate of metal uptake due to enhanced kinetic energy and increased diffusion rates. However, excessive temperatures may lead to the denaturation of biosorbent materials. The concentration of metal ions in the solution affects the capacity and rate of biosorption, with higher concentrations often leading to increased metal uptake until the biosorbent reaches saturation (Mahmoud 2021).

Biosorbent materials can be modified to improve their metal-binding capacity. Engineering of microbial strains can lead to enhanced expression of metal-binding proteins or the introduction of additional functional groups that increase metal ion affinity. Another approach is the development of composite materials that combine biological and non-biological components, such as biosorbent-coated membranes or nanoparticles, which can improve the efficiency and selectivity of biosorption processes.

Biosorption is increasingly utilized in the treatment of wastewater to remove persistent and toxic substances. This includes the treatment of wastewater from industrial processes, where dyes, heavy metals, and other pollutants are prevalent. Techniques involving biosorption and bioaccumulation have been optimized to address these contaminants efficiently. For instance, biosorption has been successfully applied to remove dyes from textile industry wastewater, where biosorbents like *S. cerevisiae* and *C. vulgaris* have been used to achieve significant decolorization and pollutant removal (Joutey et al. 2013).

Recent reviews highlight the shift toward sustainable biosorption practices, emphasizing the use of low-cost and renewable biosorbents. The development of biosorbents from agricultural and industrial waste materials, such as rice husks and sawdust, offers a cost-effective alternative to traditional biosorbents. These materials not only reduce the cost of biosorption but also contribute to waste valorization and environmental sustainability. Additionally, the integration of biosorption with other wastewater treatment technologies, such as coagulation–flocculation or advanced oxidation processes, has been explored to enhance overall treatment efficiency and pollutant removal.

11.5.3 Metabolic Transformations and Enzymatic Activities

Microbial metabolic transformations play a critical role in bioremediation, converting pollutants into less harmful substances through diverse enzymatic activities. These processes are essential for mitigating environmental contamination and involve complex interactions between microorganisms and pollutants.

Enzymes produced by microorganisms are pivotal in the degradation of organic pollutants. Among these, oxidative enzymes such as dioxygenases are crucial for the breakdown of aromatic hydrocarbons. Dioxygenases facilitate the incorporation of oxygen into the aromatic ring, leading to the cleavage of the ring structure and subsequent degradation of the compound. For example, *Pseudomonas putida* utilizes catechol 2,3-dioxygenase to degrade catechol, a common aromatic compound, into less toxic intermediates. This enzymatic pathway is instrumental in the bioremediation of hydrocarbon-contaminated sites.

In addition to dioxygenases, other enzymes such as laccases and peroxidases play significant roles in the degradation of complex organic molecules. Laccases, multi-copper oxidases produced by fungi such as *Trametes versicolor*, are known for their ability to oxidize a wide range of substrates, including phenolic compounds and dyes (Ayilara and Babalola 2023). These enzymes facilitate the polymerization and breakdown of complex organic pollutants into simpler, less toxic forms. Peroxidases, such as manganese peroxidase, are produced by various fungi and bacteria to degrade lignin and other complex organic compounds (Joutey et al. 2013).

The development of recombinant enzymes and genetically engineered microorganisms has significantly improved the degradation capabilities of these biological systems. It has been seen that engineered strains of *Bacillus* and *Pseudomonas* with overexpressed dioxygenases and laccases have demonstrated enhanced degradation of specific pollutants, such as chlorinated hydrocarbons and azo dyes (reference). These advancements highlight the potential for tailored enzymatic solutions in addressing complex pollution challenges.

Microbial interventions involve utilizing both naturally occurring and genetically engineered microorganisms to degrade pollutants. Natural microbial communities possess diverse metabolic capabilities that can be harnessed for bioremediation. For example, *Mycobacterium* spp. is known for its ability to degrade a wide range of environmental pollutants, including polychlorinated biphenyls (PCBs) and pesticides. These bacteria utilize specific metabolic pathways to transform and mineralize these contaminants into non-toxic products (Pande et al. 2022).

The field of genetic engineering has expanded the capabilities of microorganisms for pollutant degradation. Genetic modifications have been employed to enhance the metabolic pathways of microorganisms, enabling them to degrade pollutants that are otherwise resistant to natural processes. Genetically modified strains of *Pseudomonas* have been developed to degrade organophosphates, a class of pesticides that are toxic and persistent in the environment. Additionally, synthetic biology approaches have been used to construct microbial consortia with complementary metabolic pathways, improving the overall efficiency of pollutant degradation. Engineered *Bacillus* strains have been applied to treat soil contaminated with industrial solvents, showing promising results in reducing pollutant concentrations and enhancing soil health (Bala et al. 2022). Similarly, microbial consortia involving both natural and engineered strains have been utilized in the bioremediation of contaminated water bodies, achieving significant reductions in pollutant levels and improving water quality.

Sustainable bioremediation practices emphasize the use of natural microbial processes to address environmental pollution. These practices aim to minimize the use of synthetic chemicals and rely on the inherent capabilities of microorganisms to degrade pollutants. Bioremediation strategies using Indigenous microbial strains have been successfully applied to treat contaminated soils and water, leveraging the natural metabolic pathways of these organisms (Bala et al. 2022).

The exploration of novel microbial strains and biotechnological applications is a key aspect of sustainable bioremediation. Researchers are exploring new microorganisms with unique metabolic capabilities, as well as developing synthetic biology tools to engineer microorganisms for specific pollutant degradation tasks. For instance, the creation of microbial strains with enhanced tolerance to environmental stressors, such as high salinity or extreme pH, expands the range of applications for bioremediation in diverse environments (Ayilara and Babalola 2023). Additionally, biotechnological advancements in enzyme production and microbial fermentation have contributed to the development of cost-effective and efficient bioremediation technologies.

11.6 Microbial-Based Treatment Technologies

11.6.1 Microbial Activated Sludge Systems for Sewage Treatment

In the activated sludge process, microorganisms are introduced into wastewater to facilitate the biodegradation of organic materials. These microorganisms utilize the biodegradable compounds present in the wastewater as a nutrient source. During this process, bacteria develop a sticky extracellular polymeric substance (EPS) or slime layer around their cell walls, which enhances their ability to aggregate and form bio-solids or sludge. This aggregation is critical for the separation of solids from the liquid phase.

The effectiveness of wastewater treatment in this process is largely dependent on two key factors: the efficiency with which microorganisms metabolize organic materials and their ability to aggregate into flocs that can settle out of the bulk fluid. The flocculation properties of the microorganisms in the activated sludge allow them to form aggregates large enough to settle at the bottom of the settling basin or clarifier. As the flocculation characteristics improve, there is a corresponding improvement in sludge settling and overall wastewater treatment efficiency (Metcalf & Eddy 2003).

After the aeration basin, the mixture flows into a secondary clarifier. Here, the sludge settles, allowing for the separation of the treated effluent from the sludge. A portion of the settled sludge is recirculated back into the aeration basin as Return Activated Sludge (RAS). This recycling ensures a sufficient concentration of microorganisms in the aeration tank, maintaining a high level of biological activity necessary for the continuous treatment of incoming wastewater. The process is thus cyclic, with microorganisms repeatedly exposed to fresh organic nutrients and reactivated to sustain the treatment process (Tchobanoglous et al. 2014).

The activated sludge process, when operating under optimal conditions, is highly efficient, typically achieving the removal of 85–95% of solids and demonstrating a similar reduction in biochemical oxygen demand (BOD). The effectiveness of this system is influenced by various factors, including the characteristics of the wastewater and the prevailing climatic conditions. The introduction of toxic substances into the treatment system can significantly disrupt biological activity, as noted by Lajayer et al. (2022). Additionally, wastewaters with high concentrations of soaps or detergents can result in excessive frothing, leading to aesthetic or nuisance issues. In regions where industrial and sanitary wastes are combined, it is often necessary to pretreat industrial wastewater to remove toxic chemical components before it enters the activated sludge treatment process. Despite these challenges, microbiological treatment remains the most natural and effective method for removing contaminants from wastewater (Yapijakis and Wang 2004).

11.6.1.1 Microbial Community Dynamics

The effectiveness of an activated sludge system depends heavily on the composition and activity of its microbial community. Bacteria are the primary drivers of organic pollutant degradation, with different bacterial species specializing in various biochemical pathways (Wagner and Loy 2002).

11.6.1.2 Bacterial Populations

Heterotrophic bacteria, such as those belonging to the genera *Pseudomonas*, *Acinetobacter*, and *Bacillus*, play a significant role in the breakdown of organic carbon compounds. Other bacteria, such as nitrifying bacteria (*Nitrosomonas* and *Nitrobacter*), are involved in the oxidation of ammonia to nitrate, a crucial step in nitrogen removal (Jenkins et al. 2003).

11.6.1.3 Protozoa and Metazoa

Protozoa and metazoa also contribute to the treatment process by grazing on bacteria and organic particulates, enhancing the clarification of treated water. These organisms, including ciliates and rotifers, are indicators of system health and stability (Curds and Hawkes 1975).

11.6.2 Constructed Wetlands

Constructed wetlands (CWs) are engineered ecosystems designed to mimic the functions of natural wetlands to improve water quality. These systems are deliberately created to simulate natural processes using engineered techniques that combine various plants, substrates, and microbial communities to effectively treat wastewater. Constructed wetlands have proven to be an efficient and cost-effective method for treating various types of wastewater, including brackish water, urban stormwater, landfill leachate, and municipal, industrial, and agricultural wastewater (Ahn et al. 2007; Akpor et al. 2014; Andersson et al. 2005).

11.6.2.1 Types of Constructed Wetlands

Constructed wetlands are generally categorized into surface flow and subsurface flow systems. Surface flow wetlands resemble natural wetlands with shallow water flowing over the substrate. In contrast, subsurface flow wetlands direct water flow below the surface, which can be further divided into vertical flow (VF) and horizontal flow (HF) systems. VF and HF wetlands are often combined to form hybrid systems, which utilize both vertical and horizontal flows to enhance treatment efficiency (Babatunde et al. 2016; Bahr et al. 2005; Baptista et al. 2008).

11.6.2.2 Role of Wetland Plants

Wetland plants, also known as macrophytes, play a crucial role in the functioning of constructed wetlands. Macrophytes are typically classified into four types: emergent, floating-leaved, submerged, and freely floating. Common species used in constructed wetlands include *Phragmites*, *Typha, Scirpus*, *Phalaris arundinacea*, and *Iris* (Bastviken et al. 2003). The selection of specific plant species can significantly impact the treatment efficiency of constructed wetlands. For example, some plants, like *Scirpus grossus*, maintain sustainable biomass above the soil, which enhances their effectiveness in pollutant removal. In contrast, other species, such as *Typha angustifolia*, require periodic replacement to maintain optimal performance (Białowiec et al. 2011). The primary mechanisms for pollutant removal in constructed wetlands include filtration, microbial-mediated processes, chemical reactions, volatilization, sedimentation, sorption, photodegradation, plant uptake, and transpiration flux. These processes often work in combination to enhance the overall efficiency of the system. Microorganisms, including bacteria, fungi, and algae, play a vital role in the biogeochemical cycles within wetland systems, contributing significantly to the removal of organic pollutants (Morvannou et al. 2014).

11.6.2.3 Nitrogen Removal in Constructed Wetlands

Nitrogen is a common pollutant in wastewater, existing in both organic and inorganic forms. Organic nitrogen compounds include amino acids, urea, uric acid, purines, and pyrimidines, while inorganic nitrogen is found as free ammonia, ammonium salts, and nitrogen gas (Ospina and Darwich-Cedeño 2024). Nitrogen removal in constructed wetlands involves multiple pathways, such as ammonification, nitrification, denitrification, plant uptake as nitrates, biomass assimilation, nitrate reduction, ammonia volatilization, adsorption, and processes like anaerobic ammonium oxidation (Anammox) and Complete Autotrophic Nitrogen Removal Over Nitrite (CANON) (Lu et al. 2020).

11.6.2.4 Aerobic and Anaerobic Processes in Pollutant Removal

Microbial processes in constructed wetlands can be broadly categorized into aerobic and anaerobic pathways, both of which are essential for effective pollutant removal. Aerobic processes occur in oxygen-rich environments and are primarily facilitated by aerobic bacteria, such as *Methanotrophs*, *Nitrosomonas*, and *Pseudomonas aeruginosa*. These bacteria thrive in zones around plant roots where atmospheric oxygen penetrates the substrate, enabling the aerobic degradation of organic pollutants. In contrast, anaerobic processes take place in oxygen-depleted environments, which are typically found deeper in the substrate, away from the aerobic zones. Anaerobic degradation is a two-step process involving fermentation followed by methanogenesis (Pedescoll et al. 2011). This process is facilitated by methanogenic and sulfur-reducing bacteria, which convert complex organic molecules into methane and other simpler compounds. Anaerobic processes are particularly efficient for the removal of pollutants such as BOD (Biological Oxygen Demand) and COD (Chemical Oxygen Demand), as they can break down complex organic materials that are less easily degraded aerobically (Chan et al. 2008).

11.6.3 Membrane Bioreactors

Membrane bioreactors (MBRs) have emerged as a highly effective and advanced technology for sewage treatment, combining the biological degradation processes of conventional activated sludge systems with membrane filtration. This integration allows for high-quality effluent suitable for various reuse applications while minimizing the footprint of the treatment facility (Tan et al. 2019).

11.6.3.1 Principles of Operation

At the core of MBR technology is the combination of biological treatment and membrane filtration. In a typical MBR setup, wastewater is treated in a bioreactor where microorganisms decompose organic matter and pollutants. The mixed liquor, which contains both the treated water and biomass, is then passed through a membrane. This membrane acts as a physical barrier, allowing clean water (permeate) to pass while retaining the biomass and other suspended solids (Meng et al. 2009). The membranes used in MBRs can be made from various materials, including polymeric substances, and are designed to have pore sizes that prevent the passage of microorganisms and larger particles, typically around 0.1–1 μm (Le-Clech et al. 2006). This capability allows MBRs to achieve high levels of contaminant removal, including suspended solids, bacteria, and even some dissolved organic compounds, resulting in effluent that meets stringent discharge standards and is suitable for reuse in irrigation or industrial applications (Yang et al. 2006).

11.6.3.2 Advantages of MBRs (Judd 2010)

(a) High Effluent Quality: MBRs produce effluent with low concentrations of biochemical oxygen demand (BOD), total suspended solids (TSS), and pathogens, which is crucial for meeting environmental regulations.
(b) Reduced Footprint: The compact nature of MBR systems allows for smaller treatment plants, which is particularly beneficial in urban areas where space is limited.
(c) Lower Sludge Production: MBRs typically generate less sludge compared to traditional systems, reducing disposal costs and the environmental impact associated with sludge management.
(d) Operational Flexibility: MBRs can effectively handle variations in wastewater composition and flow rates, making them suitable for diverse applications, including industrial wastewater treatment and municipal sewage.
(e) Enhanced Nutrient Removal: The ability to maintain a high concentration of biomass allows MBRs to achieve better nitrogen and phosphorus removal, addressing nutrient pollution in receiving waters.

11.6.3.3 Applications of MBR Technology (Jyoti et al. 2013)

(a) Municipal Wastewater Treatment: Many cities are adopting MBRs for municipal sewage treatment to improve effluent quality and comply with stringent discharge regulations. The high-quality effluent produced by MBRs is often suitable for reuse in irrigation or industrial processes.
(b) Industrial Wastewater Treatment: Industries such as food and beverage, pharmaceuticals, and petrochemicals generate wastewater with complex compositions. MBRs can effectively treat these effluents, removing contaminants that traditional methods may struggle with.
(c) Decentralized Treatment Systems: In areas where centralized wastewater treatment is not feasible, MBRs can be deployed as decentralized treatment systems, providing effective sewage treatment in remote or rural locations.
(d) Water Reuse Applications: The ability of MBRs to produce high-quality effluent makes them ideal for water reuse applications, where treated wastewater can be repurposed for non-potable uses, helping to conserve freshwater resources.

11.6.4 Emerging Technologies

11.6.4.1 Microbial Fuel Cells (MFC)

MFC converts wastes directly into clean electricity or high-value energy and chemical products is increasingly viewed as a superior method for addressing the issues of excess sludge and energy consumption in traditional wastewater treatment systems

(Logan and Rabaey 2012). Bioelectrochemical systems (BESs) are a class of biological systems that transform chemical energy, present as organic substrates in wastewater, into electrical energy or other valuable products (Kumar et al. 2014). These systems utilize indigenous exoelectrogenic bacteria to harvest clean energy from organic waste sources. This harvested energy can be converted into bioelectricity in microbial fuel cells (MFCs) or into valuable biofuels such as ethanol, methane, hydrogen, and hydrogen peroxide in microbial electrolysis cells. A cation exchange membrane, commonly referred to as a proton exchange membrane (PEM), is employed to separate the anode and cathode compartments in these systems (Lovley 2006).

Advantages of MFCs in Sewage Treatment (He et al. 2017)

(a) Electricity Production: MFCs can produce electricity from the organic content in wastewater, potentially offsetting some of the energy expenses associated with conventional wastewater treatment processes.
(b) Efficient Pollutant Removal: MFCs are effective in removing a wide range of pollutants, including organic compounds, dyes, and certain heavy metals, leading to cleaner effluent.
(c) Environmental Sustainability: MFCs provide a more sustainable alternative to traditional treatment methods, reducing greenhouse gas emissions and operational costs associated with energy use.

11.6.4.2 Algal Bioreactors

Microbial-based algal bioreactors represent an innovative approach for treating sewage waste, leveraging the synergistic relationship between microorganisms (such as bacteria) and algae. These systems combine the capabilities of both algae and bacteria to enhance the removal of nutrients, organic matter, and emerging pollutants from wastewater (Yang et al. 2022).

Microbial-Based Algal Bioreactors Work

(a) Symbiotic Relationship: In these bioreactors, algae and bacteria form a symbiotic relationship. Algae perform photosynthesis, producing oxygen as a by-product. This oxygen is then utilized by aerobic bacteria to degrade organic pollutants in the wastewater. In turn, bacteria release carbon dioxide through respiration, which is utilized by the algae for photosynthesis, creating a self-sustaining loop (Abudaqqa et al. 2024).
(b) Nutrient Removal: Algae are particularly effective at removing nutrients such as nitrogen and phosphorus, which are present in high concentrations in sewage. Nitrogen is typically removed through the uptake of ammonia and nitrate by

algae, while phosphorus is removed through uptake and incorporation into algal biomass (Kendrick 2011).

(c) dPollutant Degradation: The microbial community in these bioreactors can degrade a variety of emerging pollutants, including pharmaceuticals, personal care products, and endocrine-disrupting chemicals. The algae can adsorb some of these contaminants, while bacteria metabolize others, breaking them down into less harmful compounds (Zahmatkesh et al. 2023).

(d) Operational Setup: These bioreactors can be designed in various configurations, including open ponds, closed photobioreactors, or hybrid systems. Closed systems, like photobioreactors, offer more control over environmental conditions and reduce contamination risks, while open ponds are simpler and more cost-effective (Shareefdeen et al. 2023).

Types of Algal Bioreactors (Spier et al. 2011)

(a) Open Ponds: Simple and cost-effective, these systems utilize sunlight for algal growth but may be less efficient in terms of nutrient removal.

(b) Closed Systems: These include photobioreactors that provide controlled environments for algal growth, enhancing efficiency and preventing contamination.

(c) Membrane Bioreactors (MBRs): Algal-based hollow fiber membrane bioreactors (AMBRs) combine algal growth with membrane separation, allowing for efficient nutrient removal and biomass harvesting.

  a) **see** Enhanced Treatment Efficiency: By combining the strengths of both algae and bacteria, these systems can achieve higher removal rates of organic matter, nutrients, and pollutants than traditional treatment methods.
  b) Sustainable and Cost-Effective: Algal bioreactors are considered more sustainable because they use sunlight as an energy source, reducing the need for external energy inputs. They also have the potential to generate valuable by-products, such as algal biomass, which can be used for biofuels or as a fertilizer.
  c) Reduction of Greenhouse Gases: The photosynthetic activity of algae reduces carbon dioxide levels in the environment, contributing to greenhouse gas mitigation.
  d) Versatility: These bioreactors can be tailored to treat different types of wastewater, including municipal sewage, industrial effluents, and agricultural runoff (Table 11.3).

Table 11.3 Different methods of treatment of sewage waste, microbes involved, and mode of action

Sewage treatment method	Type of microorganism	Treatment used	Mode of action	Examples of microorganisms
Primary treatment	None (Physical Process)	Screening and sedimentation	Sedimentation and filtration remove solids and floating materials from sewage (Akpor et al. 2014)	–
Secondary treatment	Aerobic bacteria	Activated sludge process, trickling filters	Degrade contaminants using oxygen, converting them into energy for growth and reproduction	*Pseudomonas, Acinetobacter*, *Nitrosomonas, Nitrobacter*
	Anaerobic bacteria	Anaerobic digestion	Reduce sludge volume and produce methane gas; do not require oxygen from the environment	*Methanobacterium, Methanobrevibacter, Methanosarcina*
	Facultative bacteria	Stabilization ponds	Can switch between aerobic and anaerobic conditions depending on the environment	*Bacillus, E. coli, Enterobacter*
Tertiary treatment	Various microorganisms	Membrane bioreactors, advanced oxidation processes	Further filtration and removal of nutrients; may include additional biological processes to eliminate remaining pollutants	*Chlorella, Spirulina, Azolla, Lemna*
Sludge treatment	Anaerobic bacteria	Anaerobic digestion	Used in sludge digestion to break down organic matter and reduce volume, often producing biogas as a by-product (Akpor et al. 2014)	*Methanobacterium, Methanobrevibacter, Methanosarcina*

11.6.5 Microbial Community Dynamics and Adaptation

Microbial sewage systems, notably activated sludge (AS) systems, are highly dependent on the dynamic behavior and adaptability of microbial communities for effective wastewater treatment. The efficiency of these systems is impacted by multiple factors, including the specific composition of microbial communities, prevailing environmental conditions, and key operational parameters.

11.6.5.1 Microbial Community Composition

The microbial communities within wastewater treatment plants (WWTPs) exhibit significant variation, influenced by factors such as influent characteristics, treatment technologies, and operational parameters. In activated sludge (AS) systems, the microbial population is largely dominated by Proteobacteria, Bacteroidota, and Actinobacteriota, which are integral to the breakdown of organic matter and the removal of nutrients, especially nitrogen and phosphorus (Ju et al. 2014; Yang et al. 2020). The diversity within these communities is key to maintaining stable and efficient sewage treatment, as a richer microbial diversity enhances the system's ability to withstand environmental fluctuations and changes in substrate availability. For instance, the ratio of biological oxygen demand (BOD) to chemical oxygen demand (COD) plays a critical role in shaping the community structure, thereby affecting both microbial diversity and the efficiency of pollutant removal (Liu et al. 2023).

11.6.5.2 Dynamics and Adaptations Mechanism

Microbial communities in sewage systems display dynamic behaviors, adjusting to shifts in environmental factors like temperature, dissolved oxygen, and hydraulic retention time. These communities adapt through processes such as niche differentiation, where certain species dominate under specific conditions, thereby boosting the overall functional potential of the community. Another critical aspect of adaptation is metabolic flexibility, which allows these microbial communities to metabolize diverse substrates. This flexibility is crucial in environments with variable organic loads, enabling the community to sustain functionality despite changes in influent composition. Additionally, co-occurrence networks have been employed to pinpoint key microorganisms, which can be strategically manipulated to enhance community stability and improve treatment efficiency (Yang et al. 2020).

11.6.5.3 Implications for Sewage Treatment Efficiency

Improving the efficiency of microbial sewage systems hinges on understanding the interplay between microbial community dynamics and treatment performance

(Fetzer et al. 2015). Optimizing operational parameters, such as sludge retention time and aeration conditions, along with strategies like enhancing microbial diversity through inoculation or bio-stimulation, can lead to more effective treatment outcomes. Additionally, the development of predictive models that combine environmental data with insights into microbial community structures can support the design and optimization of wastewater treatment plants (WWTPs), ensuring consistent operation and high treatment efficiency (Liu et al. 2023).

11.7 Advances in Microbial Ecology and Biotechnology

Microbial-based systems present promising strategies for the elimination of emerging pollutants (EPs) from sewage waste. Further advancements in microbial ecology and biotechnology hold considerable potential to enhance the development and optimization of these systems.

11.7.1 Elucidation of Microbial Mechanisms and Degradation Pathways

A comprehensive understanding of microbial mechanisms involved in the degradation of EPs is imperative. Research efforts should focus on elucidating specific metabolic pathways, enzymes, and cofactors responsible for the transformation and mineralization of diverse EP classes, including pharmaceuticals, personal care products, and industrial chemicals. This knowledge can facilitate the identification of pivotal microbial species and optimize their proliferation and efficacy within treatment frameworks (Rusu et al. 2023).

11.7.2 Exploration of Microbial Diversity and Interactions

Investigation into the diversity of EP-degrading microorganisms and their interactions within intricate microbial communities can yield valuable insights. Advancements in omics technologies, such as metagenomics, metatranscriptomics, and metaproteomic, offer avenues to elucidate the functional capabilities and dynamics of microbial consortia engaged in EP removal from sewage waste. Such insights are pivotal for the development of robust and efficient microbial consortia tailored for EP remediation (Gondi et al. 2022).

11.7.3 Bioprospecting and Strain Enhancement

Screening and characterization of novel microbial strains exhibiting enhanced EP degradation capabilities can uncover potent bioremediation agents. Techniques such as directed evolution, genetic manipulation, and synthetic biology can be leveraged to further optimize the performance of these microorganisms, rendering them more suitable for large-scale deployment (Sun et al. 2024).

11.7.4 Bioprocess Engineering and Optimization

Optimization of operational parameters and design aspects of microbial-based systems such as hydraulic retention time, nutrient availability, and aeration can significantly augment EP removal efficiency. Integration of advanced bioprocess engineering principles with microbial ecology promises to foster the development of scalable and resilient treatment solutions (Rusu et al. 2023).

11.7.5 Modeling and Predictive Tools

The development of computational models and predictive tools capable of simulating the fate and behavior of EPs within microbial-based systems can boost technology design, optimization, and scale-up efforts. These models should encompass factors like microbial kinetics, mass transfer phenomena, and environmental conditions to enhance the reliability and efficacy of EP removal processes (Rusu et al. 2023).

By harnessing cutting-edge insights from microbial ecology and biotechnology, researchers can advance microbial-based systems to proficiently address the challenge of eliminating emerging pollutants from sewage waste. This approach underscores a pathway toward sustainable and environmentally friendly wastewater treatment solutions.

11.7.6 Integration of Microbial-Based Systems with Conventional Wastewater Treatment Processes

The integration of microbial-based systems with conventional wastewater treatment processes presents substantial potential for augmenting the removal of emerging pollutants (EPs) from sewage waste.

11.7.6.1 Synergy of Biological and Advanced Treatment Processes

Integrating microbial-based systems with conventional activated sludge or membrane bioreactor processes can synergistically enhance the overall efficiency of EP removal. Biological treatment mechanisms can effectively degrade diverse organic EPs, while advanced treatment methodologies, such as advanced oxidation processes or adsorption techniques, can specifically target the more persistent compounds. This combined approach leverages complementary strengths to achieve comprehensive removal of EPs from wastewater (Hernandez and Osma 2020).

11.7.6.2 Optimizing Operating Conditions

Systematically optimizing the operational parameters of the integrated system, including hydraulic retention time, sludge retention time, and aeration rate, can establish conditions conducive to the proliferation and metabolic activity of EP-degrading microorganisms. This optimization aims to enhance the biotransformation and mineralization of EPs throughout the treatment process (Hernandez and Osma 2020) (Sciences 2001).

11.7.6.3 Hybrid System Configurations

Developing hybrid systems that amalgamate biological treatment with advanced technologies can synergistically augment EP removal efficiency. For instance, integrating microbial-based systems with membrane filtration or electrochemical oxidation exploits the complementary strengths of diverse treatment modalities. This integrated approach enhances the comprehensive remediation of EPs in wastewater (Hernandez and Osma 2020).

11.7.6.4 Addressing Challenges

The integration of microbial-based systems with conventional processes offers potential solutions to challenges concerning process stability, scalability, and cost-effectiveness. This combined approach capitalizes on the strengths of both biological and physicochemical treatment methods to develop robust and efficient strategies for removing emerging pollutants (EPs) (Hernandez and Osma 2020).

11.7.6.5 Collaborative Efforts

Achieving successful implementation of integrated microbial-based systems for EP removal necessitates collaboration among academia, industry, and regulatory bodies.

Such partnerships can facilitate the research, validation, and adoption of advanced wastewater treatment technologies (Sciences 2001; Hernandez and Osma 2020).

By integrating microbial-based systems with conventional treatment processes, researchers can optimize the synergy between biological and advanced treatment methodologies, thereby enhancing the comprehensive and efficient removal of emerging pollutants from sewage waste. This integration underscores the potential for advancing sustainable practices in wastewater management.

11.7.7 Potential for Upscaling and Commercialization

Achieving successful upscaling and commercialization of microbial-based systems for EP removal from sewage waste is essential for their widespread adoption and impact. Addressing several key factors is crucial to realizing the potential of these technologies.

11.7.7.1 Validation Through Pilot-Scale and Full-Scale Demonstrations

Conducting effective pilot-scale and full-scale demonstrations of microbial-based systems for EP removal is critical to validate their feasibility, performance, and reliability under practical conditions. These demonstrations are instrumental in identifying and overcoming challenges related to process stability, scalability, and cost-effectiveness (Gondi et al. 2022).

11.7.7.2 Process Optimization and Automation

Achieving optimal performance of microbial-based systems for large-scale applications requires careful optimization of operational conditions and design parameters. This encompasses configuring reactors, adjusting hydraulic and solids retention times, optimizing nutrient delivery, and enhancing aeration. Integration of advanced process control and automation technologies is pivotal for maintaining peak efficiency and reducing operational expenses (Rusu et al. 2023).

11.7.7.3 Techno-economic Analysis and Life Cycle Assessment

Conducting comprehensive techno-economic analyses and life cycle assessments of microbial-based systems offers crucial insights into their economic feasibility and environmental sustainability. These assessments aid in identifying cost-effective strategies for scaling up and commercializing these technologies, considering factors such as initial investment, operational costs, energy efficiency, and potential for resource recovery (Sun et al. 2024).

11.7.7.4 Collaboration and Knowledge Sharing

Effective collaboration among academia, industry, and regulatory bodies plays a pivotal role in advancing the development, demonstration, and commercialization of microbial-based systems for emerging pollutant (EP) removal. Facilitating knowledge exchange and technology transfer accelerates the adoption of these innovations, ensuring their sustainable implementation and long-term viability (Sun et al. 2024).

By addressing these critical factors and harnessing the potential of microbial-based systems, researchers and practitioners can advance toward the upscaling and commercialization of these technologies. This approach aims to achieve more efficient and economically viable removal of emerging pollutants from sewage waste streams.

11.7.8 Regulatory Considerations and Policy Implications

Successful integration and widespread adoption of microbial-based systems for emerging pollutant (EP) removal from sewage waste necessitate careful consideration of regulatory frameworks and policy implications.

11.7.8.1 Regulatory Frameworks and Guidelines

Establishing comprehensive regulatory frameworks and guidelines for monitoring and controlling EPs in sewage waste is pivotal to driving advancements in treatment technologies, including microbial-based systems. These regulations should define permissible EP levels, standardize analytical methodologies for detection and quantification, and mandate the adoption of EP removal technologies in wastewater treatment facilities (Bala et al. 2022).

11.7.8.2 Standardized Analytical Methods

Developing and standardizing analytical methods for detecting and quantifying EPs in environmental matrices such as sewage waste, surface water, and groundwater is critical for effective monitoring and risk assessment. Reliable analytical techniques are essential for supporting regulatory decisions and evaluating the performance of EP removal technologies (Gondi et al. 2022).

11.7.8.3 Incentives and Policy Support

Implementing policies and incentives that promote the development and adoption of sustainable wastewater treatment technologies, including microbial-based systems for EP removal, can expedite their deployment. These incentives may include financial mechanisms like tax incentives or subsidies, along with regulatory mandates requiring the integration of advanced EP removal processes in wastewater treatment plants (Sun et al. 2024).

11.7.8.4 Environmental and Health Impact Assessments

Conducting comprehensive environmental and health impact assessments of EPs and the efficacy of microbial-based removal systems is crucial for informed regulatory decisions. These assessments should evaluate potential risks to aquatic ecosystems, wildlife, and human health, as well as the long-term sustainability and environmental benefits of treatment technologies (Bala et al. 2022).

By addressing these regulatory considerations and policy implications, policymakers, regulators, and stakeholders can establish an enabling environment that supports the development, implementation, and broad adoption of microbial-based systems for effectively removing emerging pollutants from sewage waste. This contributes to a more sustainable and environmentally responsible approach to wastewater management.

11.8 Conclusion

Microbial-based systems offer a significant solution for the removal of emerging pollutants from sewage waste, utilizing the diverse metabolic capabilities of microbes to degrade or transform a wide range of contaminants. Systems, such as activated sludge, biofilm reactors, and constructed wetlands, utilize various microbial communities to break down complex organic compounds, pharmaceuticals, personal care products, and other pollutants that are not effectively removed by conventional treatment processes. Each of these systems has unique advantages; for instance, activated sludge processes are widely used and effective in removing biodegradable organic matter and nutrients, whereas biofilm reactors offer greater resistance to toxic shocks and more stable operation under varying conditions. Constructed wetlands, on the other hand, provide a low-energy option and more sustainable option, utilizing natural plant-microbe interactions to treat wastewater while enhancing the ecological value of the environment.

However, the efficiency of these microbial-based systems in removing pollutants depends significantly on the specific characteristics of the microbial communities, as well as the environmental conditions. Factors such as pH, temperature, oxygen availability, and the presence of co-substrates can influence the activity of microbes and consequently, the degradation of pollutants. Furthermore, the development of resistant microbial strains and the application of advanced molecular tools, such as proteomics and metagenomics, can enhance the understanding of microbial dynamics and optimize treatment processes. Despite the challenges and limitations, microbial-based systems continue to be a focal point of interest due to their cost-effectiveness, adaptability, and sustainability, making them a crucial component of integrated wastewater management strategies aimed at mitigating the impact of emerging pollutants on public health and the environment.

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Chapter 12
Traditional Enzymatic Methods for the Removal of Hazardous Environmental Pollutants: A Detailed Critique

Freny Shah and Sandhya Mishra

Abstract Conventional activated sludge techniques have trouble breaking down resistant contaminants including oil, grease, chemicals, insecticides, and plastics in wastewater. Because they are poisonous, and do not naturally degrade causing other major issues, these pollutants are widespread and pose a substantial threat to aquatic habitats and organisms. Enzymes are suggested for the treatment of these resistant contaminants as a high-efficiency biocatalyst. The roles and uses of enzymes in wastewater treatment is the key point of this review. Enzymatic processes in remediating resistant pollutants, the identification and ecotoxicity assessment of enzymatic transformation products, the impact of different types of enzymes and their suppliers, and commonly used enzymatic wastewater treatment methods are important factors and will be discussed in this review.

Graphical Abstract

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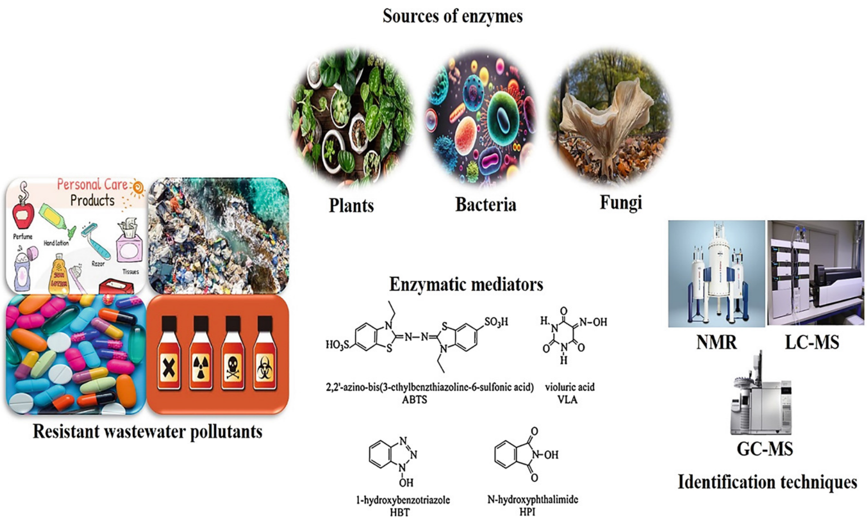
S. Dey and M. P. Shah (eds.), *Biotechnological Removal of Emerging Pollutants from Wastewater Systems*, Advances in Wastewater Research,
https://doi.org/10.1007/978-981-96-3945-8_12



Keywords Bioremediation · Enzymatic degradation · Enzymatic wastewater treatment · Enzyme mediator · Hazardous pollutant · Microbial enzymes · Toxicity study · Transformation products

12.1 Introduction

A wide range of contaminants have been released into aquatic habitats in frighteningly high concentrations in recent years. The most popular kind of wastewater treatment, conventional activated sludge can efficiently clean up most pollutants, but it might be challenging to completely remove resistant substances including plastics, oil, grease, medications, and pesticides. Wastewater containing oil and grease is typically generated by oil mills, slaughterhouses, and dairy farms (Ahmad et al. 2020). The pace at which substrates, products, and oxygen transfer will be hampered by oil and grease that floats on water surfaces (Cammarota and Freire 2006). Grease and floating oil can result in a filamentous microbe bloom and poor activated sludge performance, which can produce floating sludge, poor sedimentation, and a decrease in sludge biomass (Cammarota and Freire 2006). As stated by Teodosiu et al. (2018), other pollutants that are classified as micropollutants, such as plastics, pesticides, pharmaceuticals, and personal care items, are also referred to as emerging pollutants or emerging concern contaminants. Because of their nanogram-to-microgram-per-liter quantities in the environment (Virkutyte and Varma 2010), these substances are difficult to detect or manage in most settings (Mishra et al. 2020). They pose a serious hazard to the environment and all living things since they are usually poisonous, readily bioaccumulate, and resistant to natural biodegradation (Varga et al. 2019).

The two primary types of wastewater treatment procedures used nowadays are biological and physiochemical. Wastewater treatment has made use of physiochemical processes such as chemical oxidation, distillation, membrane-based separation techniques, and adsorption (Alshabib and Onaizi 2019). Although these tactics are treatment-oriented, they come at a high cost and have the potential to exacerbate pollution and harm (Bhatnagar and Anastopoulos 2017). Most contaminants in wastewater can be eliminated by biological processes, which are also more environmentally friendly. These techniques which treat wastewater using bacteria, plants, and enzymes eliminate the majority of contaminants found in wastewater. The organisms used in these technologies have the potential to break down or absorb pollutants as they work. However, while enzymes may function quickly and selectively, plants and microorganisms are susceptible to some harmful contaminants from wastewaters (Sharma et al. 2019).

When conditions are mild, enzymes can be an effective biocatalyst that breaks down chemicals (Yao et al. 2020). In order to lower the activation energy during enzymatic activities, enzymes have distinct active sites that can bind with particular substrates. These procedures therefore have good specificity and reaction kinetics. Moreover, enzymes may reduce the time needed for the entry of substrates into cells, making these more efficient procedures. According to Shah and Mishra (2020), there are six different types of enzymes, with hydrolases and oxidoreductases being the most commonly employed types in wastewater treatment. Due to their broad range of chemical compatibility, these two enzymes can catalyze the majority of contaminants in wastewater. Enzymes such as lipase, laccase, and peroxidase are currently used in industry. Because of their broad substrate specificities or promiscuity, laccase and peroxidase are frequently used to remove various organic micropollutants (Zerva et al. 2017). Enzymes won't be consumed by reactions and can therefore be recycled because enzymatic procedures have greater reaction kinetics and need less energy and water than typical chemical processes (Summerscales 2021). Enzymes don't compete with other microbial lifeforms, in contrast to bacteria and other biological processes (Demarche et al. 2012). Thus, the removal of refractory pollutants from wastewater, such as oil, grease, and organic micropollutants, appears to be a promising application for enzymatic methods.

Numerous enzymes have been researched and found to be effective in treating wastewater containing resistant contaminants. This chapter offers an outline and a critical analysis of the roles and uses of enzymes in wastewater treatment to remove resistant contaminants. This study presents an organized overview of the types and sources of enzymes, their effects, enzyme-based wastewater treatment, issues related to enzymatic transformation products, and commonly used enzyme systems. To support the sustainable development of enzymatic processes for green wastewater treatment technologies, future studies on enzymes for real wastewater with larger scale applications, enzymatic byproduct monitoring, enzyme ability enhancement, and multiple enzyme system constructions were suggested.

12.2 Enzymatic Treatment for Different Pollutants from Wastewater

12.2.1 Enzyme Selection

The types and sources of enzymes have a significant impact on the efficiency of enzymes in wastewater treatment. Enzymes are specific, meaning they can only catalyze a certain kind of reaction. For example, protease can break down proteins, but lipases can stimulate the breakdown of fat, grease, and oil. Carboxylesterases accelerated the hydrolysis of ester bonds of carbamates, organophosphates, and other chlorinated organic compounds (Cummins et al. 2007). According to Romeh and Hendawi (2014), phosphotriesterases have the ability to hydrolyze a broad variety of organophosphate compounds, whereas haloalkane dehalogenases are responsible for cleaving the carbon–halogen link in halogenated aliphatic substances (Mishra et al. 2020). Laccase and peroxidase exhibit great selectivity even if they contain a broad variety of chemicals (Varga et al. 2019). According to related studies, horseradish peroxidase and *Pleurotus ostreatus* laccase has the ability to efficiently and selectively eliminate a few medications. While the *Pleurotus ostreatus* laccase required 20 min to convert diclofenac (DCF) and sotalol (STL), the horseradish peroxidase was able to totally change these substances after 4 h acetaminophen (APAP) right away (Stadlmair et al. 2017). However, according to Stadlmair et al. (2017), neither enzyme was able to change sulfamethoxazole (SMX), carbamazepine (CBZ), ibuprofen (IBP), or naproxen (NAP).

According to a different study, enzyme sources have a big impact on how well wastewater treatment works. Several fungal laccases were utilized by Daâssi et al. (2016) to biotransform BPA, and the *Coriolopsis gallica* laccase had a higher rate of oxidation than laccases from other fungi. Additionally, according to Garg et al. (2020), mesquite peroxidase can remove over 90% of phenol from wastewater in just 30 min. In contrast, peroxidases from potato, soybean, and horseradish, as well as horseradish (Al-Ansari et al. 2010), require longer residence times to achieve the same degree of elimination. When 0.5 mL of crude soybean peroxidase was used for azo dye methyl orange treatment, it produced a maximum decolorization of 81.4% when incubated for 1 h at 30 °C with 2 mM hydrogen peroxide and 30 mg/L of methyl orange at pH 5.0. In the meantime, 1.5 mL of flufa peroxidase produced a maximum decolorization of 75.3% when used in conjunction with 2 mM hydrogen peroxide and 10 mg/L methyl orange at pH 3.0 for 40 min at 40 °C. Three lipases—Lipase-I, Lipase-II, and Lipase-III—were utilized by Meng et al. (2017) to hydrolyze vegetable oil, animal fat, and floating grease. The outcomes demonstrated that Lipase-I and Lipase-II efficiently liberated long-chain fatty acids from these pollutants under hydrolysis settings of 24 h, 40–50 °C, and 1000–1500 μL lipase inoculum. Lipase-III was shown to have a comparatively low rate of hydrolysis, indicating the significance of enzyme sources and types in the treatment of wastewater.

Enzymes are generally very important to life activity (Shah et al. 2021), and every living cell has the capacity to manufacture enzymes for use as biocatalysts.

The typical enzyme sources used and the contaminants they target are displayed in Table 12.1. Animals could serve as a source of lipase, although there are few research using animals as sources of enzymes to treat wastewater. For the treatment of wastewater, several plants are significant suppliers of enzymes, particularly peroxidases (Ely et al. 2017). Enzymes produced by bacteria and fungi are frequently used to clean wastewater. For example, hydrolytic enzymes produced by hydrolytic microorganisms, such as cellulase, amylase, lipase, and protease, can break down carbohydrates, lipids, protein, and other complex chemicals that are generally found as simple molecules in wastewater (Liew et al. 2020). Triglycerides in palm oil mill effluent were successfully treated with exocellular lipase that was isolated from *Candida rugosa* (Theerachat et al. 2017). Chlorpyrifos was broken down using laccase derived from *Trametes versicolor* (Das et al. 2017). Production of enzymes is not limited to a particular strain. Reports had indicated that extracellular enzymes taken out of the microbial populations in wastewater had superior catalytic capacity compared to intracellular enzyme and particularly noteworthy transformation of antibiotics (Zumstein and Helbling 2019). The crude preparations of two co-cultured yeast's exocellular enzymes, *Yarrowia lipolytica* rM-4A and *Candida rugosa,* were able to eliminate 98.5% of triglycerides within 120 h of undiluted palm oil mill effluent (Theerachat et al. 2017). Although plants, bacteria, and fungi are significant sources of enzymes for the removal of pollutants from wastewater, further research is still needed to identify the most appropriate enzymes for a particular wastewater treatment.

12.2.2 The Biodegradation of Wastewater Contaminants Using Enzymes

12.2.2.1 Grease and/or Oil

Massive quantities of meat and edible oil are produced, but there is also a significant quantity of waste associated with the world's unbridled population expansion and resource demands. The value of the world's oil market was estimated by one analysis to be US$83.4 billion in 2015 and US$130.3 billion in 2024. According to Luo et al. (2020), there was a production of around 203.8 million metric tons of edible vegetable oils in 2018 and a consumption of 197.3 million. In addition, during the past few decades, there has been a sharp rise in the production of meat, slaughterhouses, and animals. A significant volume of wastewater including oil and grease is produced by the booming meat and edible oil industries (Lee et al. 2019). These effluents have an elevated organic and inorganic load, which, if released without effective treatment, harms aquatic habitats (Lee et al. 2019), even surface water, and merely contributes to global pollution.

Since lipases may break down oil and grease into simpler free fatty acids and glycerol, they are the most often used enzymes in wastewater treatment systems that

Table 12.1 Commonly used enzyme sources and their targeted contaminants for wastewater treatment include plants and animals, bacteria, and fungi

Animal-based enzyme source	Types of enzymes	Pollutant to be targeted	Source of waste water
Luffa acutangula	Peroxidase	Methyl orange	Synthetic
Horseradish	Peroxidase	Phenols, Methyl orange	Textile/ Leather
Pig pancreas	Lipase	Crude fat	Swine slaughterhouse
Prosopis juliflora	Peroxidase	Phenols, Methyl orange	Textile/ Leather
Turnip	Peroxidase	Phenolic compound	Coffee processing
Potato pulp	Peroxidase	Phenols	Synthetic
Bacterial enzyme sources			
Candida rugosa	Lipase	Triglyceride	Palm oil mill
	Laccase	Phenolic compounds	
Aeromonas hydrophila	Ligninolytic enzyme, including	Crystal violet	Synthetic
	Laccase and LiP enzymes		
Pseudomonas aeruginosa	Lipase	Oil	Oily water
Ideonella sakaiensis	PETase	PET	
Fungal enzyme source			
Trametes versicolor	Laccase	Phenol, SMX and IPN, CBZ	Synthetic
		Chlorpyrifos, BPA	
Coriolopsis gallica	Laccase	BPA	Synthetic
Aspergillus oryzae	Laccase	BPA, DCF	Synthetic
Pleurotus ostreatus	Laccase	TrOCs	Synthetic
Thermomyces lanuginosus	Lipase	Tributyrin	Synthetic
Caldariomyces fumago	CPO	Pesticides, Lincomycin	Synthetic
		Antibiotics	

contain oil and grease. Lipases have been used commercially. It has been observed that lipase works well in oil and grease hydrolysis. For instance, commercial lipase was utilized to break down the floating fatty wastes from the food processing businesses that deal with dairy and meat. Theerachat et al. (2017) found that after 48 h, extracellular lipase produced by *Candida rugosa* could remove 93% of the triglyceride in palm oil effluent. Nevertheless, the application of lipase on oil and grease hydrolysis ought to be considered a pretreatment technique, given that the enzyme's transformation products (TPs) consist of glycerol and simple free fatty acids. Activated sludge and anaerobic fermentation are two further techniques that must be added to these enzymatic processes in order to finish the treatment (Valladao et al. 2009).

12.2.2.2 Pharmaceutical Materials

In the aquatic environment, pharmaceuticals are a typical organic micropollutant that has been found in recent decades. Due to the widespread use of pharmaceuticals, more than 200 distinct active pharmaceutical chemicals have been found in water bodies. Common medications found in wastewater include anti-infectives, cardiovascular drugs, central nervous system agents, metabolic agents, hormones, and more (Varga et al. 2019). Pharmaceuticals can currently not be sufficiently removed by traditional activated sludge systems. According to a study, only four out of 35 pharmaceuticals were able to remove more than 90% of the substance using activated sewage sludge from municipal wastewater treatment plants, whereas 17 compounds exhibited less than 50% removal (Joss et al. 2006). According to a different study, wastewater treatment plants could only passively remove 20–90% of antibiotic residues. It is challenging for natural degradation to take place for antibiotics such as cephalosporins, tetracyclines, and fluoroquinolones (Becker et al. 2016). Pharmaceuticals are common because leftover medications in treated wastewater are continuously released into the aquatic environment. Even if pharmaceuticals are present in released wastewater at low amounts, their bioaccumulation is minimal. In freshwater environments, concentrations of ciprofloxacin, norfloxacin, and oxytetracycline up to 6.5, 0.52, and 0.71 mg/L, respectively, were noted (Hughes et al. 2013). Because of their potential for bioaccumulation and ecotoxicity, medicines that are not adequately treated constitute a serious hazard to aquatic habitats.

According to some study, oxidoreductases are useful enzymes for eliminating pharmaceuticals, and enzymatic methods for treating wastewater with pharmaceuticals are feasible. For example, Song et al. (2019) treated wastewater with immobilized chloroperoxidase (CPO) for the antibiotics levofloxacin and rifaximin. It is important to emphasize that since drugs like CBZ and DCF will be converted into hazardous byproducts, the enzymatic process may result in further pollution. Sadly, over 3000 distinct compounds have been utilized as constituents in medications, and because the biodegradation pathways of most pharmaceuticals are complicated and poorly understood, little is known about the environmental impacts of most pharmaceuticals (Stadlmair et al. 2017). The employment of enzyme-based medicines with wastewater treatment is hampered by the complicated structures of pharmaceuticals. Thus, additional research is required to understand the mechanisms and pathways underlying the transformation of medications based on enzymes.

12.2.2.3 Pesticides

According to Maier et al. (2015), the extensive use of pesticides poses a significant risk to human health and aquatic ecosystems worldwide because of its high residue rate, limited usage, and significant waste. Pesticides are extremely toxic, and their residues will find their way into water bodies through percolation and runoff. They will also negatively impact the water's quality, have an adverse effect on the aquatic creatures' metabolic, regulatory, and biochemical processes (Villarroel et al. 2009), and upset the delicate balance of aquatic ecosystems. Pesticides that function as cholinesterase inhibitors, such as organophosphorus and carbamate, are currently widely used, and they have a devastating negative impact on the environment and animal health. There have been other toxicities that are not connected to cholinesterase yet can be fatal. Important enzymes involved in the breakdown of pesticides have also been documented. For instance, in 12 h at pH 7 and 60 °C, the laccase immobilized on magnetic iron nanoparticles demonstrated a more than 99% clearance of chlorpyrifos (Das et al. 2017). Organophosphate degrading enzyme A (OpdA) might be covalently immobilized on nonwoven polyester textiles to efficiently breakdown small amounts of organophosphate insecticides (Gao et al. 2014). In addition to the destruction of pesticides based on mono-enzymes, a successful outcome may also be obtained through the synergistic transformation of numerous enzymes. Acetylcholinesterase could convert acetylcholine chloride (Ach) into choline in a double-enzyme reaction, and choline oxidase (CHO) may further break down choline into betaine and hydrogen peroxide (Wu et al. 2021). A safe enzymatic method can be achieved by mixing many enzymes, as many enzymatic pesticide TPs are not environmentally benign.

12.2.2.4 Products for Personal Care/Hygiene

Nowadays, millions of individuals use personal care products (PCPs) on a daily basis, such as shampoos, creams, sunscreens, detergents, and UV filters. Both directly and indirectly, these PCPs penetrate the aquatic environment. One way that PCPs get into aquatic habitats is by recreational swimming and outdoor bathing (Balmer et al. 2005). On the other hand, inadequate removal of these pollutants by wastewater treatment facilities and outdoor swimming and bathing by humans (Balmer et al. 2005). On the other hand, human activities including cleaning, laundry, and showering contribute indirectly to PCP intake due to inadequate removal of these contaminants by wastewater treatment plants. Benzophenone-3, oxybenzone, octocrylene, and triclosan (TCS) are UV-filters that are frequently employed as organic chemicals in PCPs (Sendra et al. 2017). These substances are hazardous. *Trametes versicolor* (ATCC 7731), an extracellular enzyme extract with a laccase predominance, has been shown to be able to efficiently breakdown oxybenzone when a redox mediator is present. After an hour of treatment at 40 °C and pH 4, laccase from the white-rot fungus *Coriolopsis polyzona* in combination with mediator 2,2′-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid (ABTS) could successfully eliminate TCS (Cabana et al. 2007). Even though treating PCPs with enzymes has a lot of promise, there aren't many studies on the subject; thus further research is required.

12.2.2.5 Industrial Chemical Compounds

Phenolic Compounds/Phenols

Phenols and phenolic compounds are essential industrial materials that are used in the textile, paper, plastic, pharmaceutical, and other sectors. Even at low concentrations, these substances pose a serious risk to aquatic life and humans, making the ecosystem extremely vulnerable. Currently, research is being done on enzyme-based phenol and phenolic compound elimination. After 40 min at 35 °C and pH 4.5, an immobilized laccase was able to completely remove 0.4 mM of phenol (Fathali et al. 2019). Peroxidases are useful enzymes for changing phenolic substances because of their active sites, which include redox-activated cysteine and hemoglobin cofactor. Similar to this, Rezvani et al. (2015) used a packed bed bioreactor to remove phenol from refinery effluent by immobilizing soybean seed coat powder as soybean peroxidase. Under ideal circumstances, which included 1 mM initial phenol, 56 °C, 14 mM H_2O_2 concentration, and 5.5 mL/min flow rate, up to 97% phenol elimination was seen.

Dyes

The textile and apparel industries are experiencing growth, which has resulted in an increase in the production of dyes containing wastewater due to incomplete fixation on fabric. Additionally, the printing, leather, and plastic industries have been identified as sources of dye containing wastewater production (Zare et al. 2015). Most dyes have complex structures with high stability that prevents them from naturally degrading. Artificially colored and highly visible synthetic dyes have the potential to impact the food chain and transform into harmful compounds that could endanger the aquatic environment and its inhabitants. According to Bilal et al. (2017), the three primary categories of enzyme-based dye therapy currently available are biodegradation, decolorization, and detoxification. The oxidoreductases are the enzymes most frequently employed to treat wastewater that contains dye. Horseradish peroxidase immobilized on cross-linked polyacrylamide gel demonstrated efficacy in the degradation of methyl orange, an azo dye. The highest percentage of methyl orange degradation (93.5%) was observed at pH 6 (Bilal et al. 2017). A micro toxicity study on the inhibition of bacterial growth revealed that the laccase could effectively remove two sulfonamides when 1-hydroxybenzotriazole (HBT) was present as a mediator. However, as almost all wastewater was created artificially and studied in labs, research focusing on actual dye-containing wastewater is required and is not suitable for use in real-world applications.

Plastics/Microplastics

Plastics are widely used in daily life, particularly in packaging, which not only makes products more convenient but also renders them non-biodegradable. Commonly used plastics include polyethylene (PE), polyamide (PA), polyethylene terephthalate (PET), polystyrene (PS), polyvinyl chloride (PVC), polyurethanes (PUR), and polypropylene (PP) (Danso et al. 2019). However, fossil hydrocarbons are the source of polymers like ethylene and propylene, which are resistant to biodegradation. As a result, in the environment, they will accumulate rather than break down. Moreover, the low recycling rate and extensive plastics manufacture exacerbate the situation. Of the plastics manufactured in 2015, over 6.3 billion tons were recycled; however only 9 percent were. The world's oceans, in particular, are home to a large number of plastic ecosystems. Some studies have even found plastic in drinking water. Although plastics are not biodegradable, there are enzymes that can break them down, such as PET hydrolase, tannase, and MHETase (Danso et al. 2019). Unfortunately, the breakdown of plastics using enzymes is not very effective. PETase, an effective and selective depolymerase from *Ideonella sakaiensis*, will require weeks to hydrolyze PET entirely (Zurier and Goddard 2021).

Recent research concentrating on boosting PETase's thermostability and enzyme activity has shown remarkable success and involved in PET and PA. While more information regarding PVC, PP, PE, and PUR hydrolase enzymes and potential routes has been discovered, degradation has not (Danso et al. 2019). Enzymes, however, can break down these polymers because numerous bacteria have been identified that are capable of doing so (Danso et al. 2019). The breakdown of plastics by enzymes is a viable and encouraging approach; nevertheless, more investigation is required to optimize the enzyme's effectiveness and diversity for the purpose of effectively treating plastics that become entangled in wastewater treatment processes.

12.3 Enzymatic Product Transformation and Their Monitoring

12.3.1 Requirement/Importance

Enzymatic TPs can occasionally offer serious risks to the aquatic environment due to their intricate routes, particularly when their substrates are micropollutants (Table 12.2). As per Ji et al. (2016), laccase transformed CBZ, a medication that is typically found in wastewater, into three different forms: 10,11-dihydro-10,11-dihydroxy-carbamazepine (CBZD), 10,11-dihydro-10,11-epoxy-carbamazepine (CBZE), and acridone. Because of its varied catalytic activity, CPO might change CDF into either monohydroxylated or dihydroxylated forms (Lee et al. 2019). The laccase-immobilized chlorpyrifos TPs on magnetic iron nanoparticles consisted of 1,2 benzenedicarboxylic acid, bis(2-methyl propyl) ester, and 2,4-bis(1,1 dimethylethyl) phenol (Das et al. 2017). Consequently, the problems associated with TPs—particularly their potential for toxicity—are minimal because the breakdown of parent drugs does not signal the end of treatment. Different parent drugs and mediators have different toxicity interactions with TPs (Table 12.3). For example, TPs of TCS and lincomycin by chloroperoxidase were less hazardous than the original lincomycin molecule. When vanillin (VA) or HBT was used as the mediator, the treated effluent of some trace organic contaminants (TrOCs) biodegraded by laccase with mediator ABTS showed equal toxicity to influent (Ashe et al. 2016). In contrast, the effluent indicated increased toxicity to the influent. As previously mentioned, several compounds have environmentally hazardous materials in their TPs, yet many studies solely address the removal of parent pollutants and ignore their TPs. The response mechanisms of certain contaminants and enzymatic TPs remain poorly understood to date. As such, enzymatic TPs ought to be observed in order to mitigate this environmental hazard as well as to gain additional insight into the pathways and likely response mechanisms of enzymatic activities.

12.3.2 Identification of the Transformed Products

Table 12.2 lists the common techniques used to identify TPs. Common techniques for detecting enzymatic TPs include nuclear magnetic resonance (NMR), mass spectrometry (MS), and their based approaches (Stadlmair et al. 2017). While MS-based identification methods are the most widely used technologies because they can simultaneously detect substrates, products, and even ionized intermediates, NMR is a method that can accurately determine molecular structure but has low sensitivity and flexibility. Consequently, MS-based approaches are more useful. For example, two peroxidases were used to degrade the color thioflavin (ThT): soybean peroxidase and chloroperoxidase. TPs of the two peroxidases were observed to differ following High Performance Liquid Chromatography (HPLC) tests. According to one study, horseradish peroxidase and laccase from *Pleurotus ostreatus* can effectively monitor the breakdown of various medications and their byproducts using direct infusion mass spectrometry. Understanding the mechanics of enzymatic processes depends heavily on the exact study of enzymatic TPs and mixture effects that MS and MS-based techniques can provide quickly and sensitively. Of course, additional techniques were also used to analyze enzymatic TPs, including atomic force microscopy (AFM), scanning electron microscopy (SEM), and Fourier transform infrared spectroscopy (FT-IR) (Fathali et al. 2019).

12.3.2.1 Toxicity Assay of Transformed Products

A toxicity assay is required to assess the potential for enzymatic TP contamination in water. For toxicity assays, bacteria, fungus, algae, and plant seeds are commonly used indicator organisms (Table 12.3). By tracking the growth inhibition to various

Table 12.2 Enzymatic TPs and their identification methods

Enzyme	Mediator	TPs	Compounds	Methods used for identification
CPO		3-chloro-1,4-dimethylpyrrolidine-2-carboxamide; 2-(1-amino-2-hydroxypropyl)-6-(methylation) tetrahydro-2H-pyran-3,4,5-triol	Lincomycin	HPLC-MS
Soybean peroxidase		Seven different compounds	TCS	LC-MS
	HOBT	3-methylhex-4-enoic acid	ThT	LC-MS-MS
Laccase	PCA	CBZD, CBZE, and acridone	CBZ	LC-MS
	HBT	Tartaric acid, Pyroglutamic acid	BPA	GC-MS
		2,4-bis(1,1 dimethylethyl) phenol, and 1,2 benzenedicarboxylic acid	Chlorpyrifos	GC-MS
	ABTS	CBZD and CBZE	CBZ	LDTD-MS and LDTDMS-MS

Table 12.3 Enzymatic TPs and organisms/plants used for their toxicity assay

Enzyme	Compounds	Organism/plants used for toxicity assay
Peroxidase	SMX	*Lactuca sativa* seeds
Laccase	Orange G dye	*Trigonella foenum-graecum* L seeds
	Tartrazine	*Pseudokirchneriella subcapitata*
	SMX and IPN	*Pseudokirchneriella subcapitata*
	CBZ	Yeast, *C. marina* (CMPL01), and M. *aeruginosa* (PCC 7806)
	Ketoconazole	*Pseudokirchneriella subcapitata*,
		Candida albicans, Cryptococcus neoformans, and *Saccharomyces cerevisiae*
	TrOCs	Bacterial luminescence
	Cibacron Blue 3GA	*Daphnia magna, Chlorella vulgaris*
Horseradish peroxidase	Methyl orange	*A. salina* and *D. magna*, erythrocyte, *T. aestivum*

bioindicators, the toxicity data is obtained. Using bacteria as indicator species, *Photobacterium phosphoreum* or *Aliivibrio fischeri* (Gros et al. 2014) is a popular toxicity assessment technique known as the bioluminescence inhibition test, or microtox assay. *Bacillus subtilis*, *Bacillus megaterium*, *Escherichia coli*, and *Saccharomyces* were among the Gram positive and Gram negative bacteria that were cultivated in both treated and untreated solutions. The growth of these bacteria was used to determine the toxicity of wastewater. Regarding other bioindicators, *Daphnia magna* was employed as a test organism for the toxicity assessment of Cibacron Blue 3GA dye and its metabolites (Bayramoglu et al. 2019). Enzyme-based wastewater treatment depends heavily on identifying and toxicity testing of enzymatic TPs, particularly in cases where the enzymatic byproducts have the potential to be hazardous. Even though a lot of scholars have been interested in this topic, more research must be done before enzymes may be used further in wastewater treatment.

12.4 Enzymatic Wastewater Treatment

12.4.1 Crude/Purified Free Enzyme System

There are two types of enzymes in free enzyme systems: crude enzymes and refined enzymes. Pollutant removal was successfully accomplished by both types of enzymes (Zhang and Geißen 2010). But since procedures like membrane separation, size exclusion chromatography, and column chromatography are needed for the purification of enzymes, the cost of purified enzymes is high. Because crude enzymes contain mediators, purified enzymes were occasionally less effective than crude enzymes at eliminating wastewater contaminants. Naproxen (NPX) has been reported to be totally removed by crude laccase isolated from *Trametes versicolor*, but commercial laccase derived from *Myceliophthora thermophila* (Lloret et al. 2010) was only able to remove the drug to 60%. That does not imply, however, that unpurified enzymes are better than pure enzymes. Since enzymes are costly, these systems are impractical for treating wastewater due to the high demand for enzymes that cannot be recycled. Any leftover enzymes should be eliminated at the conclusion of the treatment process. There is more work to be done to address the expense and/or contamination issues if free enzymes are used to treat wastewater.

12.4.2 Immobilized Enzyme System

Enzymatic systems are frequently investigated and employed with immobilized enzymes. Enzymes are mixed with or physically connected to different matrices in these systems while maintaining their catalytic properties. These systems are simple to manage since the enzymes are affixed to the matrix, making it straightforward for the enzymes to separate from wastewater. Additionally, immobilized enzymes have a long shelf life, which reduces the need for additional pollution control and treatment expenses significantly. However, compared to cell-free enzymes, immobilization decreases the loss of enzyme activity, increases the service life of enzymes, and improves resilience to pH and temperature (Fan et al. 2018). The cost of enzymatic processes, enzyme activity, treatment efficiency, and enzymatic kinetics are all significantly influenced by immobilization techniques and support materials in these systems (Quintanilla-Guerrero et al. 2008). Immobilization techniques which include adsorption, trapping, covalent attachment, and cross-linking are frequently used. The two categories of immobilization techniques are chemical and physical techniques. Physical immobilization and entrapment techniques have less of an impact on the native structure of the enzyme but still result in poor enzyme stability. Chemical immobilization, on the other hand, generally provides good enzyme stability but will reduce enzyme activity due to the covalent bonds formed between the enzyme and support materials. But the finding is not conclusive. Through physical means, carrier surfaces can be altered to increase the stability of the enzyme. Compared to employing free laccase, immobilized laccase was shown to have better stability, pH, and storage. Even if physical techniques have less of an impact on enzyme function, it is still important to consider the loss of enzyme activity.

Chemical immobilization techniques are more intricate than physical techniques because they involve chemical reactions throughout the immobilization process. The execution of the enzymatic process may be impacted by immobilization techniques. Two immobilized peroxidases were found to have differing effects on the elimination of phenol under identical circumstances (Quintanilla-Guerrero et al. 2008). When the initial phenol concentration was between 0.2 and 0.8 mM, there was similar phenol removal; however, at 1.4 mM, Quintanilla-Guerrero et al. (2008) found that the alginate-entrapped turnip peroxidase showed superior phenol removal over the covalently immobilized turnip peroxidase. As previously said, application demand should dictate immobilization techniques. To prevent environmental issues, it is important to take into account the toxicity of the chemicals used during immobilization operations. Important considerations for matrix selection include material cost, toxicity, surface area, and mechanical strength. Three categories of support materials exist: inorganic matrix, organic matrix, and organic–synthetic matrix. According to Hettiarachchy et al. (2018), inorganic supports with good diffusion and flowing properties include activated carbon and silica gel. Moreover, they are typically inexpensive and resistant to microbial contamination. The organic matrix, which is cheap and abundant, is made up of proteins and carbohydrates like cellulose and chitin. These supports, however, have restricted diffusion and flowing capabilities and are often contaminated by microorganisms. In enzymatic methods, organic–synthetic matrix supports are frequently utilized because they are easily accessible and resistant to contamination by microbiological lifeforms (Tischer and Wedekind 1999).

However, because of their hydrophobicity or water-repellent qualities, these supports may result in the loss of enzymes and decrease enzyme activity (Tischer and Wedekind 1999).

However, more labor and an examination of the carrier costs are required for the manufacture of immobilized enzymes. In order to create a better system that takes cost, stability, and enzyme activity into account, immobilization techniques should be chosen in accordance with the study purpose. Additionally, more appropriate immobilization materials need to be investigated.

12.4.3 Mediator-Driven Enzyme System

Enzyme mediators are low-weight, stable substances that have the potential to function as an electron shutter between substrates and enzymes. By generating extremely reactive radicals, mediators may increase the variety of substrates for enzymes. Additionally, these tiny molecules enhance the effectiveness of eliminating the targeted contaminants and facilitate the enzymatic process.

There are two categories of enzyme mediators: synthetic and natural. While ABTS, HBT, and violuric acid (VLA) are synthetic mediators, syringaldehyde (SA), AS, VA, acetovanillone, methyl vanillate, and 4-hydroxybenzyl alcohol (HBA) are natural mediators (Cañas and Camarero 2010). They can enhance the enzymatic process and the activity of the enzymes.

Orange G dye decolorization was achieved by Bibi et al. (2019) using laccase; the results indicated that mediator might enhance both laccase activity and orange G dye removal. Horseradish peroxidase was used to remove tetracycline, and the results showed that the maximum degradation of tetracycline was approximately 53% in a pure enzyme system and more than 95% in a mediator added system. The reaction time for these results decreased from 1 to 0.5 h (Leng et al. 2020). Becker et al. (2016) employed immobilized laccase to study the biodegradation of

38 antibiotics. According to the findings, laccase alone was unable to significantly reduce the amount of antibiotics; however, when mediator SA was added, 32 out of 38 antibiotics exhibited greater than 50% clearance.

The elimination of contaminants is significantly impacted by the concentration of mediators. Different mediators may affect the same reaction differently, resulting in varying TP toxicity (Ashe et al. 2016). Inadequate performance can also result from the mediators' combination. According to reports, the independent addition of mediators SA and VLA may increase the pace at which TrOCs are broken down by laccase, but when combined with other medications, such as CBZ, IBF, and primidone, it may slow down the breakdown of those medications. It is important to note that mediators have the ability to alter the enzymatic process' mechanism, producing distinct TPs and making it more difficult to regulate the enzymatic process (Varga et al. 2019). According to one study, adding mediator SA would make the effluent more hazardous when laccase was used to cure TrOCs. It is unclear if the harmful enzymatic TPs or the interaction between laccase and mediator caused this event, even though it is connected to the dose of SA (Nguyen et al. 2016).

According to Varga et al. (2019), the majority of synthetic mediators are costly and will result in additional pollution. Moreover, the substantial consumption of mediators impedes the implementation of this technique. According to Ashe et al. (2016), enzyme activity was suppressed even when mediators were able to enhance the enzymatic process.

However, because mediators are hazardous (Becker et al. 2016), using them may result in additional environmental issues; however, this is dependent on the dose of the mediator. Although mediators are hazardous, they are required for the treatment of substances such as TCS and oxybenzone (Cabana et al. 2007). Finding an affordable and suitable mediator concentration is therefore crucial for enhancing the stability and effectiveness of the enzymatic process.

12.5 Future Prospects

Enzymatic processes have a lot of potential for treating wastewater, as was previously indicated (Wilkinson et al. 2016). Enzymatic processes are significantly influenced by the types and sources of enzymes. Therefore, additional research is required to examine how well enzymes function with particular wastewater types. The elimination of resistant contaminants from wastewater has demonstrated the viability of enzyme-based treatment. Unfortunately, a lot of research was done in experimental or laboratory settings, and the wastewater used in those studies was synthetic (Table 12.1), which makes it unsuitable for real-world use. Therefore, there is an urgent need for larger scale studies and further research on actual wastewater.

Enzymes are unable to break down certain resistant contaminants, such as plastics and medications, or can only break them down poorly. Although using mediators to improve enzymatic efficiency is a practical approach, it is important to consider the toxicity of mediators. It is preferable to employ mediators as little as possible, even though some studies are dedicated to discovering natural mediators that could reduce the undesirable results. Enhancing enzymes' catalytic capacity through genetic engineering is a workable strategy that promotes the breakdown of these recalcitrant pollutants. Another practical approach is to discover additional novel enzymes that can catalyze the breakdown of resistant pollutants. Because of their potential for toxicity, it is important to note that enzymatic TPs are crucial to the treatment of wastewater. Many researchers disregarded the byproducts in favor of concentrating solely on the transformation of the main substrates. Thankfully, there has been an increase in interest in TPs in recent years, which has allowed us to understand more about the workings of enzymatic processes and the practical uses of enzymatic wastewater treatment. Under some conditions, free enzyme systems in wastewater treatment systems related to enzymes can achieve good treatment performance; nevertheless, these systems may not be economical or environmentally benign.

Because of their potential for toxicity, it is important to note that enzymatic TPs are crucial to the treatment of wastewater. Many studies ignored the byproducts in favor of concentrating solely on the transformation of the parent substrates. Thankfully, there has been an increase in interest in TPs in recent years, which has allowed us to understand more about the mechanisms underlying enzymatic processes and the practical uses of enzymatic wastewater treatment. Under some conditions, free enzyme systems in wastewater treatment systems related to enzymes can achieve good treatment performance; nevertheless, these systems may not be economical or environmentally benign. To cut costs, it's imperative to locate commercial enzymes with high efficiency. The majority of research using free enzyme systems for wastewater treatment nowadays exclusively consider the removal of tar-treated pollutants, ignoring the impact of leftover enzyme additions.

Therefore, action must be taken to stop the detrimental effects of the enzyme additives. The effectiveness of immobilized enzymes is dependent on the immobilization carriers and techniques used. Enzyme activity loss is essentially accompanied by the immobilization processes, and the lifetime of immobilized enzymes is brief. Therefore, it is essential to identify appropriate immobilization supports and techniques for enzyme immobilization in order to minimize the loss of enzyme activity and improve enzyme reusability. As of right now, methods for locating appropriate carriers include surface modification and functionalization, as well as research into enhanced support materials. Enhancing comprehension of the properties of enzymes, such as their structures and methods of action, can further improve the immobilization of enzymes. While specificity is a benefit of enzyme-based wastewater treatment, it is also a drawback because the majority of research exclusively addresses the removal of a single type of pollutant from synthetic wastewater using a single enzyme. On the other hand, the actual wastewater is complicated, and one enzyme could not break down every contaminant—not to mention the issues with enzymatic TPs.

Consequently, the development of immobilization systems that facilitate the cooperation of many enzymes is crucial. Enzymes can only convert one substrate into more basic molecules; therefore this approach cannot eliminate contaminants entirely on its own. Consequently, the combination of enzymatic breakdown with anaerobic fermentation or other methods such as activated sludge is a good place to start.

12.6 Conclusion

The breakdown of pollutants is greatly aided by enzymes, and enzymatic bioprocesses have proven to be the preferred method of treating wastewater. When it comes to the biodegradation of refractory pollutants including grease, oil, medications, personal care items, insecticides, and industrial chemicals, enzymatic processes show promise. However, as enzymes can only break down complex molecules into simpler ones, this approach can only be used as a pretreatment step and must be used in conjunction with other techniques to achieve full therapy. There are now several barriers to the wider deployment of this technology, including the need for different enzyme system constructions, enzymatic TP monitoring, enzyme ability augmentation, and investigations into real wastewater and larger scale applications.

Acknowledgements The authors wish to express their gratitude to the Director of CSMCRI for his support. The CSIR Emeritus Scientist Scheme provided financial support to FS and SM throughout the writing of this book chapter.

Declaration of interest The authors state that none of the work described in this publication appears to have been influenced by any known competing financial interests or personal ties.

Ethical statement The investigation has not involved any human trials or the use of animals.

Use of AI and AI generative assistance The author(s) did not employ any artificial intelligence (AI) or AI-assisted technology to write this chapter.

Contribution statement by the author SM came up with the notion. The first draft was authored by FS. SM has read the work over. FS completed the final formatting and editing.

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Chapter 13
Emerging Pollutants in Wastewater and Its Biomonitoring

Sandhya Maurya, Anju Patel, Garima Gupta, and Ashok B. More

Abstract The escalation of industrialization and urbanization has led to the proliferation of emerging pollutants in wastewater, posing significant threats to environmental and human health. This chapter provides a comprehensive review of the various emerging pollutants found in wastewater, encompassing pharmaceuticals, personal care products, endocrine-disrupting compounds, microplastics, nanomaterials, and other contaminants. Furthermore, the chapter explores the methodologies and techniques employed in the biomonitoring of these pollutants, including the use of bioindicators, biomarkers, and advanced analytical tools. The significance of biomonitoring in assessing environmental contamination levels, understanding pollutant fate and transport, and evaluating the efficacy of wastewater treatment processes is emphasized. Moreover, the chapter discusses the challenges and limitations associated with biomonitoring approaches, such as the identification of appropriate biomarkers, standardization of methodologies, and interpretation of data. Additionally, it highlights the emerging trends and future directions in the field, including the integration of omics technologies, development of biosensors, and implementation of innovative monitoring strategies. Overall, this chapter serves as a valuable resource for researchers, policymakers, and practitioners involved in wastewater management and environmental monitoring, offering insights into the characterization and biomonitoring of emerging pollutants to mitigate their adverse impacts on ecosystems and human health.

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S. Dey and M. P. Shah (eds.), *Biotechnological Removal of Emerging Pollutants from Wastewater Systems*, Advances in Wastewater Research,
https://doi.org/10.1007/978-981-96-3945-8_13

Keywords Emerging pollutants · Biomonitoring · Wastewater · Bioindicators · Biomarkers

13.1 Introduction

The rapid acceleration of industrialization and urbanization has led to the emergence of various pollutants increasingly detected in wastewater. These pollutants, including pharmaceuticals, personal care products, endocrine-disrupting compounds, microplastics, and nanomaterials, pose growing concerns due to their persistence in the environment and potential adverse effects on both ecological systems and human health. Unlike traditional pollutants, these emerging contaminants are characterized by their complex chemical nature and the challenges they present to conventional wastewater treatment processes (Cao et al. 2024; Perveen et al. 2023; Vasilachi et al. 2021).

Pharmaceuticals and personal care products (PPCPs) are significant contributors to wastewater pollution, entering aquatic systems through human excretion, industrial discharges, and agricultural runoff. Endocrine-disrupting compounds (EDCs) can interfere with hormonal systems, causing widespread ecological and health impacts (Nishat et al. 2022). Additionally, microplastics and nanomaterials, with their minute sizes and diverse forms, introduce complexity by potentially absorbing and transporting hazardous substances and affecting ecosystems over the long term.

Traditional chemical analysis methods have limitations in detecting these emerging pollutants, making biomonitoring a crucial tool. This chapter reviews the types of emerging pollutants in wastewater and explores methodologies and techniques used in their biomonitoring. It examines the role of bioindicators, biomarkers, and advanced analytical tools in assessing environmental contamination, understanding pollutant fate and transport, and evaluating the effectiveness of wastewater treatment processes.

Biological indicators, including organisms, plants, and microbes, play a vital role in identifying contaminants in ecosystems. These indicators provide insights into pollutant persistence and ecosystem health over time, known for their reproducibility, simplicity, reliability, and applicability across different scales. Naturally occurring biological indicators are often used for monitoring ecosystems, capturing both positive and negative environmental changes. Khatri and Tyagi (2015) emphasized the importance of considering environmental factors such as light, moisture, temperature, and suspended particles when using biological controls.

Despite advances in biomonitoring, challenges persist, including the identification of suitable biomarkers, standardization of methodologies, and data interpretation. The chapter also highlights emerging trends and future directions, such as integrating omics technologies, developing biosensors, and innovative monitoring strategies. Through this review, the chapter aims to provide valuable insights for researchers, policymakers, and practitioners in wastewater management and environmental monitoring, emphasizing the need for comprehensive strategies to address the complex issues posed by emerging pollutants.

13.2 Types of Emerging Pollutants in Wastewater

Emerging pollutants commonly originate from the release of hospital and factory wastewater, residential sewage, and agricultural runoff and include endocrine-disrupting chemicals (EDCs), microplastics (MPs), pesticides, nanomaterials, pharmaceutical, and personal care products (PPCPs). Emerging pollutants in wastewater are a significant environmental concern due to their persistence and potential adverse effects on human health and ecosystems. These pollutants can be categorized into several groups as given in Fig. 13.1.

13.2.1 Microplastics

Microplastics (MPs) represent a significant category of emerging pollutants, prevalent across both land and aquatic environments (Cao et al. 2024). Pan et al. (2023) reported that approximately 76% of the total plastic produced ends up as waste, with 12% incinerated, 79% either landfilled or released into the environment, and a mere 9% recycled. The incineration process releases pollutants such as carbon monoxide, dioxins, dioxin-like compounds, and nitrogen oxides, exacerbating air pollution and hindering effective plastic waste management. Once in the environment, plastics fragment into smaller particles (ranging from 1 μm to 5 mm, and insoluble in water) due to exposure to sunlight, wind, and other environmental factors (Abad López et al. 2023). These microplastics can absorb and transport hazardous substances, including polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), persistent organic pollutants (POPs), polystyrene, and heavy metals (Abad López et al. 2023). The presence of these toxic chemicals on microplastics can lead to various adverse effects such as oxidative stress, metabolic disruptions, immune system alterations, neurotoxicity, reproductive and developmental issues, and potential genotoxicity (Lee et al. 2023). Current methods for removing microplastics from wastewater include physical, chemical, and biological techniques, such as filtration, coagulation and flocculation, and advanced oxidation processes. While these approaches can be effective, especially for larger particles, challenges persist in removing smaller microplastics, achieving high removal efficiencies, and avoiding the generation of secondary pollutants. Additionally, there is a need for standardized protocols to accurately measure and report microplastics in wastewater, which would enhance the development of more effective treatment technologies.

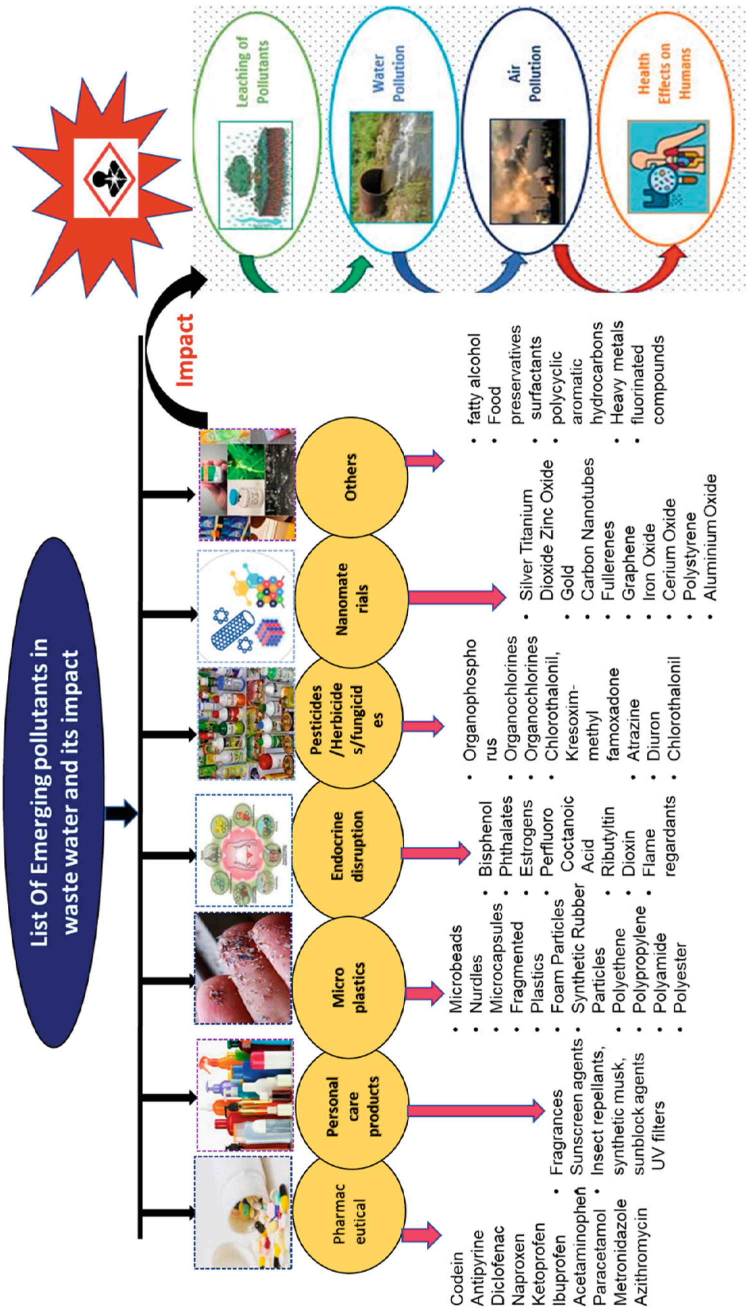

Fig 13.1 List of emerging pollutants in wastewater and their impacts

13.2.2 Pharmaceuticals

Pharmaceutical pollutants in wastewater have emerged as a pressing environmental issue due to their persistence in the environment and potential negative impacts on both aquatic ecosystems and human health. These pollutants primarily enter wastewater systems through three main routes: human excretion, industrial discharges, and agricultural runoff. A significant amount of pharmaceuticals consumed by individuals is excreted and eventually finds its way into sewage systems and wastewater treatment plants (WWTPs). Additionally, the pharmaceutical industry contributes to the contamination of wastewater by discharging drug residues during the manufacturing process. Agricultural practices also play a role, as the use of veterinary medicines and various agricultural chemicals can lead to pharmaceutical residues being carried into water bodies through runoff (Naghdi et al. 2018).

A wide range of pharmaceutical compounds have been detected in wastewater, including commonly used analgesics like ibuprofen and paracetamol, antibiotics such as sulfonamides and tetracyclines, and hormones and endocrine disruptors. These compounds pose various risks, particularly the potential for antibiotics to foster the development of antibiotic resistance in pathogenic bacteria (Ashiq et al. 2019). Hormones and endocrine disruptors can have profound ecological effects, especially on the reproductive systems of aquatic organisms. In addition, personal care products are increasingly recognized as emerging contaminants that are found alongside pharmaceutical pollutants in wastewater (Miller et al. 2019).

The environmental impact of these pollutants is significant. Even at low concentrations, pharmaceutical residues can be toxic to aquatic life, leading to disruptions in ecosystems and affecting species diversity and health. For humans, the presence of these contaminants in drinking water sources is a growing concern, though the full extent of the health risks is still being investigated. One of the major challenges in addressing pharmaceutical pollution is the inadequacy of conventional wastewater treatment methods. These methods often fail to remove pharmaceutical residues effectively, allowing these pollutants to persist in the environment.

In response to these challenges, various advanced treatment technologies are being developed. Biological treatments, which enhance the natural degradation processes of pharmaceuticals in wastewater, are one approach. Advanced oxidation processes, which involve breaking down complex pharmaceutical compounds that are resistant to traditional treatments, offer another promising solution. An emerging and innovative method is mycoremediation, which uses fungi to degrade pharmaceutical pollutants in wastewater. While these technologies represent significant advancements, further research and development are necessary to fully address the challenges posed by pharmaceutical pollutants and to protect both the environment and public health from their potential impacts (Sá et al. 2022).

13.2.3 Personal Care Products

Pharmaceuticals and personal care products (PPCPs) enter wastewater from various sources, each contributing to environmental pollution. Household products such as shampoos, soaps, and detergents are significant contributors, as residues from their use are washed down drains and into sewage systems. Medical facilities, including hospitals and long-term care centers, add to the problem through the disposal of unused medications and treatment-related waste. Additionally, industrial processes involved in manufacturing these products result in wastewater with high PPCP concentrations. Landfill leachate, from the disposal of expired or unused products, also contains PPCPs that can contaminate groundwater and surface water.

The environmental impact of PPCPs is concerning. Many of these compounds persist in ecosystems due to their resistance to degradation, leading to bioaccumulation in aquatic organisms. This can disrupt endocrine systems, causing reproductive issues among wildlife. There are also health risks associated with PPCPs; residues have been found in drinking water, potentially contributing to antibiotic resistance and hormonal disruptions in humans. The presence of PPCPs in mixtures with other pollutants can exacerbate these effects, even at low concentrations (Ismanto et al. 2022).

Treatment of PPCPs in wastewater poses challenges. Wastewater treatment plants (WWTPs) are not always equipped to effectively remove these compounds. While some plants can achieve high removal rates for certain PPCPs, such as up to 100% for ibuprofen, others, like triclosan, show much lower removal efficiencies, sometimes as low as 57%. This variability means that untreated or inadequately treated wastewater may still discharge significant levels of PPCPs into natural water bodies, leading to ongoing environmental and health concerns.

13.2.4 Endocrine-Disrupting Compounds

Endocrine-disrupting compounds (EDCs) are pollutants in wastewater that pose serious risks to human health and the environment. These compounds interfere with hormonal systems, leading to issues such as reproductive abnormalities, cancers, and metabolic disorders. EDCs often enter water systems through human activities, including pharmaceutical excretion, agricultural runoff, and the use of personal care products (Annamalai and Namasivayam 2015; Ismanto et al. 2022).

Common sources of EDCs in wastewater include pharmaceuticals like carbamazepine and sulfamethoxazole, industrial chemicals such as bisphenol A (BPA) and nonylphenols, and both natural and synthetic hormones. Despite their presence in small concentrations, these compounds can have significant impacts, causing chronic health issues and disrupting endocrine functions in both humans and wildlife.

One of the main challenges in managing EDCs is the inefficiency of conventional wastewater treatment plants (WWTPs). Traditional treatment processes often fail to remove EDCs effectively, allowing these harmful compounds to persist in treated water and continue contaminating the environment. This can lead to bioaccumulation in food chains, further amplifying the risks to public health.

To combat this issue, researchers are exploring advanced wastewater treatment technologies. Some promising methods include advanced oxidation processes (AOPs) that break down EDCs into less harmful substances, adsorption techniques using activated carbon or nanomaterials, bioremediation through microorganisms or plants, and membrane filtration methods like ultrafiltration and reverse osmosis. While these technologies show potential, challenges such as cost, scalability, and the need for further research remain before they can be widely implemented. Adsorption, especially using activated carbon, has proven effective, but newer materials are being researched to make the process more cost-effective and environmentally sustainable.

13.2.5 Nanomaterials

Engineered nanoparticles and other nanomaterials are increasingly recognized for their potential environmental hazards, particularly concerning their toxicity to aquatic organisms and their tendency to bioaccumulate. As these materials become more prevalent across industries, there is growing concern about their unintended impacts on ecosystems (Abdoul Magid et al. 2021).

13.2.5.1 Environmental Impact and Toxicity

Nanomaterials can enter the environment through both planned and accidental releases, such as industrial activities, atmospheric emissions, and the breakdown of consumer goods like cosmetics and textiles. Engineered nanomaterials (ENMs) are of particular concern due to their varied forms, such as carbon nanotubes and metal nanoparticles, which interact differently with aquatic environments compared to their larger counterparts.

13.2.5.2 Sources and Release Mechanisms

These materials can be released through various channels, including manufacturing processes, airborne particles, and wear-and-tear of everyday products. Their small size and diverse forms contribute to their unique behavior in water bodies, often leading to environmental challenges.

13.2.5.3 Toxicological Effects

Studies reveal that nanomaterials can be harmful to aquatic life, even at low concentrations. Nanoparticles can cause metabolic disturbances in fish and other organisms, leading to chronic exposure issues. These particles can accumulate in the bodies of aquatic species, potentially affecting essential organs such as the liver and brain. The high reactivity and surface area of nanomaterials heighten their interaction with biological systems, raising concerns about their long-term effects on ecosystems.

13.2.5.4 Bioaccumulation and Ecological Risks

A major concern is the potential for nanomaterials to accumulate in food chains, where they persist and enter the diets of various organisms. This bioaccumulation can lead to harmful effects on individual species and disrupt entire ecosystems, impacting biodiversity and ecological stability. Understanding these interactions requires detailed research to grasp how nanomaterials behave and persist in the environment.

13.2.5.5 Need for Research and Regulation

The rapid development of nanotechnology underscores the need for extensive research to evaluate the ecological risks of nanomaterials. Investigating their toxicity, environmental behavior, and potential to transform into more harmful forms is essential for creating effective regulatory measures. This research should cover the entire lifecycle of nanomaterials, from production to disposal, to address and mitigate their environmental impact.

13.2.6 Fertilizers

Emerging pollutants in wastewater, particularly those from fertilizers, are becoming a critical environmental issue due to their detrimental effects on water quality and human health. High-nitrogen fertilizers contribute to nitrate pollution, with less than 50% of nitrogen being utilized by crops and the rest leaching into water bodies (Abas et al. 2022). This leads to eutrophication, harming aquatic life and exacerbating issues in developing regions with increased fertilizer use. Biosolids from wastewater treatment, used as fertilizers, can also carry emerging pollutants like pharmaceuticals, which are not effectively removed during treatment and can enter the food chain. Regulatory frameworks are currently insufficient, focusing mainly on inorganic contaminants, thus complicating efforts to manage these synthetic organic pollutants. Addressing these challenges requires improved fertilizer practices, advanced wastewater treatment, and robust regulatory measures to protect environmental and public health. Bioremediation effectively removes fertilizers from wastewater using microorganisms, plants, or enzymes to transform pollutants into less harmful substances. Common methods include microbial bioremediation, where bacteria and fungi degrade fertilizers like nitrates and phosphates; phytoremediation, which uses plants to absorb and convert excess nutrients; enzyme-based bioremediation, involving enzymes to break down specific fertilizer components; constructed wetlands that mimic natural systems to treat wastewater; and bioreactors that provide controlled environments for optimized microbial treatment (Liesch et al. 2015).

13.2.7 Pesticides

Pesticide pollution in wastewater is a critical environmental issue due to its harmful effects on aquatic ecosystems and human health. Pesticides can enter water bodies via agricultural runoff and industrial discharges, leading to contamination of drinking water sources. These chemicals are extensively used in agriculture and urban areas, and their residues can build up in wastewater. A study in Athens, Greece, over seven years, identified 40 different pesticides in untreated wastewater, with concentrations as high as 4.9 μg/L (Alengebawy et al. 2021). The most common were fungicides, followed by herbicides and insecticides. The study also found pesticide transformation products and metabolites, suggesting ongoing environmental impacts and potential human exposure through contaminated water (Baharum et al. 2020; Calvo et al. 2021; Singh et al. 2022).

The presence of pesticides in water bodies not only deteriorates water quality but also poses significant health risks, including long-term exposure to low concentrations that can lead to non-carcinogenic effects. Persistent pesticides can accumulate in aquatic organisms and sediments, further exacerbating environmental and health issues.

Addressing pesticide pollution in wastewater requires effective treatment methods. Conventional techniques like coagulation–flocculation, adsorption, and filtration can be costly and may cause secondary pollution. Advanced oxidation processes (AOPs) are emerging as efficient alternatives, breaking down pesticide molecules into less harmful substances. Additionally, reverse osmosis (RO) membranes have shown over 95% effectiveness in removing pesticides, making them a promising option for improving water quality (Calvo et al. 2021). Pesticide pollution in drinking water presents several health risks. These chemicals can disrupt the endocrine system by mimicking hormones, leading to reproductive issues, developmental problems in children, and immune system alterations. Some pesticides are carcinogenic, with prolonged exposure potentially increasing the risk of cancers, particularly those related to hormones like breast and prostate cancer. Neurological effects are also a concern, especially with pesticides like organophosphates, which can impair cognitive functions and lead to neurological disorders, including reduced intelligence in children (Jacob et al. 2022). Acute toxicity from ingesting high levels of pesticide-contaminated water can cause severe symptoms such as nausea, vomiting, and even death, particularly in areas with significant agricultural runoff. Chronic exposure to low levels of pesticides may result in long-term health issues, including immune system deficiencies and respiratory problems. Additionally, pesticides can bioaccumulate in aquatic organisms, entering the human food chain and further increasing the risk of exposure through the consumption of contaminated seafood.

In conclusion, managing pesticide pollution in wastewater necessitates a comprehensive approach, including monitoring pesticide residues, enhancing treatment technologies, and encouraging sustainable agricultural practices like Integrated Pest Management (IPM). These strategies are essential for ensuring safer drinking water and healthier ecosystems.

13.2.8 Other Contaminants

This category includes various industrial additives, flame retardants, and per fluorinated compounds (PFCs). These substances can originate from industrial processes and consumer products, contributing to environmental contamination. Surfactants are synthetic compounds used in a variety of products such as cleaning agents, emulsions, paints, insecticides, and cosmetics. They are known for their ability to disrupt marine life by penetrating and affecting cellular membranes, and they contribute to foam formation in water bodies. Common surfactants include linear alkylbenzene sulfonates, lignin sulfonates, fatty alcohol ethoxylates, and alkylphenol ethoxylates. Alkylphenol ethoxylates, like octylphenol and nonylphenol, are particularly persistent in the environment. Additionally, substances such as plasticizers (e.g., phthalates and bisphenol) and polycyclic aromatic hydrocarbons from forest fires and fossil fuel combustion are also significant pollutants. Common endocrine-disrupting pollutants in groundwater include caffeine, nicotine, and various sugar substitutes like acesulfame and saccharin. Food preservatives and additives like butylated hydroxyanisole and triacetin also contribute to pollution. Their persistence and potential toxicity make them important targets for environmental monitoring and regulation.

13.3 Methodologies and Techniques for Biomonitoring

Biomonitoring involves the use of living organisms or biological responses to assess environmental conditions, including the presence of pollutants (Burger 2006). For emerging pollutants in wastewater, several biomonitoring methodologies and techniques are employed.

13.3.1 Bioindicators

Naturally occurring bioindicators play a crucial role in evaluating environmental health and are essential for detecting environmental changes—whether beneficial or harmful—and their potential impacts on human communities. Several factors influence the presence of bioindicators in an environment, including light transmission, water quality, temperature, and the concentration of suspended solids. By utilizing bioindicators, it is possible to predict the natural condition of a specific area or assess the extent of contamination.

13.3.1.1 Plant Indicators

Plants are sensitive to environmental changes and can reflect the health of their ecosystems. For instance, lichens are indicators of air quality, as their presence or absence can signal changes in pollution levels, particularly sulfur dioxide and nitrogen compounds.

Higher plants, due to their immobility and longevity, are effective biological indicators of pollutants. They exhibit external symptoms of pollution, which can be quantified and confirmed through further analysis. For instance, plants like *Calluna vulgaris* and *Salicornia europaea* can indicate changes in soil pH and salt content. Phytoremediation studies using plants such as *T. caerulescens* demonstrate their capacity to improve ecosystem health by extracting metals and enhancing microbial activity.

Planktons, including both phytoplankton (plants) and zooplankton (animals), are critical indicators in aquatic ecosystems. Specific aquatic plants, such as *Wolffia globosa*, are used to indicate cadmium contamination, while phytoplankton diversity such as *Euglena clastica*, *Phacus tortus*, and *Trachelomonas* can reveal the health of marine ecosystems and the impact of eutrophication (Burow et al. 2017).

They are sensitive to changes in water quality and can reflect the impacts of pollutants such as phosphorus and nitrogen. Phytoplankton, which are key in the aquatic food chain, can indicate water quality through their growth patterns and are used to monitor eutrophication. Overall, both plants and planktons play essential roles in monitoring and assessing the health of ecosystems.

13.3.1.2 Animal Indicators

Various animal species, including macro-invertebrates and amphibians, serve as bioindicators. Changes in their populations or health can indicate the presence of pollutants. For example, copepods and other small crustaceans are monitored for biochemical and behavioral changes that may signal ecosystem problems (Bancel et al. 2024; Zaghloul et al. 2020). Animal indicators are crucial for monitoring ecosystem health and pollution levels. These indicators reveal changes in ecosystems due to pollution by examining animal populations and their responses to environmental stressors.

13.3.1.3 Earthworms

Earthworms are significant biological indicators in soil ecosystems. Their presence and health reflect overall soil quality and pollution levels. Earthworms can detect pollutants such as heavy metals and serve as early warning systems for environmental changes. They utilize mechanisms like lipid anti-oxidative enzyme systems and compartmentalization to mitigate the effects of pollutants. Their activity and population density can indicate soil health and the extent of pollution.

13.3.1.4 Macro-Invertebrates

Macro-invertebrates in aquatic environments, such as benthos, are valuable for assessing water quality and ecosystem health. These organisms are easy to sample and categorize, making them effective indicators of aquatic pollution and habitat destruction. Their resilience to environmental changes and ability to reflect pollution levels make them important for monitoring ecosystem health.

13.3.1.5 Frogs and Toads

Frogs and toads are sensitive to changes in their habitats, both terrestrial and aquatic. As amphibians, they absorb pollutants through their skin and gills, making them effective indicators of environmental contamination. Their health can be assessed through their population dynamics, morphological changes, and developmental abnormalities. Declines in amphibian populations often signal deteriorating environmental conditions.

13.3.1.6 Insects

Insects are abundant and diverse, making them useful biological indicators. They respond quickly to changes in their environment and can indicate pollution levels through population shifts and behavioral changes. Certain insect species are more sensitive to pollutants and can provide valuable information about ecosystem health. However, taxonomic challenges and variability in response among species can complicate their use as indicators.

13.3.1.7 Zooplankton

Zooplankton are microscopic aquatic organisms that play a key role in aquatic ecosystems. They help assess water quality and contamination levels. Their abundance and diversity are influenced by factors such as pollution, temperature, and nutrient levels. Zooplankton are crucial for understanding aquatic health and the impact of pollutants on marine ecosystems. Zooplankton are microscopic organisms found near the surface of aquatic environments, with their movement influenced by tides and currents. They feed on bacterial plankton, marine snow, and phytoplankton. As key biological indicators, zooplankton help assess pollution levels in aquatic environments. According to Ramachandra et al. (2006), *Trichotria tetrat, Alona guttata, Moscyclopesedex*, *Cyclopes* and *Aheyella* are found in aquatic environments that are high in PTEs and phosphorus, making them potential candidates for use as pollution indicators (Ramachandra et al. 2006).

They, along with shrimp, are crucial food sources for many other marine species in freshwater habitats. Factors such as the expansion of freshwater bodies, eutrophication, and aquatic efficiency significantly impact zooplankton populations. Weather variations also play a role. Research indicates that zooplankton, when combined with other biological factors like food availability, can effectively serve as indicators of environmental health.

13.3.1.8 Animal Toxins

Potential ecological pollution may be indicated by changes in animal populations and weather patterns. In animal physiology, differences in population-level morphology and behavior brought on by sub-lethal impacts of stress might act as early warning systems for potential ecosystem responses. Pollution consequences can be evaluated by keeping an eye on the amount of pollutants building up in animal tissues and the frequency of abnormalities. A range of biological indicators are suggested for soil pollution testing; however, in order to reliably determine contamination levels, these indicators must be broadly calibrated. By applying pertinent biological parameters, pollution can be evaluated qualitatively.

13.3.1.9 Microbial Indicators

Microorganisms, including bacteria and fungi, are vital for detecting pollutants. Certain bacteria, such as *Escherichia coli* and *Enterococci*, are commonly used to assess water quality and the presence of fecal contamination. Microbial communities can also indicate broader ecological changes and the presence of specific pollutants. Micro-organisms are widely used in marine and coastal habitats to monitor ecosystem pollution due to their rapid growth and sensitivity to even low pollutant levels, making them effective indicators of environmental change. Their abundance and ease of detection across diverse ecosystems make them valuable for tracking pollutants. Microbial indicators are selected based on six well-defined criteria and are particularly useful in aquatic ecosystems, where microbial toxins can be easily monitored. While microbial communities are relatively easy to track, changes in their regulation primarily reflect toxin-induced alterations. The ability of microbial consortia to adjust their functioning, biomass, and composition in response to pollutants is crucial for assessing ecosystem quality, with bioluminescent bacteria being commonly used as microbial markers for detecting toxins (Chowdhury et al. 2023; Nishat et al. 2022).

13.3.1.10 Bacterial Indicators

Bacterial indicators are specific types of bacteria, like *Escherichia coli* and *Enterococci*, used to detect and assess pollution levels in ecosystems. Their presence in certain quantities signals exposure to pollutants, making them valuable for monitoring environmental health. These bacteria are cultured on selective media, and their colonies are counted to determine pollution levels. Fecal coliforms are particularly significant in testing water safety, indicating recent fecal contamination. Advances in molecular biology, such as genetic fingerprinting and PCR, enhance the detection and identification of these bacterial indicators, making them effective tools for environmental monitoring.

13.3.1.11 Fungal Indicators

Fungal indicators, such as *Trichoderma sp., Aspergillus niger, and Candida albicans*, are crucial for detecting contaminants in both terrestrial and aquatic ecosystems due to their varied resistance to environmental changes. These fungi help monitor ecosystem health by assessing pollutant levels and ecological disturbances. For instance, moss species like Hylocomium splendens have been used in remote areas like Alaska to track pollutants in the environment, revealing higher contaminant levels near roads and decreasing with distance.

13.3.1.12 Algal Indicators

Algae, such as *Euglena* sp., *Chlamydomonas* sp., and *Scenedesmus* sp., are effective indicators of pollution in both aquatic and terrestrial ecosystems. In polluted aquatic environments, algal diversity decreases, often showing a few dominant species. Terrestrial algae are less studied but could be significant, especially in their resting stages, as they respond to changes in nutrients and pH caused by pollution. Blue-green algae can monitor pH shifts, while marine ecosystem degradation is linked to increased algal diversity. Algae are also used to track potentially toxic elements (PTEs), though routine use of these indicators is still evolving. Microalgae like *Euglena gracilis* are particularly sensitive to pollutants and useful in eco-toxicological assessments due to their rapid stress response and changes in orientation.

13.3.2 Biomarkers for Pollutant Detection

Biomarkers are essential tools in biomonitoring, offering valuable insights into the health of aquatic ecosystems and the impacts of emerging pollutants. Their application can significantly enhance environmental assessments and inform conservation efforts (Dalzochio et al. 2016). For emerging pollutants in wastewater, several biomonitoring methodologies and techniques are employed:

13.3.2.1 Molecular Biomarkers

Changes at the molecular level, such as gene expression or protein production, can be used to detect exposure to emerging pollutants. For example, upregulation of stress-related genes in organisms exposed to contaminated water can be an indicator of pollutant presence (Leprêtre et al. 2022).

13.3.2.2 Biochemical Biomarkers

These include measurements of enzyme activities, hormone levels, or other biochemical parameters in organisms exposed to pollutants. For example, measuring the levels of vitellogenin in fish can indicate exposure to endocrine disruptors.

13.3.3 Bioassays

Bioassays play an essential role in environmental monitoring and pollution management. By utilizing toxicity testing and enzyme inhibition assays, researchers and regulatory bodies can better understand the impacts of pollutants on aquatic ecosystems, leading to more informed decisions regarding environmental protection and public health (Hassan et al. 2016). The continued development and application of these methods are vital for safeguarding our natural resources and ensuring a sustainable future.

Commonly used aquatic organisms include *Fathead minnows* and *Rainbow trout* for fish, while *Daphnia magna* and *Ceriodaphnia dubia* represent invertebrates. Green algae like *Scenedesmus subspicatus* are employed to gauge water quality impacts (Mitchell et al. 2002). Terrestrial tests often involve lettuce and radish seeds to assess soil toxicity. Additionally, microorganisms such as bacteria, yeasts, and fungi are used for their rapid response to contaminants. These species help provide a detailed understanding of environmental toxicity and its ecological effects.

13.3.3.1 Enzyme Inhibition Assays

Enzyme inhibition assays play a crucial role in assessing the effectiveness of enzyme-mediated processes for the removal of emerging contaminants from wastewater. Emerging contaminants, such as pharmaceuticals and personal care products, pose significant challenges to conventional wastewater treatment facilities, which often fail to completely eliminate these pollutants. Enzymatic treatment, particularly using immobilized enzymes, has emerged as a promising solution due to its potential for high removal efficiencies and recyclability.

Enzymes, especially oxidoreductases such as laccases and peroxidases, are gaining attention for their effectiveness in breaking down organic pollutants (Sá et al. 2022). Immobilizing these enzymes on various supports enhances their stability and reusability, which is crucial for efficient and economical wastewater treatment. This process not only boosts enzyme performance but also facilitates their recovery and reuse, making them ideal for large-scale applications.

For example, in Lac-mediated oxidation, small radicals from hydroxybenzotriazole (HBT) boost the breakdown of phenolic compounds like salicylic acid (Naghdi et al. 2018). Without these mediators, Lac alone is not very effective at breaking down substances, but when combined with mediators like (3-ethylbenzothiazoline-6-sulfonic acid) diammonium salt (ABTS), it can quickly and completely break down antibiotics like tetracycline and oxytetracycline. Adding ABTS can also remove up to 95% of carbamazepine, though using too much enzyme can be counterproductive. Natural mediators like salicylic acid and vanillin are often more effective than synthetic ones. However, mediators might get used up during the reaction rather than just helping out. In the Lac-mediator system for breaking down antibiotics, mediators might create reactive radicals that interact with the pollutants, suggesting we might need a new model to understand how they work.

According to Hultberg et al. (2020), laccase enzyme derived from a mushroom substrate, consisting of sawdust and wheat bran and colonized by *Pleurotus ostreatus*, exhibit substantial efficacy in removing contaminants. Specifically, these enzymes achieve removal rates of 90% for diclofenac (DCF), 43% for bicalutamide, 73% for lamotrigine, and 49% for metformin, outperforming the control, which involves an uncolonized mushroom substrate.

Ashe et al. (2016) found that Lac with HBT achieved the highest Naproxen (NPX) removal rate, reaching 80% at a 1 mM concentration. In comparison, violuric acid (VLA), another N–OH type mediator, removed approximately 60% of NPX. Both HBT and ABTS remained effective at a lower concentration of 0.5 mM.

13.3.3.2 Significance of Biomonitoring

Biomonitoring is a crucial tool for assessing the presence and impact of emerging pollutants (EPs) in wastewater and aquatic ecosystems. EPs, such as pharmaceuticals, personal care products, endocrine disruptors, and microplastics, are increasingly being detected in water bodies, posing potential risks to aquatic life and human health. However, chemical analysis alone has limitations:

- It is expensive and requires specialized equipment that may not be readily available in developing countries (Siziba and Tapiwa Sero 2023).
- Chemical methods often fail to detect EPs at low concentrations due to poor sensitivity of available equipment.
- Analyzing water samples only provides a snapshot of EP levels at a specific time and location (Miller et al. 2019).

In contrast, biomonitoring using living organisms offers several advantages:

- It provides an integrated assessment of the overall health and toxicity effects of EPs on aquatic ecosystems.
- Biomarkers like oxidative stress proteins and gonadal histopathology can be used to detect the effects of EPs more cheaply and easily than chemical analysis.
- Biomonitoring accounts for bioaccumulation and biomagnification of EPs through the food chain.
- It can help establish cause–effect relationships between EP exposure and biological responses in organisms.

13.4 Current Challenges and Future Directions

Despite the benefits, biomonitoring of EPs in wastewater and aquatic environments is still limited, especially in developing countries (Siziba and Tapiwa Sero 2023; Vasilachi et al. 2021). Key challenges include

- Lack of awareness about EPs and their potential impacts.
- Limited funding for research and monitoring programs on EPs.
- Insufficient inclusion of EPs in routine water quality and ecosystem monitoring.
- To address these gaps, experts recommend
- Increasing awareness about EPs among stakeholders and decision-makers.
- Assessing the effectiveness of wastewater treatment plants in removing EPs.
- Incorporating EPs into regular monitoring programs by municipalities and water authorities.
- Funding more research to understand the occurrence, fate, and effects of EPs in aquatic environments.
- Developing and validating biomarkers for cost-effective biomonitoring of EPs.

13.5 Conclusion

Emerging pollutants in wastewater, such as microplastics, pharmaceuticals, personal care products, endocrine-disrupting compounds, and nanomaterials, present a significant and escalating environmental challenge due to their persistence and potential impacts on human health and ecosystems. The diverse origins and complex behaviors of these pollutants complicate their effective management and removal, highlighting the need for advanced treatment technologies and comprehensive monitoring strategies. Microplastics, with their ability to absorb and transport hazardous substances, and pharmaceuticals, with risks like antibiotic resistance, underscore the difficulties in treating these contaminants. Similarly, personal care products and endocrine disruptors add layers of complexity due to their widespread use and hormonal effects. Nanomaterials introduce additional uncertainties with their small size and potential for long-term ecological harm. Biomonitoring, utilizing bioindicators and advanced techniques, is crucial for assessing the health impacts and ecological consequences of these pollutants. Despite its advantages, biomonitoring faces challenges, particularly in resource-limited settings. Addressing these challenges requires increased awareness, funding, and integration of emerging pollutants into regular monitoring, alongside continued research and development of both treatment technologies and biomonitoring methods to safeguard environmental and public health.

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Chapter 14
Unveiling the Limitations of Existing Analytical Tools in the Detection and Removal of Emerging Pollutants in Wastewater Treatment

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Abstract The management of emerging pollutants (EPs) in wastewater treatment is a challenging task that demands a nuanced understanding of pollutant characteristics, analytical methodologies, and environmental factors. This chapter delves into the limitations encountered in the detection and removal of EPs with a special emphasis on types and analysis of pollutants, instrumentation constraints, and diverse environmental variables. Firstly, it scrutinizes the limitations arising due to the diversity of pollutants, encompassing their varied chemical compositions and behavioral characteristics. Additionally, it examines the inadequacies of existing analytical techniques in the effective detection and quantification. Apart from these challenges, the influence of environmental factors—including temperature, pH, total dissolved solids (TDS), biological oxygen demand (BOD), density, viscosity, atomic weight, and atomic mass—on pollutant detection and removal processes, highlighting their intricate interplay with treatment efficacy has been incorporated. Drawing insights from these limitations, the subsequent section delineates recommendations and suggestions to overcome these hurdles. The current proposal encompasses the innovative analytical methodologies, the use of advanced instrumentation, and improved understanding of environmental dynamics. Finally, the chapter concludes by emphasizing the imperative of continuous research and technological innovation in surmounting these limitations and advancing sustainable solutions for pollutant management in wastewater treatment systems.

Keywords EPs · Wastewater treatment · Pollutant analysis · Analytical methodologies · Environmental factors · Instrumentation constraints · Sustainable solutions

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S. Dey and M. P. Shah (eds.), *Biotechnological Removal of Emerging Pollutants from Wastewater Systems*, Advances in Wastewater Research,
https://doi.org/10.1007/978-981-96-3945-8_14

14.1 Introduction

Emerging pollutants (EPs) are defined as follows: "synthetic or naturally occurring chemicals are not commonly monitored in the environment that possess to infiltrate the water cycle and cause adverse effect on human health and ecosystem" (Sangamnere et al. 2023). Contaminants of emerging concern (CECs) are a group of compounds act as EPs that have been found in nano-materials, endocrine-disrupting chemicals (EDCs), flame retardants, and micro-plastics substances, pharmaceuticals, and personal care products (PPCPs) (Bracamontes-Ruelas et al. 2022; Inyinbor et al. 2021; Sangamnere et al. 2023). The detection and removal of EPs in wastewater have become a challenging task due to the limitations of traditional analytical tools (Bracamontes-Ruelas et al. 2022; Sangamnere et al. 2023). EPs have acute and long-term effects on the ecosystem and human health like endocrine disruption, neurological disorders, immunotoxicity, and cancer. The lack of knowledge and regulations makes it really hard to monitor EPs in the environment and wastewater effectively.

14.1.1 Types of Emerging Pollutants

EPs have come from different industrial, urban, and agricultural resources, and can harm the environment and human health. In industrial waste, the main types of EPs are synthetic chemicals such as flame retardants, polymers, and surfactants, known for their chemical stability and resistance to degradation. Dyes and solvents used for painting and textile production can interfere with wastewater treatment and harm aquatic life. Industrial areas generate a unique set of EPs through PPCPs, household chemicals, and urban runoff pollutants, heavy metals, hydrocarbons, and pesticides like insecticides, herbicides, and fungicides, and fertilizers (Abdulrazaq et al. 2021; Krishnakumar et al. 2022).

14.1.2 Sources of Emerging Pollutants

EPs come from a variety of sources, each contributing different contaminants to water system (Fig. 14.1) The sources of EPs are predominantly linked to industrial, urban, and agricultural activities. Industrial sources include manufacturing discharges, unintentional spills, and improper disposal of industrial wastes, which introduce artificial chemicals, solvents, dyes, and by-products into wastewater systems (Deblonde et al. 2011; Zhou et al. 2019). Urban sources are expanding with the growth of cities, contributing drugs, cosmetics, chemicals, and micro-plastics from impermeable sources to wastewater systems (Zhou et al. 2019). These contaminants often enter wastewater through inappropriate disposal practices, anthropogenic activities, and runoff from urban areas such as parking lots and roadways. Agricultural sources primarily involve the application, and leaching of pesticides, fertilizers, and veterinary medications. These practices introduce a variety of persistent and bioactive compounds into water bodies through bioaccumulation causing toxicity to both ecosystem disruption and impacting both ecosystem and human health (Arman et al. 2021; Deblonde et al. 2011; Zhou et al. 2019).

- **Domestic Sources**: Domestic sources are one of the primary contributors to EPs in wastewater. EPs come from everyday household activities and products used by individuals in their homes. The main categories of EPs from domestic sources are pharmaceuticals, personal care products, household chemicals, and micro-plastics (https://www.researchgate.net/figure/Examples-of-common-emerging-contaminants-and-their-properties_tbl2_338314505).
- **Industrial Sources**: Industrial activities contribute significantly to the presence of EPs in wastewater. Industries release a variety of chemicals during manufacturing processes, many of which are not fully regulated or monitored. Key industrial sources include manufacturing chemicals in the form of organic dyes, inorganic salts, catalyst, additives, by-products, and heavy metals (Bracamontes-Ruelas et al. 2022; Iqbal et al. 2021).
- **Agricultural Sources**: Agricultural activities are a significant source of EPs in wastewater, primarily due to the use of chemicals such as pesticides, herbicides, and fertilizers. Additionally, animal waste from livestock farming contributes to the contamination of water bodies (Huang et al. 2022; Pépin et al. 2014).

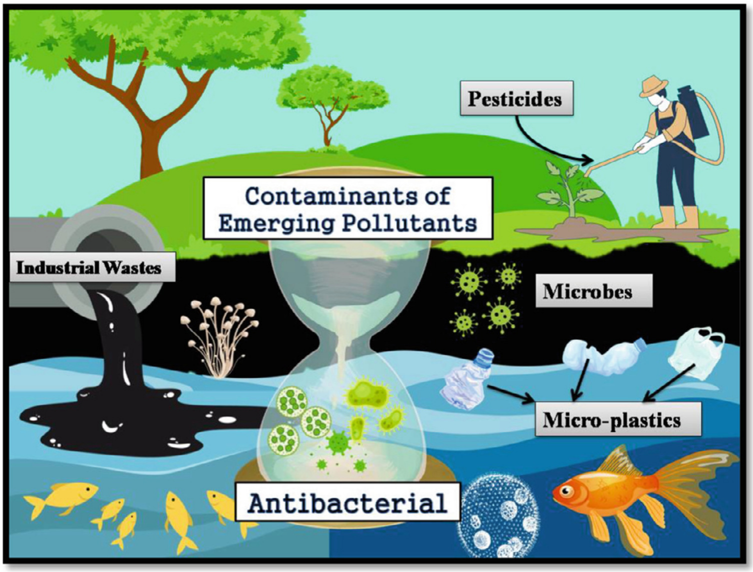

Fig. 14.1 Contaminants of emerging pollutants

- **Healthcare Facilities**: Healthcare facilities, including hospitals, clinics, and veterinary practices, are significant sources of expired and unused drug, chemical and bio chemical waste. This waste can be classified into numerous categories, as infectious waste includes blood, bodily fluids, and infectious agents and pathological waste like organs, human tissues, fluids, contaminated animal carcasses and bio waste like syringes, needles, and disposable scalpels, solvents, reagents, disinfectants, sterilants, heavy metals, etc. Pharmaceutical waste covers expired, unused, and contaminated drugs and vaccines. Cytotoxic wastes are the drugs used in cancer treatment. Radioactive waste comprises materials contaminated by radionuclides used in diagnostic and therapeutic procedures (Siziba and Sero 2023; WHO/UNICEF 2015).
- **Urban Runoff**: Urban runoff is another significant source of EPs in wastewater. It's derived from rain and outdoor water usage, includes stormwater and snowmelt that drains from roofs, sidewalks, roads, driveways, car parks, and other surfaces without soaking into the ground (Siziba and Sero 2023; WHO/UNICEF 2015). It is a carrier of EPs in urban environments and surface water bodies. EPs include heavy metals, solids, toxic chemicals, organic micro-pollutants, nutrients (nitrogen and phosphorus), biodegradable organic matter (such as polycyclic aromatic hydrocarbons and polychlorinated biphenyls (PAHs and PCBs)), pathogenic microorganisms (like E. coli), and micro-plastics (WHO/UNICEF 2015).

Understanding these sources and the pathways through which pollutants enter wastewater systems is crucial for developing effective strategies to manage and mitigate the impact of EPs. By addressing the sources and implementing better waste management practices, we can protect human health and preserve the environment for future generations (Bracamontes-Ruelas et al. 2022; Siziba and Sero 2023).

14.2 Detection Methods of Emerging Pollutants in Wastewater

The detection methods of EPs can be performed by using various analytical techniques like chromatography and spectroscopy. The screening of EPs helps to identify potential hazards linked with substances and their combinations. It is crucial to detect and remove the EPs efficiently for safety of the environment and public health and also help to create risk-based policies and regulations (Krishnakumar et al. 2022). Macro- and micro-level investigation of EPs in wastewater is essential for understanding the types and concentration of EPs. That helps to enable effective monitoring, regulation, and treatment strategies.

At the macro level, pollutants such as heavy metals and synthetic chemicals are often examined to assess their widespread distribution and concentration in large water bodies and soil systems (Inyinbor et al. 2021; Krishnakumar et al. 2022). Conversely, the micro-level analysis is frequently performed on PPCPs, and pesticides to detect trace amounts and study their specific interactions within smaller ecosystems and biological organisms (Inyinbor et al. 2021). These analyses help in understanding the pollutants' behavior, bioaccumulation, and potential effects (https://www.researchgate.net/figure/Examples-of-common-emerging-contaminants-and-their-properties_tbl2_338314505; Deblonde et al. 2011; Inyinbor et al. 2021; Krishnakumar et al. 2022). Mass spectrometry (MS), including high-resolution mass spectrometry (HRMS) tandem mass spectrometry (MS/MS), gas chromatography (GC) and liquid chromatography (LC) coupled with MS (GC-MS and LC-MS) are commonly used for its sensitivity and precision in detecting and quantifying trace EPs. Inductively coupled plasma mass spectrometry (ICP-MS) is used specifically for detecting and analyzing heavy metals. These sophisticated instruments offer the necessary analytical specificities to detect, quantify, monitor, and regulate the presence and effects of EPs in various complex matrices. These techniques include the following.

14.2.1 Chromatography

HPLC is an analytical method for identifying, quantifying, and separating different chemicals from a mixture. It's a useful tool for EPs identification. A liquid solvent containing EPs in the sample mixture is forced through a column that is packed with a solid adsorbent material by means of a high-pressure pump (Bracamontes-Ruelas et al. 2022). Different compounds react differently with the adsorbent material (stationary phase) resulting in subsequent separation of the components of EPs. Numerous detectors are utilized to accomplish detection and quantification, including UV-Vis, fluorescence, and mass spectrometric detectors, enabling precise analysis of complex samples (https://www.researchgate.net/figure/Examples-of-common-emerging-contaminants-and-their-properties_tbl2_338314505).

GC is specifically used for the examination and separation of volatile and semi-volatile substances. It works efficiently to separate contaminants present in industrial chemicals, pesticides, and medications (https://www.researchgate.net/figure/Examples-of-common-emerging-contaminants-and-their-properties_tbl2_338314505; Deblonde et al. 2011). In GC, an inert carrier gas, such as nitrogen or helium, vaporizes the sample and carries it through a column. A stationary phase in the column usually a long, coiled tube separates the compounds according to their interactions and boiling temperatures with the stationary substance. Detectors like Flame Ionization Detectors (FID), Thermal Conductivity Detectors (TCD), and Mass Spectrometric Detectors (MS) are used for detection (https://www.researchgate.net/figure/Examples-of-common-emerging-contaminants-and-their-properties_tbl2_338314505; Bracamontes-Ruelas et al. 2022; Deblonde et al. 2011). The sensitivity of the detection is increased by using mass spectrometry (GC-MS) as a detector. By breaking down each molecule into individual ions and determining their mass-to-charge ratios, the mass spectra of these ions enable accurate identification (Deblonde et al. 2011; Krishnakumar et al. 2022). This combination is especially useful for environmental study; it can identify specific compounds present in complicated mixes and detect pollutants at trace levels. Hyphenated techniques such as HPLC-GC, LC, MS, and ICP-MS can be proven useful in the precise detection of EPs (https://www.researchgate.net/figure/Examples-of-common-emerging-contaminants-and-their-properties_tbl2_338314505).

14.2.2 Mass Spectrometry (MS)

Mass spectrometry (MS) is a potent analytical method for determining the composition of a sample through mass to charge ratio of a sample ion. LC-MS and Tandem Mass Spectrometry (MS/MS) are two sophisticated modifications of MS with improved application particularly in the analysis of EPs (https://www.researchgate.net/figure/Examples-of-common-emerging-contaminants-and-their-properties_tbl2_338314505; Inyinbor et al. 2021; Krishnakumar et al. 2022).

The detection strength of MS and the separation capabilities of LC are proven helpful for assessing complicated mixtures of newly discovered EPs, like hormones, personal care products (PPCPs), and other organic contaminants (https://www.researchgate.net/figure/Examples-of-common-emerging-contaminants-and-their-properties_tbl2_338314505; Deblonde et al. 2011). MS/MS combines several phases of mass analysis that expands on the capabilities of conventional mass spectrometry. This method allows several rounds of fragmentation and analysis by sequentially using two or more MS (Inyinbor et al. 2021; Krishnakumar et al. 2022). Ions from the sample are produced and separated in the first stage according to their mass-to-charge ratios. Following their fragmentation in a collision cell, the chosen ions are examined in a second mass spectrometer. By repeating this procedure for subsequent fragmentation and analysis phases, the specificity and sensitivity of the detection can be greatly increased (https://www.researchgate.net/figure/Examples-of-common-emerging-contaminants-and-their-properties_tbl2_338314505; Deblonde et al. 2011). MS/MS is very useful for detecting EPs at the trace level because it can precisely identify and measure the target substances in intricate matrices. Because MS/MS can do many rounds of mass analysis, it is a vital technique for validating the presence of particular EPs in samples providing comprehensive structural elucidation (Krishnakumar et al. 2022).

14.2.3 Spectroscopy

Spectroscopy is an analytical technique used to examine and determine the chemical and molecular structure of materials by analyzing the interaction of light with matter (https://www.researchgate.net/figure/Examples-of-common-emerging-contaminants-and-their-properties_tbl2_338314505). Two spectroscopic techniques

(Ultraviolet–Visible Spectroscopy (UV-Vis) and Fourier Transform Infrared Spectroscopy (FTIR)) are frequently employed in the assessment of EPs (Krishnakumar et al. 2022).

- **Ultraviolet-Visible Spectroscopy (UV-Vis)**: The analytical technique known as UV-Vis measures the amount of light absorbed by the sample in the presence of visible and UV radiation of the electromagnetic spectrum. Specific wavelengths are absorbed by the EPs when a sample is placed to UV or visible light, which causes change in electronic energy inside the molecules. That results in absorption spectrum with important details of the quantity and concentration of these EPs (https://www.researchgate.net/figure/Examples-of-common-emerging-contaminants-and-their-properties_tbl2_338314505; Krishnakumar et al. 2022).
- **Fourier Transform Infrared Spectroscopy (FTIR)** measures the amount of infrared radiation absorbed by the samples and provides precise details about the molecular vibrations and functional groups that are present in the samples. Certain wavelengths of infrared light are absorbed by the sample, which causes the molecules to vibrate at distinctive frequencies. The resulting infrared spectrum can be used for qualitative and quantitative detection. FTIR is useful for recognizing the functional groups, thus provides the molecular fingerprint of the compound (https://www.researchgate.net/figure/Examples-of-common-emerging-contaminants-and-their-properties_tbl2_338314505; Krishnakumar et al. 2022).

14.2.4 Electrochemical Methods

To detect and measure EPs, electrochemical methods such as potentiometry and voltammetry measure changes in the electric potential, current, and solutions. These methods are very useful for locating heavy metals and specific chemical compounds. Voltammetry allows one to determine and measure the amount of electroactive species in a solution by monitoring the current flowing through an electrochemical cell in response to an applied voltage. To ascertain the concentration of certain ions in the sample, potentiometry, on the other hand, measures the voltage differential between two electrodes in an electrochemical cell. These electrochemical techniques are sensitive, selective, and adaptable in situ, making them valuable for real-time EP monitoring in a range of environmental matrices (Shetti et al. 2020).

14.2.5 Biosensors and Bioassays

Biosensors and bioassays are innovative tools that attached biological components to detect EPs, providing rapid and sensitive methods for monitoring environmental EPs (Wang and Liu 2019).

- **Enzyme-Linked Immunosorbent Assays (ELISA)**

ELISA is a commonly used bioassay that employs antibodies to specifically identify and quantify antigens like EPs. This technique is effective for the quantification of hormones and pharmaceuticals in environmental samples. The target pollutant is bound to a micro plate that is coated with a primary antibody specific to the antigen (pollutant). This primary antibody captures the pollutant from the sample. Environmental samples suspected of containing the pollutant are added to the plate. If the target pollutant is present, it will bind to the primary antibody (Wang and Liu 2019). After washing away excess unbound substances, an enzyme-linked secondary antibody is introduced. This secondary antibody binds to the target pollutant, forming a complex with the primary antibody. A substrate specific to the enzyme linked to the secondary antibody is then added. The enzyme catalyzes a reaction that produces a measurable signal, often a color change, and directly correlates with the concentration of the pollutant. ELISA is valued for its sensitivity, specificity, and ability to process multiple samples simultaneously, making it an essential tool in environmental monitoring and analysis (Kahn and Heller 2020).

- **Microbial Biosensors**

Microbial biosensors help to detect living microorganisms as pollutants based on their metabolic responses. These biosensors can monitor water quality in real time, providing immediate feedback on the presence of specific microbial contaminants. This approach is beneficial for environmental monitoring and their potential impact on microbial ecosystems (Ghosh and Dutta 2021).

14.2.6 Nanotechnology-Based Approaches

Nanotechnology significantly enhances detection methods by utilizing nanomaterials that improve the sensitivity and selectivity of sensors (Lim and Kim 2021; Zhang and Wang 2022).

- **Nano-material-Enabled Sensors**: These sensors utilize nano-materials to amplify the electrochemical or optical signals generated by EPs. The unique properties of nano-materials, such as increased surface area and reactivity, help these sensors to detect EPs at extremely low concentrations (Zhang and Wang 2022).
- **Nano-Enabled Spectroscopy Techniques**: Nano-enabled spectroscopy techniques, such as surface-enhanced Raman spectroscopy (SERS), utilize nanostructures to amplify the signals of pollutants (Lim and Kim 2021; Zhang and Wang 2022). This amplification allows for the detection of contaminants at very low concentrations, making it particularly effective for identifying organic pollutants in complex mixtures. SERS can provide detailed molecular structural information, aiding in the characterization of pollutants and their potential sources (Zhang and Wang 2022).

14.3 Limitations and Challenges of Current Analytical Methods

Emerging pollutant analysis faces several significant challenges related to sensitivity and selectivity, sample preparation, time and cost, and the detection of a wide range of pollutants (Lorenzo et al. 2018).

- **Sensitivity and Selectivity**: Many newly discovered EPs are found in extremely low concentrations, frequently in the range of nanograms per liter (ng/L). It's possible that conventional techniques don't have the sensitivity required to precisely identify these small amounts (https://www.researchgate.net/figure/Examples-of-common-emerging-contaminants-and-their-properties_tbl2_338314505). The existence of complex matrices in wastewater can impair the selectivity of these approaches, resulting in interference and false positives or negatives, and interference by foreign ion effect (https://www.researchgate.net/figure/Examples-of-common-emerging-contaminants-and-their-properties_tbl2_338314505; Lim and Kim 2021).
- **Sample Preparation**: The pretreatment process of the sample for traditional analytical methods can take a lot of time and effort, and sometimes requires hazardous chemicals to process (Sangamnere et al. 2023). It frequently involves multi-step procedures, including extraction, concentration, and filtering, which can lead to mistakes and unpredictability. Due to the intricate nature of wastewater matrices, a thorough sample clean-up is necessary to eliminate any interfering materials, which might make the analytical procedure even more difficult (Lorenzo et al. 2018; Sangamnere et al. 2023).
- **Time and Cost**: Analyzing new EPs with conventional techniques is costly and time-consuming. Expensive consumables, advanced equipment, and highly skilled staff are all related to high expenses (https://www.researchgate.net/figure/Examples-of-common-emerging-contaminants-and-their-properties_tbl2_338314505). The efficacy of monitoring programs might be limited by lengthy reversal times for sample analysis, which can delay the detection process (https://www.researchgate.net/figure/Examples-of-common-emerging-contaminants-and-their-properties_tbl2_338314505; Sangamnere et al. 2023).
- **Identification of a Broad Spectrum of Pollutants**: EPs comprise a wide range of chemical classes, each of which needs certain analytical conditions in order to detect them efficiently. There isn't a single technique that can reliably identify each and every kind of EP that can be detected by utilizing a solo analytical technique. This complex nature of EPs leads to employing a combination of analytical techniques in order to cover the entire range during the monitoring process (Lorenzo et al. 2018).
- **Trace-Level Concentration of EPs**: Conventional analytical techniques sometimes don't have the sensitivity needed to detect these trace level concentration of EPs in wastewater. This situation leads to hamper the analysis by giving false positive or false negative results, and the combination of techniques also leads to relative and absolute errors. The creation and implementation of these cutting-edge

detection technologies are essential to guaranteeing thorough and economical monitoring of the environment and protection (Lim and Kim 2021).

- **Limitations in Biological Treatment Process**: Biological treatment methods such as activated sludge and bio-filtration face significant limitations in the effective removal of EPs. One of the main challenges is the resistance to biodegradation of EPs, including PPCPs. This stability makes it difficult for microorganisms to degrade, which limits the overall efficiency of biological processes (Lorenzo et al. 2018). The biological treatment systems require precise operating conditions to promote optimal microbial growth, including careful ventilation control, nutrient balance, and temperature. This level of supervision can be difficult and requires qualified personnel. These systems are sensitive to environmental changes; fluctuations in pH, temperature, and the presence of toxic substances can disrupt microbial communities and reduce treatment effectiveness (Lim and Kim 2021). The slow response time associated with biological treatment is also a challenge, as microorganisms need time to adapt to changes in water composition, making it difficult to respond quickly to pollution events. Finally, these methods often have limited effectiveness in removing persistent organic compounds and heavy metals, resulting in partially treated water that can still present environmental and health risks (Lorenzo et al. 2018).
- **Limitations in Chemical Treatment Process**: Chemical treatment methods such as coagulation and chlorination also face significant limitations in combating EPs. Conventional chemical treatments often lack the specificity required to degrade the various emerging pollutants effectively (Al-Abri et al. 2019). This restriction can lead to many pollutants not being treated, allowing dangerous substances to enter and accumulate into the environment and human body. The end product of a process sometimes generates new class of EPs. Chemical processing can produce hazardous by-products, such as chlorinated organic compounds, which can pose a greater threat than the original pollutants (Lorenzo et al. 2018). The limited effectiveness of traditional chemical methods further aggravates the problem, as these methods tend to focus on specific EPs, leaving them untreated. Many new pollutants can resist complete degradation during chemical treatment, resulting in the presence of partially degraded, potentially harmful substances in treated wastewater that may have adverse effects on ecosystems and human health (Al-Abri et al. 2019).
- **Physical Treatment Limitations**: Physical treatment methods, such as sedimentation and filtration, have their own set of limitations in the removal of EPs (Ahmed et al. 2021). One significant challenge is their ineffectiveness against small molecules as these method processes are designed to remove larger particles and are often inadequate for small, dissolved contaminants that can easily pass through treatment systems. Many emerging pollutants are also characterized by high water solubility, which complicates their removal through physical processes that rely on gravity or size exclusion. Furthermore, physical treatment methods generally lack specificity, meaning they do not target specific chemical structures. This can lead to inefficient removal of contaminants that do not exhibit distinguishable physical characteristics (Lorenzo et al. 2018). The inability of physical

treatments to capture small, dissolved pollutants can result in their environmental persistence in treated effluent, posing ongoing risks to aquatic ecosystems and humans. As such, while physical treatment methods play a role in wastewater management, they are often insufficient on their own for effectively addressing the challenges posed by EPs (Ahmed et al. 2021).

After the detection of EPs with the above analytical techniques, the effective removal strategies of these EPs can be designed easily. The removal strategy encompasses a variety of physical, chemical, and biological processes designed to address the limitations of conventional treatment methods (Tran et al. 2014). These strategies aim to degrade, remove, or neutralize the EPs present in complex media, ensuring that the treated water meets safety standards and possesses minimal risk to human health and ecosystem (Kümmerer 2009). The various innovative and effective techniques used for the removal of EPs and their action mechanism along with pros and cons are discussed below.

14.4 Advanced Removal Strategies and Their Action Mechanism

The removal process involves developing more effective wastewater treatment systems, enacting laws to restrict the release of EPs, and launching public awareness efforts (Bracamontes-Ruelas et al. 2022; Deblonde et al. 2011). For the removal of this contaminant, there is the requirement of new treatment technologies such as membrane filtration, advanced oxidation processes (AOPs), and biological treatments. Precise identification of newly developing contaminants aids in determining the shortcomings of current treatment procedures and directs the creation and application of cutting-edge technology.

The inadequacy of current analytical instruments fails to detect and eliminate newly developing EPs from wastewater. These developments are essential for maintaining public health, safeguarding water resources, and advancing environmental sustainability (Siziba and Sero 2023). Many cutting-edge technologies have been created to overcome the shortcomings of conventional therapeutic approaches. These technologies, which include revolutionary material-based adsorption techniques, membrane filtering technologies, and sophisticated oxidation processes, provide improved capacities for eliminating developing contaminants (Kümmerer 2009; Tran et al. 2014).

14.4.1 Advanced Oxidation Processes (AOPs)

Advanced oxidation processes produce extremely reactive oxidative species (ROPs), like hydroxyl radicals (˙OH), that can oxidize and degrade a variety of organic pollutants in a non-selective manner. Photo catalysis is the process that generates reactive radicals which helps in breaking down the EPs by using light-activated catalysts, such as titanium dioxide (TiO_2). Pesticides, medications, and substances that disrupt hormones are among the targeted molecules (Sanches et al. 2012). Ozonation is a process used to remove pharmaceuticals, personal hygiene items, and certain industrial chemicals by utilizing ozone for effective oxidization and neutralized ozone. Fenton-like and Fenton reactions are used to create hydroxyl radicals (utilizing iron peroxide, iron salts, and hydrogen peroxide (H_2O_2)). Persistent organic pollutants (POPs) can be effectively degraded by these processes (Bolong et al. 2009).

14.4.2 Membrane Filtration Technologies

Membrane filtration technologies use selective barriers according to chemical affinity, size, or charge to separate contaminants from water (Michael et al. 2014; Snyder et al. 2007). Although they are less effective against dissolved emerging EPs, microfiltration (MF) and ultra filtration (UF) can remove bigger particles and bacteria. For the elimination of tiny organic compounds, multivalent ions, and certain medicines, Nanofiltration (NF) is used because of its smaller pore size and higher rejection rate. Reverse osmosis (RO) process removes a high degree of impurities through a semi-permeable membrane that rejects almost all dissolved substances. The EPs which can be removed are industrial chemicals, medicines, and endocrine disruptors.

14.4.3 Adsorption Methods Utilizing Innovative Materials

Adsorption is the process by which contaminants adhere to the surface of solid materials. Innovative adsorbents/resins/ion exchange materials have been designed to improve effectiveness. Due to its large surface area and strong adsorption capacity, activated carbon is widely employed and proven efficient against a variety of organic EPs, including industrial chemicals and PPCPs. Biochar is black carbon (plant residues, wood and manure), has high adsorption effectiveness for both organic and inorganic contaminants, and is a sustainable substitute for activated carbon. Because of their large surface area and distinctive structural features, carbon nanotubes (CNTs) have remarkable adsorption capabilities that enable them to target heavy metals, insecticides, and medicines. Metal-Organic Frameworks (MOFs) are extremely porous substances with adjustable qualities for specific contaminants.

Adsorbing gases, volatile organic compounds (VOCs), and other organic substances are an efficient use of MOFs (Arnold et al. 2013; Richardson and Ternes 2018; Zwiener and Frimmel 2000).

14.5 Advantages of Advanced Detection Technologies

Advanced technologies offer several advantages in the analysis of EPs (Table 14.1), addressing many limitations of traditional methods.

- **Sensitivity and Selectivity**: Selectivity and sensitivity have been significantly improved by HRMS-TOF and Orbitrap mass spectrometry because of their remarkable mass precision and resolution. This technique can accurately measure the chemical composition of EPs even at trace quantity and complex mixture (Bracamontes-Ruelas et al. 2022; Mahmood et al. 2022; Zhang and Wang 2022).
- **Specificity**: One is high specificity, wherein advanced mass spectrometry (such as an Orbitrap) allows for undeniable identification of compounds. This makes possible high-resolution studies that could distinguish similar compounds by inclusivity and eliminatory mass-to-charge ratios, increasing the probability of non-false/false positive results. This specificity is required when analyzing the complex ecosystem environment, where multiple compounds may be present.
- **Real-Time Monitoring**: Real-time monitoring of EPs has been successfully transformed with the help of sophisticated sensor technologies (biosensors, optical sensors) and electrochemical detectors. Continuous data analysis utilizing these sensors helps us to identify and address EPs. Furthermore, a combination of sensors with automated systems and remote sensing technologies expedites extensive aqueous body monitoring, hence diminishing the necessity for labor-intensive manual sampling and time-consuming laboratory examination (Ahmed et al. 2016; Hazarika and Ahmaruzzaman 2023).
- **Onsight detection**: Advances in nanotechnology have produced Lab-on-a-Chip (LOC) systems, which simplify intricate laboratory procedures onto a single nano-chip. For onsight detection and analysis of EPs, these portable devices are perfect since they can carry out several analytical processes in a small package, such as sample preparation, separation, and detection. Comparably, the advent of portable mass spectrometers makes it possible to conduct analysis on location and provides quick, accurate findings removing the chances of contamination sample degradation and vigorous analytical process (Ahmed et al. 2016; Pal et al. 2014).
- **Advanced Data Analysis**: The interpretation of complicated information produced by sophisticated analytical procedures is improved by the use of machine learning and artificial intelligence (AI) in data analysis. These instruments can enhance detection accuracy, spot trends, and forecast the behavior of EPs. Moreover, big data analytics integration makes it possible to handle and analyze huge amounts of data without any human error, and data representation is much easier

Table 14.1 Advantages and disadvantages of analytical techniques

S.N	Sources	Pollutants	Techniques	Advantages	Disadvantages	References
1	Hospitals	Pharmaceuticals	Membrane filtration	Efficient removal	High energy consumption	Mahmood (2022)
2	Industrial	Anti-bacterials	Adsorption	Selective removal	Costly	Abdelbasir and Shalan (2019)
3	Agricultural	Hormones	Coagulation-flocculation	Reduced effluent levels	Limited efficiency	Petrie et al. (2015)
4	Other sources	Synthetic dyes	Solvent extraction	Minimized aquatic impact	Technological limitations	Ghamari (2023)
		Flame retardants	Ion exchange	Improved water quality	Scale-up challenges	Zhang et al. (2019)
			Photodegradation	Environmentally friendly	Implementation costs	
			Catalytic oxidation	Effective degradation	Operational complexity	
			Electrochemical oxidation	Advanced treatment	Energy-intensive	
			Ozonation	Rapid pollutant removal	High capital investment	
			Precipitation	Versatile application	Residual sludge handling	

with graphical representation and statistical data analysis (Arman et al. 2021; Lapworth et al. 2012; Peterson et al. 2014).

- **Multidisciplinary Approaches**: Combining many analytical methods can yield a more thorough monitoring of EPs. For example, combining sophisticated spectrometry and sensor technologies with chromatography improves detection performance and provides a more comprehensive understanding of the dynamics of EPs. More collaborative research is required between various branches of science such as chemistry, biology environmental science, mechanical engineering, medicine and toxicology, for increase the efficacy of surveillance initiatives (Hernández et al. 2007; López-Ruiz et al. 2019).

Technological developments can greatly improve the identification and management of EPs in several critical areas, including enhanced sensitivity, real-time monitoring capabilities, downsizing, and improved data analysis. Adopting these innovative approaches is essential to safeguarding public health, preserving water resources, and advancing environmental sustainability.

14.6 Limitations of Advanced Detection Technologies

When compared to conventional analytical techniques, advanced detection technologies provide considerable gains in sensitivity, selectivity, and efficiency. Their efficacy in identifying newly developing EPs in wastewater may be impacted by some restrictions. These restrictions can be divided into groups according to the types of pollutants, analysis, tools used, and other factors like environmental, chemical, and physical (Table 14.1) (Daughton 2004; Gogate and Pandit 2004).

- **Pollutant-Wise Limitations**: The detection of specific classes of EPs may be difficult with advance detection methods because of their continuous changing chemical structure (Gogate and Pandit 2004).
- **Highly Polar Substances**: Polar substances present in several medications and insecticides can have poor retention values on chromatographic columns, which lowers the sensitivity and resolution of the chromatography. Non-volatile Organic Compounds: These substances might not be able to be analyzed using the gold standard of detection and analytical technique GC-MS, necessitating the use of alternate methods such as direct injection techniques or LC-MS.
- **Complex Mixture**: Degradation products, resultant by product, metabolites of poison and drugs catalysts, and ROS are just a few examples present which can make it difficult to identify and quantify the target compounds.
- **Analysis-Wise Limitations**: The effectiveness of advanced detection methods can be impacted by several analytical process-related interferences (Gogate and Pandit 2004), such as

Effects of the Matrix: Presence of different nature of elements in sample matrix targeted analytes produces inaccurate results. Ion suppression/ enhancement in MS, co-elution in chromatography, and background noise are the examples of matrix effects.

Analyte Stability: During sample pretreatment and analysis, some EPs may degrade or convert, hampering the integrity of analyte and produce false negative results.

Quantification Limits: The capacity of modern detection technologies to detect trace-level contaminants may be limited by their lower detection limits, which might vary based on the analytical technique, instrument sensitivity, and sample matrix complexity (Daughton 2004).

- **Instrument-Wise Limitations:** Various kinds of sophisticated detection instruments could have restrictions that have an impact on how well they work in wastewater analysis (Gogate and Pandit 2004). Examples of these restrictions include

Sensitivity of an Instrument: Although sophisticated instruments are highly sensitive for detecting low levels of EPs, the faulty sample pretreatment, sample preparation, leads to distorted picture structure.

Specificity of Instrument: Co-elution of interfering chemicals or spectrum overlap due to presence of closely correlated compound can affect the specificity of detection techniques, MS-based procedures, resulting in false positive identifications.

Calibration of Instrument: Accurate and trustworthy results depend on the regular calibration of analytical instruments. Sample processing can be delayed and analysis timetables can be upset by instrument downtime brought on by maintenance or repairs (Mahmood et al. 2022).

- **Other Influencing Factors**

The detection of EPs in various water bodies such as lakes, wells, ponds, and rivers is a complex process influenced by several factors (Daughton 2004; Gogate and Pandit 2004). These factors include the presence of diverse chemicals due to waste management practices, and the natural variability of water bodies in terms of flow, source, and composition. Each of these factors can affect the detection process, leading to challenges in sample preparation, purification, and accurate identification of EPs (Gogate and Pandit 2004).

- The existence of microorganisms and diatoms in wastewater samples can cause the introduction of extra organic matter and impede analytical measures, which can impact the operation of the instrument and the interpretation of the findings (Mohan and Gupta 2018).
- pH and temperature fluctuations can affect chromatographic separations, analyte stability, and chemical reactions, which can affect the outcome of analytical procedures (Baker and Hurst 2020).

- Total Dissolved Solids (TDS), Density, and Viscosity: Elevated TDS concentrations, distinct density patterns, and varying viscosities in wastewater samples can all have an impact on the precision and accuracy of analytical results by impacting sample injection, chromatographic flow rates, and detector response (Baker and Hurst 2020).
- Atomic Weight and Mass: Variations in the analyses of atomic weight and mass can impact how well they ionize in MS-based techniques, leading to variations in detection sensitivity (Baker and Hurst 2020; Mohan and Gupta 2018).

14.7 Technological Interventions for Removal of EPs

The effective elimination of EPs from wastewater requires high-tech solutions that cause different significant risks to human health and the ecosystem. This section addresses the shortcomings of current wastewater treatment techniques in managing EPs and suggests a variety of advanced treatment systems, including their mechanisms and targeted pollutants.

Traditional wastewater treatment plants (WWTPs) typically employ a combination of physical, chemical, and biological processes to remove contaminants, each stage addressing different types of pollutants to ensure comprehensive treatments (Mompelat et al. 2009).

14.7.1 Primary Treatment

The goal of this first phase is to get rid of particles and particulates using physical means of wastewater. WWTPs are capable of effectively addressing suspended particles and gross pollutants by the process of screening and sedimentation. Heavier particles fall at the bottom of sedimentation tanks and generate sludge that can be further treated or disposed of. The larger debris are captured by screening, which uses mechanical filters or grates (Petrie et al. 2015; Zhang and Jiang 2019).

14.7.2 Secondary Treatment

Biological processes are used in secondary treatment, which comes after the primary one, to break down organic materials in wastewater. To break down nutrients like phosphate and nitrogen as well as biodegradable organic molecules, this stage utilizes microbial activity. Trickling filters, bio-film reactors, and activated sludge are common secondary treatment techniques. Aeration tanks combine wastewater with a microbial rich sludge in the activated sludge process, which encourages the decomposition of organic materials. Utilizing a bed of media (such as pebbles or plastic) that wastewater is spread across, bio-filters enable microorganisms to proliferate on the media's surface and break down EPs as water trickles through. In contrast, biofilm reactors facilitate microbial growth on their surfaces, offering an environment conducive to efficient breakdown of EPs (Wang et al. 2020).

14.7.3 Tertiary Treatment

To guarantee that the treated effluent satisfies strict quality criteria, the advanced tertiary treatment step focuses on removing any leftover inorganic compounds, nutrients, and pathogens. At this point, both chemical and physical processes are involved. Filtration is frequently used to separate the coagulated particles from the water after chemical coagulation, which is used to aggregate and remove fine particles and dissolved compounds. Disinfection techniques like ultraviolet (UV) radiation and chlorine treatment are used to get rid of harmful microbes. Furthermore, residual organic substances and trace contaminants that were not addressed in previous treatment phases are removed using active carbon adsorption (Sharma et al. 2021).

Even though many pollutants can be effectively removed by standard WWTPs, new pollutants can still be present after these processes, including endocrine-disrupting chemicals, medicines, and personal care items. To effectively remove these compounds, more sophisticated treatment technologies are frequently needed. This emphasizes the necessity of ongoing innovation and the incorporation of sophisticated detection and treatment techniques into contemporary wastewater management procedures (Cristaldi et al. 2020).

14.8 Factors Affecting Detection Process

14.8.1 Complex Sample Preparation Techniques

The presence of diverse chemicals in wastewater samples from different sources requires complex sample preparation techniques. Waste management practices, which include the discharge of industrial, municipal, and agricultural wastes, introduce a variety of EPs into water bodies. These EPs can interact and form new compounds, complicating the sample matrix. Sacred rituals, such as religious offerings and ceremonial baths, can introduce additional organic and inorganic substances, further complicating the chemical composition of the water. Preparing these complex samples for analysis involves multiple steps such as filtration, extraction, and concentration to isolate the EPs of interest. Each step must be carefully optimized to ensure the accurate detection of the pollutants, which can be time-consuming and resource-intensive (Almeida 2021).

14.8.2 Variability of Water Bodies

Different water bodies, such as lakes, wells, ponds, and rivers, have distinct characteristics and bio media, microorganism that influence the nature of pollutants, and the detection process.

14.8.3 Flow and Source

- Rivers have continuous flow and can carry pollutants from various upstream sources, leading to dilution and dispersion of EPs. This variability can make it challenging to obtain representative samples and detect low-concentration pollutants.
- Lakes and ponds, being stagnant or slow-flowing, can accumulate EPs over time, leading to higher concentrations of contaminants. However, the lack of flow can result in stratification, where different layers of water have varying chemical compositions, requiring careful sampling to avoid biased results.
- Wells, often sourced from groundwater, can have EPs leached from soil and rock, which might be less variable but can contain complex mixtures of naturally occurring and anthropogenic substances (Westrich Förstner 2007).

14.8.4 Composition

The natural composition of water bodies, including pH, temperature, metal content, and organic matter content, can affect the stability and behavior of EPs. For example, acidic or alkaline conditions can cause certain chemicals to degrade or precipitate, altering their delectability. High organic matter content can interfere with analytical methods by binding to pollutants and reducing their extraction efficiency (Babiak and Krzemińska 2021).

14.8.5 Nature of Pollutants

The variability in the nature of pollutants, from simpler to more complex compounds, poses significant challenges in detection. Simpler pollutants, such as nitrate or ammonia, may be easier to detect using straightforward analytical techniques. In contrast, complex EPs, such as pharmaceutical compounds or industrial chemicals, often require advanced analytical methods like GC-MS or LC-MS/MS. These techniques involve sophisticated instrumentation and expertise, increasing the complexity and cost of the detection process (Schmidt et al. 2004).

14.8.6 Purification of Highly Contaminated Samples

Highly contaminated samples require extensive purification to remove interfering substances and concentrate the pollutants of interest (Guttikunda et al. 2014). This purification process often involves multiple steps, such as solid-phase extraction (SPE) or liquid–liquid extraction (LLE), which can be labor-intensive and prone to sample loss or contamination. Efficient purification is crucial to ensure that the analytical instruments can accurately detect and quantify the pollutants without interference from other substances present in the sample (Guttikunda et al. 2014; Mohan and Gupta 2018).

14.9 False Negative or False Positive Results

The complexity of wastewater samples and the nature of EPs can lead to false negative or false positive results in the detection process (Eduok et al. 2013).

False Negatives results occur when EPs are present but not detected due to inadequate sample preparation, insufficient purification, and other analytical interferences. The complex matrices can mask the presence of certain EPs or reduce their delectability by binding to other substances or undergoing chemical transformations (Eduok et al. 2013).

False Positives results occur when substances are incorrectly identified as pollutants due to analytical interferences or cross-reactivity. The presence of similar compounds in the sample matrix can lead to misidentification, especially in methods relying on non-specific detection techniques (Baker and Hurst 2020). False positive and false negative results in detecting EPs can occur due to several reasons related to sample preparation, instrument sensitivity, contamination, and human error. False positives, where pollutants are incorrectly detected, often arise from interferences in the sample matrix, where non-target substances mimic the target analytes, leading to misidentification (Müller and Huber 2018). Contamination during sample collection, handling, or within analytical instruments can introduce extraneous substances, falsely identified as pollutants. Improper calibration of instruments can also result in incorrect readings, detecting substances that are not actually present. Additionally, highly sensitive methods may pick up trace amounts of irrelevant substances due to environmental exposure or sample handling, resulting in over-sensitive responses. Human errors, such as misinterpretation of data or mistakes in documentation, can further contribute to false positives (Zhang and Wang 2022).

Conversely, false negatives, where pollutants present are not detected, often result from inadequate sample preparation (Baker and Hurst 2020; Müller and Huber 2018). Inefficient extraction methods may fail to isolate target analytes, or sample loss during preparation steps like filtration or evaporation can lead to non-detection. Analytical methods with low sensitivity or those unable to detect EPs below a certain concentration threshold may miss low-concentration substances (Müller and Huber 2018).

Instrumental issues, such as malfunctions or signal suppression caused by other substances in the sample, can also affect detection. Chemical interferences, such as the formation of complexes or degradation of target analytes, can render them undetectable (Baker and Hurst 2020). Improper calibration, leading to underestimation of analyte concentration, and human errors in data analysis or documentation can also result in false negatives. Understanding these factors is crucial for improving the accuracy and reliability of detecting EPs, ensuring more precise and dependable results (Baker and Hurst 2020; Müller and Huber 2018; Zhang and Wang 2022).

14.10 Limitations of Phenomenated Techniques, Biosensors, and Approaches Based on Nanotechnology

Although hyphenated methods (LC-MS, GC-MS, and GC-GC), biosensors, and nano-based technologies have distinct benefits in the identification of EPs, they are not without limits. Hyphenated procedures come with a high price tag and high technical difficulty since they need complex instrumentation and specialized knowledge and training to operate and interpret data.

- **Biosensor Sensitivity**: When dealing with complex sample matrices that have a lot of background interference, biosensors may not be as sensitive or selective as they may be.
- **Nano-material Stability**: The long-term performance, repeatability, and stability of nano-materials under extreme environmental conditions are potential issues for nano-material-enabled sensors and nano-enabled spectroscopic techniques (Arora et al. 2011; Arugula and Simonian 2014).

In order to overcome these constraints, continuous research and development activities are needed to improve the resilience, adaptability, and suitability of sophisticated detection systems for wastewater analysis. To overcome these obstacles and progress the subject of environmental monitoring and management, collaboration among academic institutions, regulatory bodies, and other stack holders is crucial (Dueñas-Muñoz et al. 2022).

A comparison table summarizing the limitations of existing analytical tools for detecting and removing EPs from wastewater, along with potential solutions is given (Table 14.2).

Table 14.2 Limitation of existing analytical tools with potential solutions

Sl. No	Techniques	Limitations	Overcoming of the limitations	Solutions/suggestions	References
1	Low concentration measurement	Analytical methods struggle to measure emerging contaminants (ECs) at low concentrations (usually in parts per billion or parts per trillion levels)	Develop more sensitive techniques for detecting EPs at extremely low levels	Explore advanced analytical methods, such as mass spectrometry (MS), to enhance sensitivity and accuracy	Sangamnere et al. (2023)
2	Diversity of chemical properties	ECs exhibit diverse chemical properties, making uniform analysis challenging	Adopt versatile techniques capable of handling different types of ECs	Consider using LC and GC coupled with MS for comprehensive analysis	Sangamnere et al. (2023)
3	Complex matrices	Environmental samples (e.g., wastewater, soil, sediment) contain complex matrices that interfere with accurate EC detection	Improve sample preparation and cleanup methods	Optimize extraction and cleanup procedures to minimize matrix effects and enhance specificity	Sangamnere et al. (2023)
4	High operating costs	Conventional treatment techniques for removing ECs can be expensive to operate	Explore cost-effective alternatives	Investigate nanotechnology-based approaches, which may offer better efficiency and cost-effectiveness	Sangamnere et al. (2023)

(continued)

Table 14.2 (continued)

Sl. No	Techniques	Limitations	Overcoming of the limitations	Solutions/suggestions	References
5	Limited flow-through capacities	Existing treatment plants may have limitations in handling large volumes of wastewater containing ECs	Enhance treatment plant design and capacity	Consider modular or decentralized treatment systems to accommodate varying flow rates and pollutant loads	Tian et al. (2021)
6	Selective de-contamination	Some existing techniques selectively remove specific ECs, leaving others untreated	Develop multifunctional approaches	Combine different treatment methods (e.g., adsorption, oxidation, biological processes) to target a broader range of ECs	Sangamnere et al. (2023)

14.11 Recommendations and Suggestions Based on the Limitations of Existing Analytical Tools in Detecting and Removing EPs in Wastewater Treatment

- **Improve Analytical Capabilities**: Develop more sensitive and selective analytical methods to detect a wider range of EPs at lower concentrations in wastewater (Dueñas-Muñoz et al. 2022). Utilize advanced analytical techniques like LC-MS, GC-MS, and spectroscopy coupled with chemo metrics to comprehensively monitor EPs in water, soil, and air. Adopt emerging tools like sensors, miniaturized probes, and bioassays to enhance real-time monitoring and eco-toxicological assessment of EPs.
- **Enhance Removal Efficiency**: Investigate and optimize biological, physical, and chemical advanced oxidation processes to improve the removal of resistant EPs like pharmaceuticals, personal care products, and industrial additives (Dueñas-Muñoz et al. 2022). Explore innovative green sorbents and membrane-based technologies for more effective removal of emerging contaminants. Integrate multiple treatment techniques in a treatment train to achieve higher overall removal rates for a broader spectrum of EPs (Dueñas-Muñoz et al. 2022).
- **Strengthen Regulatory Framework**: Establish comprehensive regulations and monitoring programs for EPs in water, wastewater, and the environment to drive technological advancements and mitigation efforts. Promote collaboration between researchers, policymakers, and water utilities to develop evidence-based guidelines and standards for EPs (Dueñas-Muñoz et al. 2022).

14.12 Conclusion

This chapter offers an in-depth overview of the obstacles encountered in the management of emerging pollutants (EPs) within wastewater systems. Managing emerging pollutants (EPs) in wastewater treatment presents significant challenges that require a deep understanding of the pollutants' characteristics, the analytical methods employed, and the environmental conditions affecting treatment processes. Emerging pollutants (EPs) have a diverse chemical composition; as a result their detection and removal are difficult. EPs are not accurately detected and quantified with conventional analytical methods. Environmental factors (temperature, pH, and biological oxygen demand) have a crucial role in determining the effectiveness of EP detection and removal. For overall management, it is crucial to effectively remove EPs by developing advanced/innovative analytical methods. To address these limitations, continuous research and technological advancements are essential to manage EPs in wastewater treatment systems.

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Chapter 15
A Weal Against Woe: Detection of Pharmaceutical Remnants in Water Using Nano Sensors

Bidisha Ghosh and Subhasis Sarkar

Abstract An array of newer emerging pollutants gain entry into the aquatic ecosystem that endangers not only the aquatic fauna and flora but also makes human life precarious at the global scenario. Stemming out of newer alternatives in treatment, antibiotics are the main therapeutic regimes in recent times. This however poses threat as derivatives of these antibiotic products released from municipalities as well as from different livestock waste water enters into major water bodies. Antibiotics thus are a newer addition of persistent organic pollutants (POPs) in the aqueous milieu due to their indiscriminate use. Thus the treatment of this antibiotic infested water becomes a major imperative besides other irritant pollutants like heavy metals, microorganisms, organic compounds are mostly subjected to regulation and monitoring. Techniques are prevalent for the effective removal of these pharmaceutical wastes, but their presence in water and thereby sensing still remains as a cardinal challenge. Nanomaterial by virtue of their noted tunable size, large surface to volume ratio and excellent optical properties & reusability provides a broad avenue for the sensing of the residual antibiotics in waste water. This review thus focusses on the recent developments of sensing of vast categories of antibiotics exploiting the benevolence of nanomaterials. The different developments in techniques concerning the sensing of the pollutant through colorimetric, fluorescence, photoluminescence, chemiluminescence, Surface Plasmon Resonance (SPR), Surface Enhanced Raman Spectroscopy (SERS), etc. are been discussed in this chapter along with their future prospects to develop a ready potable nanosensor for effective antibiotic sensing.

Keywords Antibiotics · Nanomaterials · Nanosensor · Persistent organic pollutants (POPs) · Waste water

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S. Dey and M. P. Shah (eds.), *Biotechnological Removal of Emerging Pollutants from Wastewater Systems*, Advances in Wastewater Research,
https://doi.org/10.1007/978-981-96-3945-8_15

15.1 Introduction

Nanomaterials with its diverse functions are being utilized and fabricated in several ways to meet the increasing demands of modern civilization. Nanoparticles are generally categorized as having a dimension less than 100 nm (Popescu et al. 2013). The properties of the nanomaterials can differ depending upon the type of the nanomaterial used. In recent times with ancillary applications and advantages in several domains nanomaterials has gained significant attention in sensing. Nano based Sensors can be developed in broad arenas that encompass bioremediation (Patra 2022), aerospace (Edwards et al. 2017), medicinal research (Kim et al. 2017). In this context sensors can be harnessed for sensing various irritable xenobiotics in the environment. The sensors under this context should be reliable in terms of biocompatibility, its prompt applicability measured through sensitivity and selectivity. Water pollution has been the biggest quagmire of the century that has mainly stemmed from the past pace in population and urgency of rapid urbanization and progress through technology. Rapid industrialization has led to the influx of a large number of potential toxic compounds into the environment. These are been categorized under persistent organic pollutants" (POP) (Zhang et al. 2020) that dictates major natural bodies from air, soil water. Water pollution among all has gained considerable attention as water forms the elixir of life and scarcity down the line is likely to change the entire ecosystem slaying majority of organisms in the food chain. The WHO has enlisted a number of toxic products that potentially reign the aqueous milieu that entails a number of organic and inorganic products like phenol derivatives (Mohd 2022), heavy metals (Karvelas et al. 2003) to name a few. Alongside one of the alarming reports hint at the presence of antibiotic and their remnants in the waterbodies (Xue et al. 2022).

Over the years the rampant use of antibiotics has already set to the global concern of antibiotic resistance (Manaia et al. 2024). To add to the concern the presence of antibiotics and their residual products in water arising out of environmental and metabolic breakdown has heaped in perturbation. The slow yet steady entry of antibiotics chiefly to treat diseases and infections concomitantly in humans as well as in animals has necessitated the development of a biocompatible sensor. Of the various detection methods available for the quantification of the antibiotics in water like liquid chromatography (Nebot et al. 2007) and fluorescence (Škrášková et al. 2013), mass spectrophotometry (Hirsch et al. 1998), ratiometric sensing (Wu et al. 2020), capillary electrophoresis (Díaz-Quiroz et al. 2018). In this review we are going to delve into the origin of antibiotics their various categories along with their origin. The detection of different nanosensors and their mechanism of sensing are also discussed that are effective in sensing various antibiotics and their remnants in waste water.

15.1.1 Antibiotic as Persistent Organic Pollutant (POPs) in Natural Bodies: A Potential Threat to Aquatic System

Chemical substances known as persistent organic pollutants, or POPs, have garnered a lot of attention on a global scale in recent decades. These substances have a mix of chemical and physical characteristics that enable them to withstand deterioration, bioaccumulate, and move across great distances. Both humans and wildlife have been linked to a variety of symptoms following exposure to these substances. These days, antibiotics are regarded as one of the newer, persistent organic pollutants. These are starting to generate serious problems for public health because they are the source of the environment's bacteria developing antibiotic resistance.

Therapeutic substances are widely employed to cure diseases in humans and/or other animals nowadays since they have ingrained themselves into our daily lives (Gothwal and Shashidhar 2015). In this situation, the antibiotic compounds that demonstrate the ability to eradicate germs are extracted from the organism and synthesized (Tong et al. 2014). Antibiotics have been used to treat various diseases brought on by pathogenic bacteria ever since they were discovered (Dong et al. 2016; Jin et al. 2017). These days, both humans and animals are exposed to antibiotics since they are used to treat a variety of illnesses, including gonorrhea, syphilis, pneumonia, and TB (Gothwal and Shashidhar 2015).

Given that human urine and feces both contain antibiotic compounds that are digested and eliminated (Xu et al. 2016; Almeida et al. 2014). The effluents from pharmaceutical industries, wastewater treatment plants, hospitals, and other sources are the reason antibiotics are present in wastewater. The significant amount of antibiotics that have been released into groundwater, surface water, and even drinking water are the result of the wastewater treatment plant.

15.1.1.1 Common Antibiotics Found in in Water

Based on their molecular makeup, antibiotics are divided into 11 groups, which include tetracyclines, lactams, glycopeptides, aminoglycosides, oxazolidinones, polymyxins, quinolones, streptogramins, and sulfonamides (Zhang and Li 2011). In both human and veterinary medicine, tetracyclines, sulfonamides, and macrolides are frequently used antibiotics. In addition to being utilized to identify and treat infectious diseases in humans, these antibiotics are also employed to maintain and safeguard the health of animals (Kim and Carlson 2007). Penicillin, a class of lactam antibiotics that includes aminopenicillins–ampicillin, naturally occurring penicillin G, and extended spectrum penicillin–piperacillin—is the most widely used and oldest antibiotic (Al-Riyami et al. 2018). Sulfonamides, macrolides, and quinolones are the most often detected antibiotics in sewage sludge, sediments, soils, and wastewater as well as foods. Because antibiotics can bioaccumulate in aquatic organisms and cause a loss of biodiversity, antibiotic contamination has thus become a serious concern in many rivers and seas (Li et al. 2012; Rosal et al. 2010). Antibiotics may increase bacterial resistance, impede soil decomposition, endanger marine, freshwater, and terrestrial life, and harm the food chain (Chen and Zhou 2014; Yang and Carlson 2004).

15.1.1.2 Origin of Contamination

As was previously recognized, antibiotic contamination can be found in soil, water resources, and sewage (Hubeny et al. 2021; Ebrahimi et al. 2020). Because of its negative effects on ecosystems and human health, its presence needs to be addressed very away. Moreover, it causes bacterial resistance, which makes infection treatments ineffective. By contaminating water or food that has been prepared with it, these antibiotic-resistant bacteria can spread to humans and other animals. They then modify the hosts' gut flora, leading to a range of ailments (Kumar et al. 2020). Antibiotics cannot enter the human body or any other biological system unless the source of contamination is found. The sources of antibiotics are then discussed.

- *Domestic Wastewater*

Due to improper disposal by users or insufficient treatment, antibiotics find their way into municipal and surface waterways (Sun et al. 2019). The two main sources of antibiotics are domestic home waste and the meat and poultry industries. Antibiotics ingested by humans and animals pass through the intestines, are eliminated, and ultimately end up in wastewater treatment facilities (Gao et al. 2012). Pharmaceuticals enter the environment mostly through municipal wastewater, although there are other sources as well, such as improperly treated manufacturing effluents and the direct disposal of unneeded medication. The kinds and concentrations of antibiotics vary depending on the substances that the consumer or company uses. The antibiotics are altered physically or chemically once they get at the treatment plants, and the sort of treatment and procedure used will determine the medicines' next course of action. Antibiotics belonging to the six major classes—tetracyclines, β-lactams, quinolones, macrolides, and sulfonamide—are frequently found as pseudo-persistent pollutants in activated sludge, sewage, digested sludge, and effluents (Zhang and Li 2011). Municipal wastewaters contain the most diverse and abundant populations of micro- and macroorganisms, which encourages the development of drug-resistant organisms. It is not surprising that these organisms would exhibit antibiotic-resistant traits, whether they are commensals, pathogens, or ambient bacteria, protozoa, or fungi (Kumar and Pal 2018; Teixeira et al. 2020). The primary concern in this case is managing the emergence of resistant pathogenic microorganisms, even in the presence of heavy metals, pesticides, endocrine disruptors, and hormones in wastewater (Magureanu et al. 2010, 2011).

- *Effluent from Hospitals*

Hospitals that have contaminated water may have remnants of chemicals used in labs, organic halogens, radioisotopes, heavy metals, cytostatic agents, disinfectants, medicinal ingredients, and microbes of all types. Among many other substances used in medical therapy, anti-neoplastic drugs are believed to be environmentally hazardous due to their potential for mutagenicity, teratogenicity, and carcinogenesis, while cytostatic drugs are governed by stringent production and handling guidelines (Verlicchi et al. 2010; Wegrzyn et al. 2015; Capoor and Bhowmik 2017). Because it is a major source of bacteria and genes resistant to antibiotics, hospital wastewater is therefore particularly harmful (Wang et al. 2016). Hospital wastewater is typically too difficult for traditional wastewater treatment systems to handle, and as a result, there is a chance that these pollutants will leak entirely or partially into the ecosystem (Arslan et al. 2014). Hospitals' contribution to the pharmaceutical load in wastewater is difficult to assess because most people use medications and contraceptives. A number of programs are currently in place to evaluate and screen hospitals, investigating their possible role as reservoirs for medications and other materials that can give rise to germs resistant to several medicines (Escher et al. 2011). Hospital wastewater has more than 25% more antibiotics than regular wastewater, with gene concentrations varying from about 0.4 to 1.8 log (Paulus et al. 2019). Apart from medications, a variety of substances are utilized for medical purposes in hospitals and operations, including disinfectants and diagnostics (Orias and Perrodin 2013). Numerous antibiotics have been detected at higher concentrations in hospital effluent, including ciprofloxacin, enrofloxacin, oxalinic, ofloxacin, norfloxacin, sulfapyridine, trimethoprim, and metronidazole (Khan et al. 2020; Carraro et al. 2016).

- *Effluent from Slaughter Houses*

Since the clinical administration of antibiotics to animals plays a key role in their diffusion in the environment, animal slaughterhouse wastewater is regarded as another substantial source of resistant bacteria (Savin et al. 2020a, b). Due to the incorrect and frequent use of antibiotics in treatments, as well as the physical manipulation of growth hormones in animal husbandry, which has stimulated the establishment of new resistances, antimicrobial resistance in bacteria associated to livestock has developed significantly in recent times (Savin et al. 2020a, b; Tang et al. 2020). Large amounts of effluents from the slaughtering process may contain bacteria resistant to antimicrobials (Homeier-Bachmann et al. 2021). Meat processing effluents are considered harmful globally due to their high concentrations of lipids, proteins, fibers, organic substances, microorganisms, and veterinary drugs (Bustillo-Lecompte and Mehrvar 2017). For instance, in countries in central Africa, drugs like procaine penicillin G and oxytetracycline are frequently used to treat cattle. The animals excrete these drugs in the form of urine or feces, which then find their way into the sewage water system (Masse et al. 2021).

- *Surface Runoffs*

Due to their broad over-the-counter availability, antibiotics have a substantial impact on consumption patterns in poor nations due to their misuse and overuse. Antibiotics are present in many environmental sectors in these nations as a result of their widespread usage, continuous surface runoff, and discharge from wastewater treatment facilities (Lucas et al. 2016). Antibiotic concentrations in the environment rise as a result of antibiotic contamination. Therefore, a range of sources, such as veterinary waste, human waste streams, livestock husbandry waste, stored animal faeces, etc., are introducing antibiotics into the environment. These resources have the potential to release antibiotics into surface and groundwater, which is often initiated by moderate to heavy precipitation. As a result, this is now the most typical reason why antibiotics contaminate the environment. Moreover, in fertilized agricultural fields, this runoff has the potential to transfer pollutants from manure to surface water systems. Thus, the chance of bacterial resistance or resistance genes being released into surface water is increased when manure, insecticides, and pesticides are used on crops. Furthermore, seasonal variables that affect stream velocity, nutrients, precipitation, and snow have an impact on the amount and mobility of pollutants (Beattie et al. 2018). The type of antibiotic has a significant impact on how antibiotic losses are distributed between runoff and sediment (Davis et al. 2006). Antibiotics have migrated across the environment considerably more quickly and extensively because of their strong water affinity or solubility in water (Christy et al. 2018; Tasho and Cho 2016). One of the main causes of antibiotic contamination in this situation is the direct discharge of wastewater from healthcare facilities into a system without any prior treatment (Hocquet et al. 2016). This exacerbates the issue. Antibiotics disposed of as solid waste can, as previously indicated, be carried to adjacent water bodies or seep into groundwater from disposal sites (Anthony et al. 2018; Tarrass et al. 2008).

15.2 Development of Nanomaterial Based Sensing Systems for Rapid Detection of Antibiotics

As mentioned earlier in this section that there is a rapid urgency for the development of sensor which will be rapid in terms of sensitivity and selectivity. In this context nanomaterials are been selected as efficient candidates that sense the presence of antibiotics in water either colorimetrically, or through fluorescence or electrochemically. Here is a succinct review of the different methodologies that are harnessed for the sensing of antibiotics in water.

15.2.1 Plausible Ability to Sense Antibiotics in Water Through Gold and Silver Nanoparticles: Role of Colorimetric Sensors

Colorimetric sensors are very much in vogue for sensing trace amount of analytes and ligands in diverse environments known. In most of the colorimetric assays employing nanoparticles surface modification of the nanoparticles through colorimetric sensors will detect the presence of analyte at a negligible concentration. The color change

Table 15.1 Sensing of antibiotics by surface functionalized gold (Au) and silver (Ag) Nps with their limit of detection (LOD)

Nanoparticle	Antibiotic detected	LOD	References
Au@CTAC*	TC[1], OTC[2], DC[3], CTC[4]	TC, OTC, CTC: 0.17 μg/ml DC: 0.25 μg/ml	Shen et al. (2014)
Au@Chitosan	Kanamycin	8 nM	Lai et al. (2017)
Ag@Quercetagetin	Amoxicillin	4.46 μM	ul Ain et al. (2018)
Ag@Chlortetracycline	Streptomycin Kanamycin	2000 pM 120 pM	Saratale et al. (2020)
Ag@Citrate	Neomycin	70.8 pM	UshaVipinchadran et al. (2022)

* CTAC: Cetyltrimethylammonium Chloride
TC[1]: Tetracyclin
OTC[2]: Oxytetracyclin
DC[3]: Doxycylin
CTC[4]: Chlortetracyclin

produced can be visualized and ultimate quantification can be analysed through UV Vis spectrophotometry. A significant number of reports are cited in support of nanoparticles like gold (Au), silver (Ag) that are used for the colorimetric assay for a wide array of analytes ranging from biomolecules like carbohydrates to various inorganic ions and other organic compounds (ul Ainet al. 2018). The color of AuNps differ a lot than their bulk counterparts, and upon binding with various analytes a sudden color change due to aggregation causes the absorption peak in UV Vis spectroscopy to have higher wavelengths (Nath and Chilkoti 2002). This colorimetric change is attributed to the plasmonic oscillations of the free electrons present on the surface of the metal nps (Amendola et al. 2017). A table hinting at the colorimetric detection of various antibiotics by gold and silver nanoparticles is been cited in Table 15.1.

15.2.2 Nanosensors for Detecting Antibiotics

The basic concept for the development of a biosensor device is its ability to recognize a particular analyte by virtue of its surface mediated action. This roughly translates into enhanced detection by a material whose surface to volume ratio is higher. Nanomaterials fulfil the above criteria and thus it has been observed that the electron transfer efficiency of the nanomaterials are ideal candidates for sensing performances (Sargazi et al. 2022).

For real time, detailed analysis fluorescent based nanomaterials like quantum dots (Sun et al. 2013), carbon dots (Xu et al. 2020), use of various fluorescent labels (Oliveira et al. 2018), dyes alone or used with another nanomaterial (Zhong 2009) are effectively utilized in the detection of various ligands and analytes. Nanocomposites are tailored in such a way that they can effectively detect vast spectrum of antibiotics. It has been observed that with increasing concentration of the antibiotic engineered fluorescent nanosensors undergo drastic changes in their fluorescent intensities (Zhou et al. 2018).

15.2.2.1 Carbon Dots in Fluorometric Detection of Antibiotics in Water

With the advent of carbon dots wide variety of antibiotics can be analysed in water. Carbon nanodots possess excellent stability (Wang et al. 2015), low toxicity (Zuo et al. 2015) and notable chemiluminescent properties (Shen et al. 2020). The fluorescence based detection of carbon dots are attributed to quenching mechanism between the fluorophore and the target analyte which is based upon the principle of Inner filter effect (Akhgari et al. 2017) along with other mechanisms like Fluorescence Resonance Energy Transfer (FRET) (Shi et al. 2015), Photoinduced Energy Transfer (PET) (Huang et al. 2022). Table 15.2 gives an idea about the different fluorescent carbon dots, their selectivity and sensitivity against different spectrum of antibiotics in water.

Table 15.2 Carbon dots (CDs), their mode of synthesis and selectivity towards antibiotics

Carbon dots	Synthesis	Type of antibiotic	Sensitivity	Linear range	References
N-CDs*	Solid pyrolysis	Enrofloxacin	0.16 μg/mL	1.0–15 μg/mL	Guo et al. (2019)
N-CDs	Hydrothermal	Tetracycline (TC)	0.39 μM	0.5–60 μM	Yuan et al. (2022)
R-CDs**	Hydrothermal	TC, OTC, CTC	TC: 3–35 μM OTC: 2–50 μM CTC: 5–50 μM	12 nM 23 nM 25 nM	Li et al. (2021)
S-CDs***	Hydrothermal	NOR, CIP	NOR: 0.02–1.25 μM CIP: 0.02–1.0 μM	4.6 nM 6.7 nM	Hua et al. (2018)

* N-CDs-Nitrogenous Carbon Dots
** R-CDs-Red Carbon Dots
*** S-CDs-Sulphur doped Carbon Dots
OTC: Oxytetracyclin
CTC: Chlortetracyclin
NOR: Norfloxacin
CIP: Ciprofloxacin

15.2.3 Magnetic Nanosensors in the Detection of Antibiotics in Water: Role of Surface Enhanced Raman Scattering (SERS)

Volatile chemicals can react with solvents to create unwanted byproducts. There is very little chance of thorough monitoring because it takes pretty good amount of time to deliver results. Magnetic nanoparticles (MNPs) have emerged as a powerful tool for the detection of a large number of organic compounds. Compared to non-MNPs-based technologies, sensing techniques based on MNPs offer advantages in terms of analytical figures of merit, such as quick analysis times, high signal-to-noise ratios, low detection limits (DL), and enhanced sensitivity. MNPs are used by applying labelled supports directly to the sensors that are placed inside the transducers. On the active surface of the sensors' or biosensors' detection, an external magnetic field is used to draw the MNPs into the material (Slimani and Hannachi 2020). The magnetic nanoparticles prepared through a wide variety of synthetic routes like micro emulsion (Salvador et al. 2021), co-precipitation (Daoush 2017), pyrolysis (Chen et al. 2010) etc. methods are mostly oxides of iron, ferrate and metal alloys like cobalt, nickel (Alagiri et al. 2011). Through Surface Enhanced Raman scattering (SERS) the magnetic nanomaterials which is observed when the MNPs are in close vicinity with the analytes (Pinheiro et al. 2018). Beside bare magnetic nanoparticles, a number of surface modification over magnetic nanoparticles to sense a number of antibiotics. Colloidal Au nps can be decorated over magnetite nanoparticles that upon binding with penicillin G antibiotic had been observed to generate SERS signal (Pinheiro et al. 2017). Antibiotics like chloramphenicol and tetracyclines can also be detected through nanotags that comprise core-shell structure of embedding a hybrid Au–Ag nanostar into magnetic nanoparticles with a detection limit in femtograms (Liu et al. 2022).

15.3 Discussion and Perspectives

This study was aimed to study the different antibiotics and their remnants that are present in water. The sources of antibiotics harm the sum total of all flora and fauna alongside makes the life of human beings precarious. The rise in fluoroquinolones, sulfonamides, and beta lactam group of antibiotics poses serious threat to the aqueous environment because this gives rise to an array of antibiotic resistant bacteria within the water bodies. The introduction of antimicrobial agents, disinfectants in the aqueous environment poses serious threat as this sprouts evolution of a number of resistance within the aqueous compartments. The "resistome" theory can thus be applied here where an apparently seen non-resistant gene can transform themselves into a "resistant" one depending on the load of the antimicrobials and residues in the environment (Baquero et al. 2008). The contaminated water therefore can gain entry into irrigated crops and knowledge gaps persist regarding the uptake of the contaminated water and also the influx of these antimicrobial resistant genes in to the human food chain (Hong et al. 2013). There are reports hinting at the dissemination of pathogen through water where the clinical isolates are found to be similar with the resistant gene containing environmental isolates. The surface functionalization of the nanoparticles and its fabrication thorough various chemical and biological routes had its evidence in removing various organic and inorganic xenobiotics from the environment. (Dewil et al. 2017). Besides detection of these antibiotics and their efficient removal becomes imperative. The use of colorometric assays through gold and silver nanoparticles are effective in turn for detecting antibiotic resistance (Abdou Mohamed et al. 2021). Magnetic nanoparticles are in vogue for determination of *sul 1* genes (Martín et al. 2022) The diverse application of wide variety of nanoparticles with their various properties can be utilized for meeting the challenge of antibiotic resistance genes. This review suggest nanoparticles and their effective detection mechanisms to address water bodies infested with organic pharmaceutical remnants that can be seen as a defined alternative to most of the conventional methods of sensing.

15.4 Conclusion

In conclusion, we mention that the growing concern in the occurrence of emerging persistent pollutants including residual antibiotics, originated from various municipal and industrial sources indicate the necessity to detect them in natural water bodies following their removal from the environment. In the present scenario, knowing the existence of persistent pollutants, has become extremely important as their presence may harm the biotic life forms existing in natural ecosystems to a great extent. Towards resolving the antibiotic pollution, in the current study we noted one of the potential technologies, is nanosensing which holds a promising role. In the era of nanoscience, we have been able to explore the existing sensing technologies towards detecting the traces of residual antibiotics present in natural water bodies. In context, sensing methods including colorimetric, fluorescence, photoluminescence, chemiluminescence, Surface Plasmon Resonance (SPR), Surface Enhanced Raman Spectroscopy (SERS) etc. have been discussed as they are found to be the potential ways through which the detection has become extremely efficient and convenient. In the near future, further progress in sensing technology would definitely be promising in tracing the existence persistent organic pollutants and antibiotics as well.

Acknowledgements The authors owe highly to Swami Vivekananda University for providing research funding and infrastructure.

Conflict of Interest The authors have no conflict of interest.

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Chapter 16
Application of Nanoadsorbents for Remediation of Wastewater: A Review

Shreyasi Biswas and Mahuya Myukhopadhyay

Abstract In the current scenario, nanotechnology has been widely used in different scientific applications and technologies. Nanotechnology may be used to develop some methods to solve various environmental pollution, which can be effective more than the conventional techniques to reduce water pollution. Increasing population growth and excessive industrialization result in environmental degradation which is a serious global concern. One of the most important reasons for the contamination of natural water bodies is wastewater from several industries. Discharge of hazardous material into the water bodies may cause serious health issues to mankind. Nowadays adsorption is a very important remediation process for the treatment of wastewater. Due to the unique physical and chemical features like large surface area, multiple sorption sites, tunable pore size, and surface chemistry of nanomaterials have gained tremendous attention to solve this problem. Carbon nanotubes are very popular in this purpose due to their high tensile strength, chemical and thermal stability, high Young's modulus, and good thermal and electrical conductivity. They also can interact with inorganic and organic pollutants strongly due to their porous hollow structure, low density, hydrophobic surfaces, and high specific surface area. Apart from this, there are other nanoadsorbents also used for example graphane, zinc oxide, magnesium oxide, ferric oxide, and manganese oxide. This review focused on the synthesis and classification of nanoadsorbents and their utilization for the treatment of wastewater.

Keywords Pollutants · Wastewater · Nano-based adsorbents · Carbon nanotubes · Graphane

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S. Dey and M. P. Shah (eds.), *Biotechnological Removal of Emerging Pollutants from Wastewater Systems*, Advances in Wastewater Research,
https://doi.org/10.1007/978-981-96-3945-8_16

16.1 Introduction

A healthy economy and multifaceted growth of society always depend on access to clean and safe water (Morrison et al. 2020). Rapid population growth, urbanization, increased industrialization, and widespread agricultural practices all have contributed to the production of wastewater. Due to this, not only did water become contaminated but it also showed a devastating effect on aquatic life (Mateo-Sagasta et al. 2017). Water pollution is becoming a global issue. Numerous biological infectious organisms like bacteria, virus, and parasites contaminate water through human waste, sewage, and animal excreta causing varieties of health issues starting from stomachaches and simple intoxification to fatal illness or even unexpected death. Wastewater is basically contaminated water or a by-product of agricultural, commercial, or industrial operations (Tilley et al. 2016).

Wastewater treatment using nanotechnology will undoubtedly benefit the environment and living things (Siegert et al. 2019). Nowadays, application of nanomaterials for the remediation of contaminated sites has become very popular and attracted the attention of scientists (Prasad and Aranda 2018). Due to the lack of water resources for a developing economy, efficient wastewater treatment is needed. Developing and implementing sophisticated, highly efficient wastewater treatment technology is essential. By eliminating hazardous chemicals like herbicides and insecticides as well as bacteria and pathogenic viruses, nanotechnology solves technical problems in wastewater treatment.

16.2 Nature of Water Pollution

Numerous categories contribute to water pollution. Water contamination can result from both domestic and industrial waste discharge, depending on where it comes from. There are two categories of pollutants: those originating from natural sources and those originating from human activity. Groundwater pollution occurs naturally when shallow groundwater masses are caused by geological configurations, or when low-quality surface water bodies percolate, saltwater invades, or geothermal fluids have an effect (Baba and Tayfur 2011). Water from animal feces and domestic sewage is made more nitrogenous by the breakdown of organic nitrogen via various processes. Enzymes from microbes break down the organic nitrogen in ammonia. Farmers apply a lot of nitrogenous fertilizers because it is essential for plant growth. However, there is an imbalance between the amount of nitrate available and plant uptake. For example, some fertilizers are applied when the plant cannot absorb them or because the plant density is too low. In this case, the excess fertilizer that the plant is not able to absorb becomes concentrated during evaporation and eventually contaminates the aquifer through seepage (Ahamad et al. 2018).

16.3 Nanoadsorbents and Classification

Due to superior adsorption quality nanoparticles known as nanoadsorbents can be used to remediate contaminated water. Nanomaterials have been extensively studied in the last 20 years for water and wastewater treatment applications because of their characteristics, which include specific surface area, surface functions, porosity, and ion-binding abilities. Indeed, even in minute quantities, they exhibit a great capacity for eliminating metallic ions (Parvin et al. 2019). Nanomaterials are divided into several groups, such as carbon-based, silica-based, metal, and metal oxide nanoparticles and nanocomposites.

16.4 Carbon-Based Nanomaterials

16.4.1 Carbon Nanotubes

Carbon-based nanomaterials including carbon nanotubes, activated carbon, graphane, graphane oxide, and Fullerenes have been widely used in wastewater treatment (Pyrzyńska and Bystrzejewski 2010). Their special qualities also enable the elimination of both organic and inorganic contaminants, which makes them a viable substitute for wastewater treatment. A layer of carbon atoms joined together in a hexagonal mesh forms the structure of a carbon nanotube. The carbon nanotubes are divided into two categories: one is single-walled and other is double-walled (Bassyouni et al. 2020). Four potential active sites can govern the adsorption process in the case of carbon nanotubes like (i) an internal site which is basically a hollow interior of individual carbon nanotube, (ii) an external surface, (iii) grooves between adjacent carbon nanotubes, and (iv) interstitial channels between carbon nanotubes (Arora and Attri 2020; Zhang et al. 2017). The process of adsorption is initiated at the locations of interstitial channels and grooves. Subsequently, pollutants are adsorbed on the external walls and finally accumulate on internal axial sites. The cost and complexity of CNT functionalization, the need for solid and liquid segregation, the kind of wastewater, and the effectiveness and cost of recycling are major criteria that determine whether or not carbon nanotubes can be used to treat wastewater.

16.4.2 Graphane-Based Nanoadsorbants

Another carbon-based substance that is highly effective in wastewater management is graphene. It is a two-dimensional material in which carbon atoms (hexagon arrangement) form a honeycomb lattice. There are two main forms of graphene: reduced graphene oxide (RGO), which has the potential to be used in the remediation of several types of environmental contaminants, and graphene oxide (GO), which is the oxidized form (Woo et al. 2019). The sigma bonds with three nearest atoms are arranged in a honeycomb lattice, and the planar orbitals are energetically stable. Due to this type of structure, graphane has a high surface area and electrical conductivity (Dimiev and Eigler 2016).

16.4.3 Silica-Based Nanomaterials

Inorganic materials have been widely used in adsorption methods due to their thermal and chemical stability. Silica-based nanoadsorbants have a high surface area, porosity, and superior mechanical thermal stability. Silica particles consist of oxygen bound to protons and due to the presence of hydroxyl groups these are polar in nature. As a result of this, polar groups from organic pollutants interact with the surface of silica nanomaterials through dipole–dipole and hydrogen bonding (Scott 1980). Because silica-based materials' surfaces contain acidic silanol, they exhibit intense and occasionally irreversible non-selective adsorption. Nevertheless, modified silica is more effective at the heavy metal ion and acidic dye effluent adsorption and exhibits increased interactions with dyes (Wadhawan et al. 2020; Fu et al. 2011). Amino groups are one type of functional group that is frequently used to modify the surface of silica so that it can remove both cationic and anionic pollutants from water. At low pH levels, the protonated amine groups adsorb anionic contaminants through electrostatic attraction (Aguado et al. 2009), whereas, at high pH levels, they can eliminate cationic pollutants, including heavy metals (Jal et al. 2004).

16.4.4 Metal-Based Nanoadsorbents

This comprises a number of nanoadsorbents, such as zinc oxide, hematite, and copper oxide nanoparticles. pH is a common determinant of the adsorption efficiency of pollutant removal using metal oxide nanoparticles. For example, the rate at which heavy metal ions are removed rises with pH as a result of electrostatic interactions and metal complex formation (Liu et al. 2019). These kinds of nanoparticles have a huge surface area, small particle size, and high surface activity, which make them highly effective at removing heavy metal contamination from water bodies. Studies have shown that lead (Pb^{+}) has the highest affinity of all the metals for hematite and copper oxide nanoparticles (Shipley et al. 2013; Mahmoud et al. 2021).

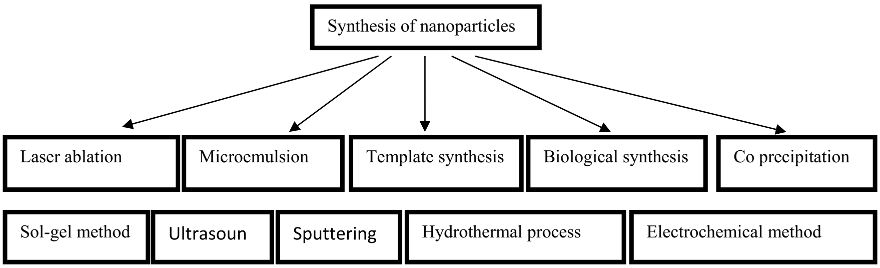


Fig. 16.1 Methods of nanoparticle production

16.5 Nanocomposites

In case of nanocomposites, one or more phases at nano-sized dimensions (zero, one, and two dimensions) are incorporated in a ceramic, metal, or polymer material. There are three types of nanofillers like one-dimensional, two-dimensional, and three-dimensional. Fillers with one dimension less than 100 nm are referred to as one-dimensional (1D) nanofillers. Typically, they take the shape of sheets that range in length from a few nanometers to hundreds and thousands. Typical examples of one-dimensional nanofillers are nanographene platelets and montmorillonite clay. Additionally, they can be found as nanodisks, nanoprism, nanosheets, nanoplates, branching formations, and nanowalls (Akpan et al. 2019). Two-dimensional (2D) nanofillers are defined as being less than 100 nm. Most of them have the form of tubes, filaments, or fibers. Gold or silver nanotubes, cellulose whiskers, boron nitride (BN) tubes, carbon nanotubes (CNTs), and two-dimensional grapheme are 2D nanocomposites (Qadir et al. 2021). Relatively equiaxed particles with all three dimensions at the nanoscopic (nanometer) size are known as three-dimensional (3D) nanofillers. Commonly these are of cubical or spherical shape and are known as isodimensional or zero-dimensional nanomaterials (Farahani et al. 2016).

16.6 Synthesis of Various Nanoadsorbents

There are various techniques for preparing nanoparticles as presented in Fig. 16.1.

16.7 Synthesis of Carbon Nanotubes

There are different methods of making carbon nanotubes. In the arc discharge method, helium is used as buffer gas in a chamber which contains a graphite anode, cathode, vaporized carbon molecules, and a small amount of metal catalysts like cobalt, iron, and nickel. For the synthesis of carbon nanotubes, the chamber is heated at 4000 K and direct current is applied under pressure. In this, half of the vaporized carbon solidified on the tip of cathode and formed a very hard deposit in a cylindrical shape. The remaining carbon became condensed and formed a cathode soot and chamber soot (Eatemadi et al. 2014). Another similar method is the laser ablation method, in which graphite inside the chamber is vaporized by laser. But one of the important points in this method is the power of laser influences the diameter of the carbon nanotubes (José-Yacamán et al. 1993). In the flame synthesis approach as compared to the other methods, it is possible to fabricate CNTs in vast quantities at a significantly reduced cost. It can create carbon nanotubes on the necessary surfaces, and it can do it in a controlled manner. The synthesis of CNTs requires the presence of three key ingredients. These are a source of heat, a source of carbon, and metallic catalyst particles. The catalytic precursors are typically added to the flame system, where they nucleate and eventually condense into solid, spherical metallic nanoparticles. Flame parameters can also be used to create the right flame conditions, which would make it possible to create catalyst particles with the right sizes for the development and initiation of carbon nanotubes (Chen and Gao 2017).

16.8 Synthesis of Graphane Oxide

In the year 1958, Hummers and Offeman had proposed a method of producing graphane oxide which was further modified by Gomes et al. (2022). As per their method, pure graphite of chemical grade was mixed in 99% H_2SO_4 under temperature control and continuously stirred. After the addition of $KMnO_4$, the mixture was left for 6 h for oxidation followed by addition of distilled water, H_2O_2. Then graphane oxide was washed in 5% HCl and distilled water and subjected to sonication for exfoliation of grapheme oxide layers and finally the suspension was obtained.

16.9 Synthesis of Silica-Based Nanomaterials

There are three main steps of making silica-based nanomaterials—(i) creating a nanoscale template, (ii) by deposition of silica precursors, a silica-based shell formed on the template, and (iii) removing the template by either high-temperature calcination or solvent dissolution, which creates a cavity inside the shell. The synthesis of this type of nanoadsorbent is divided into two types: one is the cavity-generating and another is the shell-forming method. Hard and soft templating, and the recently developed template-free syntheses are examples of cavity-generating techniques. To create the cavity in SNCs, a variety of soft (i.e., flexible solid, liquid, and gaseous) and hard (i.e., rigid solid) templates have been used, including polymer latex and inorganic nanoparticles (NPs) as well as (micro) emulsion droplets, vesicles, micelles, polymer aggregates, and gas bubbles. Conversely, supramolecular-templated deposition techniques, reverse microemulsion, and Stöber techniques are examples of shell-forming processes (Zhang et al. 2015).

16.10 Synthesis of Metal-Based Nanomaterials

Several synthetic techniques have been devised for the creation of noble metal nanoparticles. Commonly there are two strategies: (i) electrochemical deposition and (ii) electroless deposition. The first one electrochemical deposition allows metallic ions to solidify and deposit on the cathode surface. Deposition of various metal and alloys such as Pt, Ag, Au, and Pd were reported in many studies (Gao and Zheng 2009; Xiao et al. 2008; He et al. 2004; Zhao et al. 2007). Apart from a few limitations, this procedure has many advantages like less time consumption and undesired by-products (Cioffi et al. 2011). In the electroless deposition method, metal cations undergo chemical reduction and become insoluble. The limitation of the electroless deposition procedure, in contrast to electrodeposition, is that metal ions can only be converted to metal nanoparticle NPs on a carbon nanotube support when their redox potential is greater than that of the carbon nanoparticles. As a result of lower redox potentials, Cu^{2+} and Ag^{+} cannot be reduced into metal nanoparticles on carbon nanoparticles through electroless deposition (Wu et al. 2011).

16.11 Synthesis of Nanocomposites

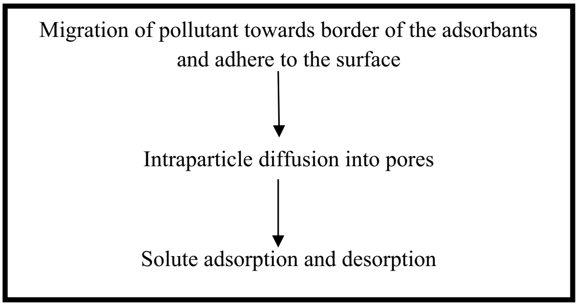
There are many methods of synthesizing nanocomposites. Polymer precursor method, vapor methodologies, sol–gel, colloidal and precipitation, and template synthesis have been widely used. But in the case of sol–gel technique, there are many factors affecting this like pH, solvent type, time, etc. Spray pyrolysis, vapor methodologies, and liquid metal infiltration are the most common types of methods for producing metal matrix nanocomposites (Camargo et al. 2009).

16.12 Role of Nanoadsorbents in Wastewater Management

16.12.1 Application of Carbon Nanotubes

The carbon nanotubes employed several mechanisms to remediate wastewater like adsorption, filtration, disinfection, etc. The adsorption method is an excellent method of water pollution remediation in which the pollutant adheres to the surface of

Fig. 16.2 A generalized method of pollutant adsorption



adsorbent without dispersing through it. The carbon nanotubes are of two types—single-walled and multi-walled. The single-walled nanotubes have comparatively small inner and outer diameters than multi-walled nanotubes (Carrales-Alvarado et al. 2020). Most importantly, those nanotubes which have a large surface area, are small in size and with a unique hollow structure may adsorb pollutants well. Figure 16.2 represents a schematic diagram of the adsorption technique. Due to the large surface area, high binding capacity multi-walled carbon nanotubes can easily bind to polycyclic aromatic hydrocarbons (PAHs). On the other hand, carbon nanotubes with smaller outer diameter adsorb microcystines. Oxidized multi-walled carbon nanotubes may eradicate the contamination of methyl orange (textile dye) from water. Carbon nanotubes purified with HNO_3 have the potential to reduce metal (lead) contamination from water (Chung et al. 2022).

The filtration method generally membrane filtration has been used extensively for drinking water treatment. For a number of reasons, including their adjustable pore size, potent antimicrobial activity, and greater water flux compared to other porous materials, carbon nanotubes are used in membrane filtering (Liu et al. 2012). When CNTs are mixed with membrane materials—also referred to as the general CNT membrane—they create an active adsorption layer that traps pollutants from wastewater, such as organic and heavy metal pollutants. Furthermore, because CNTs are a component of the membrane materials, they won't be discharged into the effluent. Another type of carbon nanotube filter is called an electrochemical filter, in which the carbon nanotubes are mixed with an anodic filter to break down organic contaminants and render bacteria inactive. Electrochemical oxidation degradation is the mechanism derived from this kind of membrane filter, in which organic pollutants are oxidized when they come into touch with the anode filter because they lose electrons (Song et al. 2018).

Moreover, in disinfection process carbon nanotube membrane has been utilized to eliminate residues. As was previously reported, the bacteria have been rendered inactive by the use of nanotubes in membrane technology (Song et al. 2018). Carbon nanotubes have the ability to disrupt the bacterial cell wall and membrane, allowing them to enter the cell body to damage DNA and cause malfunctioning proteins. Their size and form have an impact on their antibacterial potential. Such brief carbon nanotube adhesions to the cell surface will rupture the cell membrane and allow intracellular components to seep out (Song et al. 2018; Liu et al. 2018). The chemical reaction takes place when bacterial cell wall and the components of carbon nanotubes interact and give rise to reactive oxygen species (ROS). These ROS damage DNA and protein.

16.12.2 Application of Graphane Oxide

Organic pollutants such as polycyclic aromatic hydrocarbons, or PAHs, are created by both natural and anthropogenic processes linked to urbanization and industrialization (Qiao et al. 2018). Graphane oxide, due its excellent physicochemical properties, has been extensively used for PAHs removal from water. The treatment of polycyclic aromatic hydrocarbons has revealed remarkable potentials and applications for the aggregation and effective removal of PAHs using GO and GO-based nanomaterials. Adsorption is a multi-step process where molecules or adsorbates from the liquid phase are attracted to the solid phase. By regulating the creation of hydrogen bonds or the electrostatic interactions with contaminants, the oxygen-containing functional groups on the GO surface influence the adsorption capabilities for hydrophilic pollutants. Because of the availability of π–π stacking or hydrophobic interactions, the degree of GO reduction also affects the adsorption of hydrophobic chemical molecules like PAHs (Fan et al. 2012).

16.12.3 Application of Silica-Based Nanomaterials for Removal of Contaminants from Water

Four oxygen atoms bind the silicon atom, which remains in the middle of the tetrahedral structure of silica (SiO_2). SiO_2 nanoparticles are unique materials having large surface areas, superior chemical reactivity at the surface, thermal stability, and a porous framework. A removal effectiveness of more than 90% was noted for SiO_2 in the removal of Cu ions and blue 3 dye from aqueous solutions (Elbarbary and Gad 2021). In 2019, Wang et al. (2019) investigated the use of SiO_2 in the extraction of oils from wastewater and discovered that the materials have an efficiency of more than 99.9% for the efficient separation of different kinds of oil/water combinations. This is because of its exceptional hydrophilicity/hydrophobicity, surface wettability, and chemical and mechanical soundness.

16.12.4 Application of Metal-Based Nanomaterials

Nanoscale ferric oxides are inexpensive adsorbents for the sorption of hazardous metals due to their easy manufacturing and resource accessibility. Goethite is an effective sorbent for metal cations due to its chemical makeup and large specific surface area. Grossl et al. (1994) used the pressure-jump (p-jump) relaxation approach, which yields both kinetic and mechanistic information for events taking place on millisecond time scales, to assess the kinetics of Cu^{2+} adsorption/desorption on/from goethite. From 4.5 to 5.5, the adsorption of Cu (II) increased as pH rose. Because of their larger specific surface area and polymorphism architectures, manganese oxide nanoparticles have better adsorptive performance than their bulk counterpart. They have been used for decades to remove cationic or anionic contaminants from natural waters, including as phosphate, arsenate, and heavy metal ions (Hua et al. 2012). Al_2O_3, or alumina, is a commonly used adsorbent for heavy metals. It is predicted that γ-Al_2O_3 will have a higher adsorptive activity than α-Al_2O_3. These have an ability to remove trace Pb (II), Cr (III), Cd (II), Ni (II), Co (II), and Mn (II) (Yang et al. 2010). One of the cutting-edge oxidation techniques utilized to address environmental problems with pollutant management is photocatalysis (Zhao et al. 2016). It has to do with the utilization of reactive species, including OH radicals, to mineralize contaminants in wastewater by creating a catalyst by photon-induced creation of the reaction. Zinc oxide nanoparticles can degrade several dyes like methylene blue, rhodamine, congo red, malachite green, eosin Y, methyl orange, and metals such as cadmium and chromium (Aremu et al. 2021).

16.13 Conclusion

To live well, one must have access to clean drinking water. Water will always be used at a certain rate for a variety of uses, including residential, commercial, and agricultural. The contaminants are added to the several water sources as a result of population growth and industrialization. This has raised serious questions about how to manage water sources in order to lessen environmental crises. Previous researchers have used a variety of treatment techniques, including conventional treatments, but the degradation of pollutants in wastewater has been seen as being slow, costly to manage, partial in terms of removability efficiency, and producing new pollutants. It is thought that nanotechnology is a revolutionary technique that is crucial to fully mineralizing contaminants in wastewater. The application of various nanomaterials like carbon nanotubes, metal oxides, and graphane have a positive impact on the environment by reducing the pollution in water.

Acknowledgements The financial support from University Grants Commission under NET-JRF scheme is duly acknowledged.

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Chapter 17
Engineered Nanomaterials and Associated Threats in the Environment: Risk Assessment Strategies

Suneha Shukla, Sandhya Maurya, Anushka Srivastava, Umesh Jadhav, and Garima Gupta

Abstract Engineered nanomaterials (ENMs) have transformed a number of industries, thanks to their special qualities and capabilities. However, worries over their possible effects on the environment have been raised by their growing production and extensive use. An overview of risk assessment techniques for ENMs and the related environmental risks is given in this chapter. The aspects of ENMs that affect their behavior in the environment are discussed, including size, shape, and surface features. Comprehensive analyses are performed on the risk characterization, exposure assessment, toxicity assessment, and environmental destiny of ENMs. This chapter's foremost aim is to discuss the regulatory frameworks, new developments in the industry, and methods for risk management and reduction. The applicability of risk assessment approaches to particular ENMs is demonstrated through the presentation of case studies in the present work.

Keywords Nanoparticles · Risk assessment · Hazards · Regulatory frameworks

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S. Dey and M. P. Shah (eds.), *Biotechnological Removal of Emerging Pollutants from Wastewater Systems*, Advances in Wastewater Research,
https://doi.org/10.1007/978-981-96-3945-8_17

17.1 Introduction

17.1.1 Definition of Engineered Nanomaterials

Engineered nanomaterials (ENMs) are intentionally created materials that have at least one dimension within the range of 1–100 nm. ENMs, or engineered nanomaterials, frequently display distinct characteristics that deviate considerably from their larger forms. These traits encompass enlarged surface area, quantum phenomena, and improved mechanical, electrical, or optical attributes. The unique characteristics of ENMs make them extremely important in a wide range of applications, such as electronics, medicine, environmental remediation, and materials research (Bhattacharya et al. 2017).

The manufacturing of ENMs utilizes advanced methods such as chemical vapor deposition, sol-gel processes, and laser ablation, which allow for accurate manipulation of the material's dimensions, morphology, and surface properties. These techniques enable the customization of ENMs to accomplish precise purposes, such as enhancing medication delivery systems, improving catalytic activity, and increasing the efficiency of energy storage devices (Batley et al. 2013).

ENMs are classified according to their composition and structure, encompassing carbon-based nanomaterials (such as carbon nanotubes and fullerenes), metal-based nanomaterials (such silver or gold nanoparticles), and polymer-based nanomaterials. Every category has distinct characteristics that may be utilized for different technological breakthroughs. Carbon nanotubes are renowned for their remarkable strength and electrical conductivity, rendering them well suited for use in electronics and composite materials. Nevertheless, the swift advancement and use of ENMs also give rise to apprehensions regarding their possible environmental, health, and safety hazards. ENMs, because of their diminutive size, can readily traverse cellular membranes, potentially resulting in uncharted toxicological consequences. Consequently, continuous research is being conducted to examine the consequences of ENMs on human health and the environment, and regulatory frameworks are being established to appropriately oversee their production and utilization (Oberdörster et al. 2005) (Fig. 17.1).

17.1.1.1 Properties of Engineered Nanomaterial

Engineered nanomaterials (ENMs) exhibit a wide range of sizes and compositions, typically from 1 nm to several micrometers. Common examples include carbon-based materials like single-walled carbon nanotubes (SWCNTs), multi-walled carbon nanotubes (MWCNTs), graphene, and fullerenes (e.g., C60). Additionally, metal and metal oxide-based compounds such as cadmium, gold, silver, and titanium dioxide are prevalent among ENMs. Carbon-based ENMs can take various forms, including SWCNTs, MWCNTs, graphene, and fullerenes, while metal and metal oxide ENMs

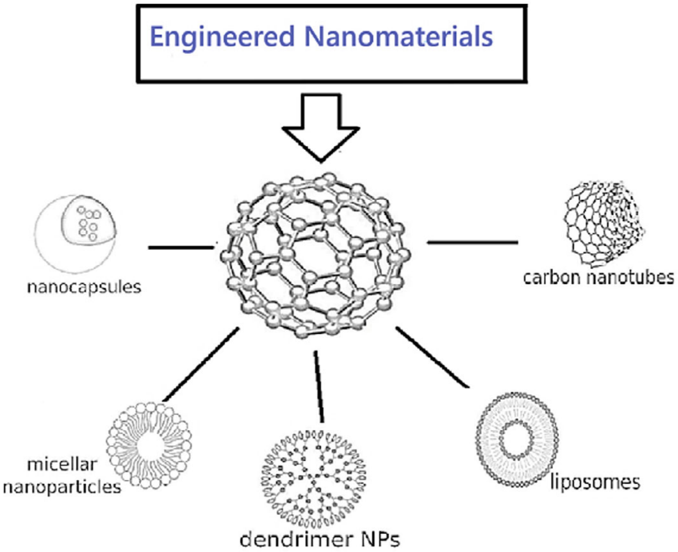


Fig. 17.1 Types of engineered nanomaterials

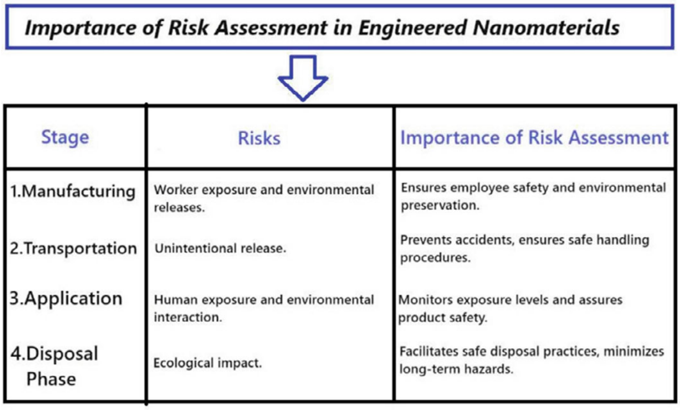
encompass substances like alumina, ceria, silica, titania, and zinc oxide (Rao et al. 2015; Mendoza and Brown 2019). Here are some properties:

A. Size and Composition: ENMs vary greatly in size and composition, ranging from 1 nm to several micrometers. Common examples include carbon-based materials (SWCNTs, MWCNTs, graphene, fullerenes) and metal/metal oxide compounds (cadmium, gold, silver, titanium dioxide) (Rao et al. 2015; Mendoza and Brown 2019).
B. Structural Variations: Carbon-based ENMs come in various forms, including SWCNTs, MWCNTs, graphene, and fullerenes. Metal and metal oxide ENMs include materials such as alumina, ceria, silica, titania, and zinc oxide (Rao et al. 2015; Mendoza and Brown 2019).
C. Contaminants and Impurities: ENMs may contain impurities like residual metal catalysts, which can enhance toxicity. The physicochemical properties of ENMs can alter over time due to factors such as agglomeration, influencing stability and reactivity (Rao et al. 2015).
D. Biological Interaction: Due to their small size, ENMs can interact with cellular components like enzymes, potentially disrupting biological functions.
E. Characterization Challenges: The well-defined nature of ENMs poses challenges for accurately estimating their toxicological and biological effects, complicating safety assessments (Rao et al. 2015; Mendoza and Brown 2019; Schwirn et al. 2020).

17.1.2 Importance of Risk Assessment Strategies

The need for strong risk assessment procedures has become more apparent as a result of the environmental hazards presented by artificial nanomaterials (NMs). Conventional regulatory risk assessment frameworks, which are intended to evaluate the dangers of traditional chemicals, frequently fail to adequately include the distinct properties of nanomaterials (NMs). These materials possess unique characteristics, such as being extremely small in size, having a huge surface area, and displaying modified reactivity. These traits can impact how they behave in various parts of the environment. Furthermore, the possible influence of NMs on vulnerable species, particularly those with distinct ecological functions, requires a reassessment of current risk assessment approaches. Failure to sufficiently account for these distinct characteristics increases the likelihood of underestimating the environmental risks associated with NMs, perhaps resulting in unforeseen ecological ramifications (Maynard et al. 2006). In order to tackle these issues, it is crucial to create novel tools and procedures that are specially designed for evaluating dangers related to nanomaterials. An essential element of this progress is the precise depiction of material characteristics, which must be beyond mere chemical composition and encompass variables such as particle size distribution, shape, surface charge, and aggregation state. Additional exposure models are required to accurately forecast the behavior of NMs in different environmental settings, encompassing their transportation, longevity, and alteration. These models must consider the dynamic interactions between NMs and environmental media, such as water, soil, and air, which can greatly affect their bioavailability and toxicity (Oberdörster et al. 2005). Furthermore, an enhanced comprehension of species susceptibility is essential for appropriately evaluating the ecological hazards of nanomaterials. This involves the identification of the species that are most susceptible to exposure to NM and the determination of the precise mechanisms via which these materials cause their toxic effects. The investigation of species-specific reactions to NMs will provide valuable insights for the creation of more precise risk assessment methodologies, which will enhance the protection of vulnerable ecosystems (Handy et al. 2012).

The suggested Environmental Risk Assessment (ERA) technique aims to meet these requirements by specifically analyzing hazards associated with the whole lifespan of NMs, with a particular focus on processes driven by exposure. This technique is crucial for the early detection of possible hazards during the development of NMs, therefore guaranteeing the preservation of environmental safety from the original design phases till disposal. The ERA technique incorporates the most recent scientific breakthroughs in various essential areas: material characterization, release, destiny, exposure, hazard, and risk characterization. The ERA plan intends to create a comprehensive framework for evaluating the environmental hazards of NMs, guaranteeing their safe use, and successfully satisfying regulatory requirements by combining the latest research in these areas (Hartmann et al. 2014). This comprehensive strategy not only improves our capacity to forecast and alleviate the ecological consequences of NMs but also promotes the advancement


Importance of Risk Assessment in Engineered Nanomaterials

Stage	Risks	Importance of Risk Assessment
1.Manufacturing	Worker exposure and environmental releases.	Ensures employee safety and environmental preservation.
2.Transportation	Unintentional release.	Prevents accidents, ensures safe handling procedures.
3.Application	Human exposure and environmental interaction.	Monitors exposure levels and assures product safety.
4.Disposal Phase	Ecological impact.	Facilitates safe disposal practices, minimizes long-term hazards.

Fig. 17.2 Importance of risk assessment in engineered nanomaterials

of safer nanotechnology applications. The ERA strategy comprehensively assesses the possible hazards of NMs at every phase of their lifecycle, guaranteeing that environmental factors are fully incorporated into the development and implementation of nanomaterials, ultimately promoting more sustainable technological progress (Fig. 17.2).

17.1.2.1 Engineered Nanomaterial Risk Assessment Strategies

A growing number of sectors use engineered nanomaterials (ENMs) because of their special qualities and prospective uses. But the introduction of these materials also brings up serious issues related to the environment and human health, which calls for effective risk assessment techniques. To ensure safety and compliance with regulatory frameworks, this chapter examines the frameworks and methodology for analyzing hazards related to ENMs (Oomen et al. 2018).

Understanding Engineered Nanomaterials: Materials that have at least one dimension less than 100 nm are referred to as ENMs. Because of their unique physical and chemical characteristics, despite their small size, they are useful in fields including environmental cleanup, electronics, and medicine. However, evaluating their possible dangers to the environment and human health is made more difficult by their distinctive qualities (Oomen et al. 2018; Schulte et al. 2014).

17.1.2.2 Importance for ENMs

a. **Health and Safety:** Understanding the potential health effects of Enzymes and Natural Minerals (ENMs) in consumer products is crucial for worker and consumer protection, as exposure can lead to respiratory issues and other toxicological effects (Oomen et al. 2018).

b. **Regulatory Compliance:** Regulatory bodies like OECD and EU mandate risk assessments for new materials before marketing, emphasizing the need for standardized testing protocols for ENMs to ensure regulatory compliance and public safety (Joseph 2023).
c. **Environmental Protection:** ENMs can enter various environmental compartments, potentially affecting ecosystems. Assessing their environmental fate and effects is crucial to mitigating wildlife and habitat risks (Yetisgin et al. 2020).

17.1.2.3 Frameworks for Risk Assessment

Frameworks have been developed to facilitate the risk assessment of ENMs. These frameworks typically encompass the following components. Hazard Identification is the process that involves assessing the potential adverse effects of ENMs by characterizing their physicochemical properties, which may impact their behavior and possible toxicity in the biological systems (Yetisgin et al. 2020) and exposure assessment, in this stage, the possibility and degree of environmental or human exposure to ENMs are assessed. It considers variables including how long ENMs last in the environment, how they are released into the air, and how exposure occurs (e.g., inhalation, dermal contact) (Joseph 2023).

- **Risk Characterization**

To calculate the danger that ENMs pose, this phase combines exposure and hazard evaluations. To forecast environmental concentrations and possible impacts on ecosystems and human health, it frequently uses models (Yetisgin et al. 2020).

- **Decision-Making Frameworks:** To assist risk managers in making well-informed decisions on the usage and regulation of ENMs, several decision-making tools have been put forth. Among these are testing schemes that assign resources according to the possible degrees of risk connected to certain ENMs (Scott-Fordsmand et al. 2017; Joseph 2023).

17.1.2.4 Challenges in Risk Assessment

Despite the development of risk assessment frameworks, several challenges remain:

- **Data Gaps:** Risk evaluations are made more difficult by the lack of appropriate information on the toxicity and environmental behavior of many ENMs. This lack of data may make it difficult to appropriately assess hazards (Joseph 2023; Oomen et al. 2018).
- **Dynamic Nature of Nanomaterials:** The dynamic nature of nanomaterials makes it challenging to forecast their long-term consequences since environmental interactions might cause changes in the characteristics of ENMs over time. To deal with

these uncertainties, adaptive risk management techniques and ongoing monitoring are required (Scott-Fordsmand et al. 2017).

- **Regulatory Heterogeneity:** There may be differences in the laws governing ENMs between nations and regions, which makes it difficult to standardize risk assessments and ensure worldwide compliance. It is imperative to harmonize these rules to effectively manage risks (Joseph 2023; Yetisgin et al. 2020).

17.1.2.5 Significance in Risk Assessment

- **Human Significance:** Nanoparticles can enhance medical therapies through targeted drug delivery and advanced imaging techniques. However, they also pose health risks, including respiratory issues, cardiovascular problems, and potential neurotoxicity. Research highlights that while nanoparticles improve treatment efficacy, their safety profiles must be carefully evaluated due to associated toxicological concerns (Mitchell et al. 2021).
- **Plant Significance:** In agriculture, nanoparticles can boost productivity by improving nutrient delivery and pest management. Nevertheless, they may disrupt plant growth, photosynthesis, and reproductive processes, necessitating a thorough understanding of their ecological impacts.
- **Environmental Significance:** Nanoparticles hold promise for environmental remediation and pollution control, yet their release can lead to soil and water contamination, threatening ecosystems and biodiversity. Studies emphasize the need for careful monitoring of nanoparticle interactions within environmental systems to mitigate potential adverse effects (Mitchell et al. 2021).

17.2 Environmental Exposure and Fate of Engineered Nanomaterials

The environmental changes caused by ENM are significantly influenced by the chemical composition, physical properties, and additives present. For instance, factors such as soil pH (Schlich and HundRinke 2015), temperature, organic matter content, and dispersing agents in water-based solutions can have a profound impact (Adeleye and Keller 2016).

The agglomeration pattern of engineered nanomaterials (ENMs) is influenced by the ionic strength and organic compound content of the media. This effect occurs via affecting the surface chemistry of ENMs, which frequently leads to a reduction in the quantity and concentration of nanoparticles (NPs). As a result, there is a decrease in the interaction between NPs and cells, leading to a drop in the specific toxicity of NPs (Wang et al. 2015).

Studies show that the destiny of engineered nanomaterials (ENMs) is strongly influenced by their physical and chemical characteristics, including their size, shape, surface charge, and coating, as well as the surrounding environmental circumstances. Nevertheless, there is a substantial lack of information regarding the extended environmental behavior of engineered nanomaterials (ENMs), particularly in real-world environmental circumstances. Additional research is required to clarify the processes that control the environmental destiny of engineered nanomaterials (ENMs) and to create prediction models that can inform their safe design and utilization (Keller et al. 2012). To tackle these difficulties, a multidisciplinary strategy that combines nanotechnology, environmental science, and toxicity is necessary (Batley et al. 2013).

17.2.1 Sources of Engineered Nanomaterials in the Environment

The sources of engineered nanomaterials encompass various manufacturing techniques used in their production, including vapor/aerosol, liquid, and solid phase synthesis methods (Virji and Stefaniak 2014). Additionally, these materials are commonly incorporated into numerous consumer products, which can lead to their eventual release into the environment (Virji and Stefaniak 2014; Yang and Westerhoff 2014). Emission of ENMs into the atmosphere occurs through indirect or diffuse sources, such as industrial processes, combustion, and degradation of items containing nanomaterials. It can also occur through direct sources, such as purposeful application or accidental spills (Virji and Stefaniak 2014).

17.2.2 Transport and Transformation of Engineered Nanomaterials

The widespread use of engineered nanomaterials (ENMs) in several industries, including disinfectants and electronics, leads to their inevitable release into the environment. This can result in the accumulation of ENMs and subsequent environmental pollution (Loureiro et al. 2018).

Engineered nanomaterials can be introduced into the environment through many pathways, such as the release of industrial waste, the discharge of wastewater, and the disposal of consumer items that include nanoparticles (Loureiro et al. 2018). Once introduced into the environment, these nanomaterials can experience a range of physical and chemical changes, including coming together, forming clusters, dissolving, and interacting with both organic and inorganic substances. These activities can greatly modify the behavior, bioavailability, and possible toxicity of nanomaterials to soil organisms and the food chain (Loureiro et al. 2018; Gardea-Torresdey et al. 2014). Existing pollutants in the environment can reduce the bioavailability of nanomaterials by causing them to aggregate with other substances, be absorbed, or form complexes.

Table 17.1 Main sources of nanomaterials in the environment

Natural sources	Types	Incidental sources	Engineered nanoparticles
Air	Volcanic eruption	Combustion processes	Nanotechnology-production processes
	Hydrothermal vent systems	Industrial emissions	
	Physicochemical wearing of rocks and dust volatilization		
	Biological processes		
	UV degradation from aquatic systems		
	Nucleation processes		
Water	Metal-sulfide nanoclusters	Deposition from atmosphere	Spillage from nanotechnology
	Hydrous iron		
	Manganese oxide		
Soil	Nanominerals (e.g., ferrihydrite)	Deposition from atmosphere	Spillage from nanotechnology
	Natural organic-material aggregates	Sorption and transport from aquatic systems	
	Biogenic origin (e.g., uraninite)		

However, these contaminants can also affect the way nanomaterials behave, move, and become toxic in a way that is mutually beneficial (Joo and Zhao 2017).

The water quality factors and physicochemical qualities of these ENMs significantly affect their bioavailability and toxicity, as shown by their colloidal behavior (Chung et al. 2021; Callaghan and MacCormack 2017) (Table 17.1).

17.3 Risk Assessment Approaches for Engineered Nanomaterials

Engineered nanomaterials (ENMs), known for their unique physical and chemical properties, are in many areas such as health care, energy, and electronics. Various materials have enabled notable progress in various domains, providing inventive solutions in areas such as medicine delivery systems, energy storage, and electronic device downsizing. Nevertheless, the swift growth of ENMs' utilization has also raised significant worries over their possible ecological and physiological effects. The need for implementing thorough risk evaluation procedures that can effectively meet the specific issues presented by ENMs has been emphasized by these concerns (Fadel et al. 2015; Hristozov and Malsch 2009).

The complicated interaction between nanoparticles and biological systems and the environment poses considerable difficulties in creating reliable risk assessment frameworks. ENMs, or engineered nanomaterials, can display unique characteristics at the nanoscale that differ from traditional materials. These qualities include heightened reactivity, improved permeability, and modified biological activity. However, these distinctive attributes make it more challenging to assess the risks associated with ENMs. The unique characteristics of engineered nanomaterials (ENMs) provide challenges in accurately predicting their environmental fate, bioavailability, and toxicity using conventional risk assessment methods (Alvarez 2006; Schwirn et al. 2020). An essential component of the risk assessment procedure for engineered nanomaterials (ENMs) is the comprehensive characterization of the nanomaterial itself. This step serves as the basis for evaluating its destiny, exposure, and related dangers. Comprehensive characterization entails a thorough analysis of the physicochemical features of the material, encompassing its dimensions, morphology, surface chemistry, and tendency to aggregate. These features are essential since they have a substantial impact on the way the material interacts with living beings and the environment (Scott-Fordsmand et al. 2017; Schwirn et al. 2020). Developing precise exposure measures and testing procedures especially tailored for nanoparticles is crucial, in addition to material characterization. Conventional techniques employed for studying materials on a broader scale may not accurately account for the intricate interactions of nanomaterials, which might result in the underestimating or incorrect characterization of possible dangers (Fadel et al. 2015; Shatkin et al. 2010). The progress in informatics and computer modeling provides exciting opportunities to improve risk assessment in this domain. These technologies have the ability to replicate the actions of ENMs in different environmental and biological situations, offering useful knowledge that can direct experimental investigations and regulatory choices. By combining these sophisticated methodologies with empirical investigation, the domain of nanotoxicology and exposure science may be greatly expedited, resulting in more precise and complete evaluations of potential risks (Fadel et al. 2015).

17.3.1 Hazard Identification and Characterization

"Hazard identification" (HI) refers to the process of identifying the potentially harmful consequences that a drug is capable of causing. Until recently, the majority of the discourse around the environmental and health hazards of ENPs was seen as more conjectural than factual. Recent experimental research have revealed that exposure to specific engineered nanoparticles (ENPs) might result in detrimental health impacts in live beings. In 2007, Hansen et al. discovered 428 pieces of research documenting the toxicity of engineered nanoparticles (ENPs). This research reported unfavorable health effects from 965 tested engineered nanoparticles (ENPs) with different chemical compositions (Hansen et al. 2007).

Engineered nanomaterials present distinct difficulties in identifying and describing their potential dangers because of their intricate physical and chemical attributes, which can differ greatly depending on the manufacturing technique, surface alteration, clumping state, and environmental circumstances (Godwin et al. 2015). Traditional toxicological techniques developed for large-scale materials may not sufficiently assess the dangers associated with nanoparticles, thereby requiring the creation of new testing approaches (MacCuspie 2018).

An important factor to consider when identifying hazards associated with engineered nanomaterials is the possibility of inhalation exposure, which has the potential to cause negative health consequences (Hänninen et al. 2009). Engineered nanomaterials possess distinct toxicokinetic and biodistribution characteristics due to their small size, which can greatly impact their biological activity and risk of injury in comparison to larger materials. Assessing the physical and chemical attributes of nanomaterials, including their dimensions, configuration, tendency to clump together, and surface qualities, is essential for comprehending and forecasting their possible dangers (Tripathi et al. 2017). In addition, it is crucial to understand how nanoparticles interact with biological systems to evaluate their possible harmful effects and guarantee the safety of manufactured nanomaterials in different uses. For example, an examination of the harmful effects of quantum dots, a type of artificially created nanomaterials, has revealed that their capacity to harm is greatly influenced by their physical and chemical characteristics, as well as the specific environmental circumstances they come into contact with (Hardman 2006).

17.3.2 Exposure Assessment

Engineered nanomaterials (ENMs) are now essential in various industrial and consumer applications because of their distinct physicochemical qualities, including high surface area-to-volume ratios, increased reactivity, and distinctive electrical, optical, and mechanical characteristics. Nevertheless, the very characteristics that render ENMs so advantageous also contribute to their inherent environmental and health hazards. Nanomaterials (ENMs) can interact with the environment at many points in their life cycle, including as during the extraction of raw materials, production, transportation, storage, industrial processing, consumer use, trash disposal, and recycling (Esposito et al. 2021). Each of these processes offers unique routes via which ENMs might be discharged into the environment, thereby amplifying the potential for workers, consumers, and ecosystems to be exposed to them.

The growing utilization of engineered nanomaterials (ENMs) has raised significant apprehensions over their possible detrimental impacts on human health and the environment. ENMs, or engineered nanomaterials, possess unique characteristics such as tiny size and strong reactivity that allow them to interact with biological systems and environmental matrices in ways that are yet not completely comprehended (Samet 2014). Studies have shown that carbon-based and metal-based engineered nanomaterials (ENMs) can build up in sediments and agricultural soils, especially in regions where biosolids are used as fertilizers. The buildup of this substance can have an impact on plants in several ways, including their physiological, biochemical, nutritional, and genetic aspects. This can result in decreased crop yields or changes in the overall health of the plants (Zuverza-Mena et al. 2017).

Although there is an increasing amount of study, there are still important gaps in our knowledge of the behavior of ENMs under complex and dynamic environmental conditions. The interactions between engineered nanomaterials (ENMs) and biological organisms are governed by several linked physicochemical parameters, including chemical composition, size, shape, surface properties, and aggregation state (Pérez-Hernández et al. 2025). These elements collectively govern the environmental destiny, conduct, and harmfulness of ENMs, rendering it difficult to precisely anticipate their effects.

To tackle these difficulties, it is essential to embrace a holistic, system-level strategy that takes into account the whole life cycle of ENMs—from their creation to their disposal. An effective strategy would entail the amalgamation of diverse scientific fields such as toxicology, environmental science, chemistry, and materials science. This integration would be aimed at constructing predictive models that may guide the secure and sustainable advancement of nanotechnology (Esposito et al. 2021). This method tries to eliminate possible dangers before they become substantial problems by concentrating on the complete life cycle of nanotechnology. It ensures that the advantages of nanotechnology may be achieved without compromising human and environmental health.

17.3.3 Toxicity Assessment

Engineered nanomaterials (ENMs) are widely used in many industrial and consumer applications, which has led to substantial concerns over their possible environmental risks. The assessment of Environmental Nanomaterial (ENM) toxicity in the environment requires a thorough examination of their impact on several ecological indicators, such as aquatic creatures, terrestrial plants, and microbes. Aquatic species, including fish and invertebrates, are especially susceptible to engineered nanomaterials (ENMs) because they are consistently exposed to particles present in water. Terrestrial ecosystems may experience the absorption of engineered nanomaterials (ENMs) by plants through their roots, which might result in the buildup of these materials in their bodies and cause toxicity. This, in turn, has the potential to alter the food chains within these ecosystems. Microorganisms, which have a vital role in the cycling of nutrients and other processes within ecosystems, may also experience negative effects from engineered nanomaterials (ENMs), leading to wider ecological impacts (Handy et al. 2012). Advancements in toxicological research, such as the combination of high-throughput screening methodologies with omics technology, have greatly improved our comprehension of the molecular pathways that cause toxicity in engineered nanomaterials (ENMs). Omics methodologies, such as genomics, proteomics, and metabolomics, offer an extensive understanding of the biological processes impacted by exposure to engineered nanomaterials (ENMs), hence aiding in the discovery of biomarkers that indicate toxicity. In addition, the increasing utilization of environmental modeling tools enables the anticipation of the destiny and movement of engineered nanomaterials (ENMs) in various ecosystems. This assists in evaluating possible risks and facilitating regulatory decision-making (Handy et al. 2012). These advancements are crucial for enhancing our capacity to mitigate the hazards linked to the extensive utilization of ENMs.

17.4 Current Challenges and Future Directions

Engineered nanomaterials (ENMs) are increasingly being used in many sectors because of their distinct physicochemical features. Nevertheless, the extensive utilization of these substances poses notable environmental obstacles, namely concerning their environmental destiny, transportation, and possible toxicity. An important issue is the limited comprehension of the behavior of engineered nanomaterials (ENMs) in several environmental matrices, including soil, water, and air. The interaction between engineered nanomaterials (ENMs) and these matrices might result in aggregation, dissolution, or chemical changes, affecting their movement, availability to living organisms, and harmfulness. Research has demonstrated that modifying the surface of nanoparticles may greatly impact how they behave in the environment. However, accurately forecasting these changes is difficult since natural systems are complicated (Klaine et al. 2012).

Furthermore, the existing techniques for identifying and measuring engineered nanomaterials (ENMs) in the environment are insufficient. Conventional analytical methods sometimes struggle to distinguish between artificially created nanoparticles and naturally existing particles at the nanoscale, resulting in uncertainty when evaluating potential risks (Lead et al. 2018). There is an urgent requirement for the creation of sophisticated analytical techniques that can precisely detect and measure engineered nanomaterials (ENMs) in complicated environmental samples. The implementation of techniques such as single-particle inductively coupled plasma mass spectrometry and field-flow fractionation paired with different detectors has shown potential. However, their use is currently restricted due to their high prices and technical difficulties (Tiede et al. 2008).

Another crucial concern is the potential toxicity of engineered nanomaterials (ENMs) to both aquatic and terrestrial creatures. ENMs, due to their tiny size and strong reactivity, can lead to oxidative stress, cellular damage, and even death in organisms that are exposed to them (Handy et al. 2008). Nevertheless, the toxicity of engineered nanomaterials (ENMs) is greatly influenced by factors such as their chemical composition, size, shape, surface charge, and the presence of other environmental pollutants. This variability makes it challenging to draw broad conclusions that apply to all types of ENMs (Nel et al. 2006).

The inquiry should emphasize the creation of standardized protocols for evaluating the adverse impacts and ecological monitoring of engineered nanomaterials (ENMs). The lack of standardized testing techniques and regulatory restrictions has led to incomplete data, making it challenging to precisely evaluate the hazards linked to ENMs. Standardization is essential to ensure that toxicological data can be compared and relied upon across various research. The task would need the establishment of standardized approaches to assess the physicochemical characteristics of engineered nanomaterials (ENMs), as well as their behavior in the environment and their impact on living organisms. The Organisation for Economic Co-operation and Development (OECD) has been developing recommendations to test chemicals, including nanomaterials, in order to provide a more unified method for assessing risks (OECD 2012). These endeavors are crucial in establishing a cohesive structure that can facilitate regulatory decision-making and guarantee the secure implementation of nanotechnology.

Moreover, there is an urgent want for multidisciplinary investigation that combines nanotechnology, environmental science, and toxicology in order to comprehensively comprehend the intricate interplay between ENMs and the environment. Nanomaterials can display distinct behaviors as a result of their extremely small size, perhaps resulting in unexpected ecological effects. By integrating knowledge from these many disciplines, scientists may create more holistic models that forecast the behavior of engineered nanomaterials (ENMs) in various environmental settings and their interactions with biological systems. Research has demonstrated that the environmental changes experienced by engineered nanomaterials (ENMs) can greatly impact their toxicity. This emphasizes the need to take environmental aspects into account when conducting toxicological evaluations (Lowry et al. 2012).

Tackling these obstacles is essential for guaranteeing the safe and enduring utilization of nanotechnology. To effectively manage possible hazards and optimize the advantages of ENMs in different applications, it is crucial to take proactive steps such as implementing standardized evaluation methods and fostering multidisciplinary research collaborations. This method will ensure the responsible progress of nanotechnology, protecting both the environment and human health.

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Chapter 18
Innovative Treatment Options for the Removal of Emerging Pollutants from Wastewater

Deeptimayee Pal and Sujit Sen

Abstract The increasing prevalence of emerging pollutants in wastewater treatment necessitates investigating advanced and scientifically innovative treatment methods. Implementing novel approaches is crucial in addressing the complex chemical compositions and persistent characteristics of emerging pollutants, such as those found in pharmaceuticals, personal care items, and industrial chemicals. Advanced Oxidation Processes (AOPs), such as photocatalysis and ozonation, use potent oxidizing agents to break down the emerging pollutant complexes. Membrane-based technologies, such as nanofiltration and reverse osmosis, facilitate the precise segregation of pollutants by exploiting their molecular size, hence aiding in removing refractory compounds. Simultaneously, nanotechnology interventions include the deliberate use of nanoparticles for specific adsorption or catalytic degradation, offering an advanced and efficient method of removing emerging pollutants. These novel treatment alternatives demonstrate the scientific community's dedication to tackling emerging contaminants. It emphasizes the necessity for collaborative research and technological progress to effectively and accurately address the complexities of modern wastewater treatment.

Keywords Emerging pollutants · Wastewater treatment plants · Advanced oxidation processes · Membrane filtration · Nanotechnology

18.1 Introduction

The rapid advancement of industry and urbanization has brought environmental degradation to the forefront of worldwide issues. With society's advancement, environmental quality deterioration has emerged as a growing and critical challenge. Many pollutants, including persistent inorganic chemicals like heavy metals

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S. Dey and M. P. Shah (eds.), *Biotechnological Removal of Emerging Pollutants from Wastewater Systems*, Advances in Wastewater Research,
https://doi.org/10.1007/978-981-96-3945-8_18

and organic substances like pharmaceuticals, personal care items, pesticides, and endocrine-disrupting agents, are widespread and pose significant global dangers. Pollution is a complex and critical issue beyond ecosystems and threatens human health, requiring immediate and coordinated global efforts (Bunke et al. 2019). The continuous growth of human activities across several sectors, such as industry, agriculture, healthcare, and transportation, has resulted in a significant increase in the production and utilization of chemicals known as "emerging pollutants (EPs)" or "contaminants of emerging concern." These compounds have spread rapidly in the environment due to uncontrolled urbanization, industrial expansion, and the essential role of healthcare practices in promoting human well-being. EPs refer to a wide range of synthetic, persisting organic substances previously not given much attention in environmental monitoring. Nevertheless, these pollutants present substantial hazards to ecological systems and human well-being. This wide range of compounds, crucial for the proper functioning of contemporary society, can negatively impact the stability of the environment and the health of living beings (Gavrilescu et al. 2015).

EPs in water are mainly determined by use patterns, individual water consumption, watershed features (such as population density and land use), sewer conditions, and environmental persistence. Although present in relatively low quantities, usually ranging from nanograms per liter (ng/L) to micrograms per liter (μg/L), extended exposure to EPs may significantly harm ecosystems' health and long-term viability. Recent research has shown that discharging EPs (emerging contaminants) into water bodies without proper treatment presents substantial hazards. The issue is worsened by ineffective laws and a lack of complete information on the destiny and harmfulness of EPs, resulting in their uncontrolled release (Xiang et al. 2021).

18.2 Sources and Fate of EP

EPs come from several sources, both specific and widespread, and may infiltrate the soil, atmosphere, or aquatic bodies via numerous routes. The functioning of these processes relies heavily on the specific attributes of EPs, including their polarity, volatility, and persistence, as well as the features of the environmental compartments they move through (Geissen et al. 2015). EPs and their byproducts are discharged into the environment via industrial operations, domestic refuse, hospital effluent, and agricultural methods, ultimately infiltrating surface and groundwater. EPs are found in surface and groundwater systems. The concentrations of EPs in surface waters are typically lower than those observed directly downstream of wastewater and sewage treatment plant discharges due to dilution and natural degradation mechanisms. Surface waters often contain greater concentrations of EP than groundwater due to direct discharges from wastewater treatment plants (WWTPs) and shorter residence durations. Elevated groundwater concentrations may occur, especially when the aquifer is close to sources of pollution. Research has shown significant variation in the presence of PPCPs in surface waters. The diversity seen may be attributed to variations in the frequency of consumption, doses administered, and the efficiency of WWTP systems in various geographical areas. Various variables impact the transportation, destiny, and prevalence of EPs. These factors include the physicochemical characteristics of the environment and water, as well as geographical parameters like longitude and latitude. Furthermore, the specific pollution source substantially impacts both the amounts of exposure and the characteristics of the chemicals (Stefanakis and Becker 2015). Figure 18.1 depicts the source and possible routes of EPs when they are discharged into the air and released into different receptors, such as groundwater, surface water, and drinking water.

PPCPs refer to a diverse array of substances, which include cosmetics and healthcare items such as over-the-counter medications, vitamins, and prescription pharmaceuticals. These contaminants often infiltrate community water systems and soil via leaching from agricultural manure or effluent from sewage treatment facilities. The pharmaceutical sector has a substantial role in functioning WWTPs (Palli et al. 2019). A study conducted in the Ter River, Catalonia, Spain, suggests that the influence of WWTP effluent on the river's total pollution is insignificant compared to the extensive occurrence of diverse chemicals. Studies conducted on groundwater in Cape Cod, Massachusetts, have identified residential and industrial sewage systems and on-site wastewater treatment from nursing homes and healthcare facilities as major contributors to EPs. Triclosan, a compound with antiseptic and antibacterial properties, is often included in many home items like toothpaste, toys, soaps, clothes, beds, plastics, and textiles. Triclosan may generate chloroform, a chlorinated by-product, when present in tap water. In addition, triclosan may break down in the environment

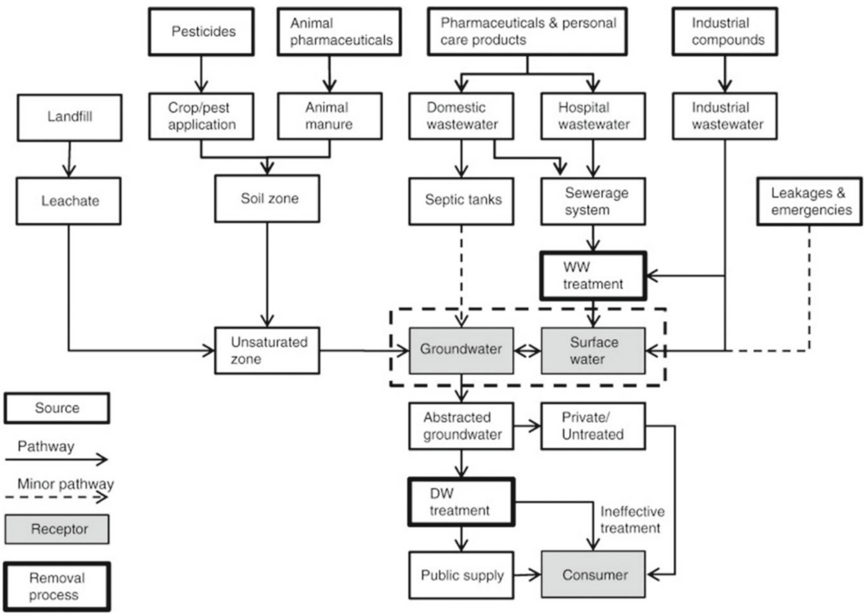

Fig. 18.1 Sources and possible pathways of EPs into the environment (Stuart et al. 2012)

and form substances such as methyl triclosan and certain dioxins, including 2,4-dichlorophenol and 2,8-dichlorodibenzo-p-dioxin. Research conducted by the United States Geological Survey (USGS) examined 95 distinct organic wastewater contaminants in streams throughout the United States. The study revealed that triclosan was one of the chemicals most often discovered and found to have the highest amounts. Triclosan has been detected in many water bodies throughout the United States, indicating that standard treatment procedures have not eliminated it. Furthermore, there are no clear safety regulations regarding the acceptable concentrations of triclosan in drinking water (Weatherly and Gosse 2017).

Within the realm of both over-the-counter and prescription pharmaceuticals, which include nonprescription treatments, there exist both synthetic and natural steroid hormones, including progestogens, androgens, and estrogens. Humans and animals extensively use these hormones because of their capacity to alter physiological processes and control essential biological functions. Ferguson et al. determined that the estrogens found in the estuary in Southeastern Australia most likely originate from a WWTP nearby. Estrogens found in freshwater indicate the existence of another origin, most likely resulting from agricultural runoff (Ferguson et al. 2013). Further research identified crop residues as the primary origin of steroid estrogens, with conjugated estrogens accounting for up to 22% of the overall estrogen burden in dairy production. Furthermore, estrogens have been detected in soil drainage water, streams that flow from grazing areas, runoff from the application of dairy manure, groundwater under unlined ponds used to contain waste, and the surrounding land. Drinking water treatment facilities (WTPs) are the main origin of disinfection by-products (DBPs). Stalter et al. studied DBPs at 15 water treatment plants WTPs in Beijing City. These WTPs obtained their water from different sources. In the treated water samples, it was discovered that halogenic acetic acids made up 38.1%, and trihalomethanes made up 42.6% of all DBPs. DBP concentrations in drinking water differed according to the water source, with surface water displaying the greatest concentrations, mixed water sources, and groundwater exhibiting the lowest concentrations (Stalter et al. 2020).

PFCs, or perfluorinated compounds, are used in various products, including fabrics, adhesives, paints, polishes, waxes, electronics, and stain repellents (Pal and Sen 2023a). Perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) are the most well-known PFCs and classified as emerging petroleum pollutants (Pal and Sen 2023b). PFOA is often found in drinking and treated water sources due to discharges from industrial sites, WWTPs, and non-point sources. Through groundwater plumes, it may pollute drinking water wells. Furthermore, pervasive industrial sites may release particulate matter into the atmosphere, which can then seep into the groundwater and soil. According to studies conducted by Pitter et al. and Steenlan et al., drinking water wells up to 20 miles away might be contaminated by industrial PFOA emissions in West Virginia and Ohio. The aquifer was refilled with contaminated surface water from the Ohio River when PFOA-laden air pollution fell to the earth, permeated the groundwater, and settled (Pitter et al. 2020; Steenland et al. 2020).

Pesticides may contaminate drinking water by inconsiderate methods, including back-siphoning, spraying on lawns and golf courses, and substantial unintentional spills. Pesticide metabolites have a high tendency to seep into the soil via a process called leaching. Reemtsma et al. detected pesticide metabolites in both ground and surface water. The differences in runoff samples were ascribed to using several pesticides in small metropolitan areas (Reemtsma et al. 2013). Detecting several compounds in water matrices suggests extensive pesticide use in metropolitan areas. According to Belenguer et al., the occurrence and levels of pesticides such as prochloraz, clofenvinphos, pyriproxyfen, imazalil, and dichlofenthion in water are linked to the extensive agricultural practices in the area (Belenguer et al. 2014).

EPs have the potential to readily pollute river ecosystems, especially when untreated effluents from WWTPs are released. EPs can accumulate in sediments, plants, and animals in river systems because they persist for a long time and degrade extremely slowly via biodegradation, chemical degradation, and photodegradation (without light). As a result, their removal from aquatic ecosystems is very insignificant. While certain microbial populations can withstand the biocidal effects of EPs and perhaps increase their breakdown rates, there is a lack of research on the natural biodegradation of EPs, including hormones, some detergents, and medications. This research is often undertaken in controlled laboratory environments, which may not exactly simulate real-world environmental circumstances, and the practical application of these results on a wide scale is still uncertain (Gavrilescu et al. 2015). Hence, the research progress in identifying and harnessing customized microbial communities for various environmental pollutants or even individual substances presents substantial scientific opportunities.

18.3 Toxicity and Effects of EP

The detrimental impacts of emerging pollutants (EPs) have sparked considerable apprehension among society and the environment, owing to the potential to induce cancer and interfere with endocrine systems. Endocrine-disrupting chemicals (EDCs) are molecules, whether man-made or occurring naturally, that can disrupt the normal functioning of hormones. They could accomplish this by blocking or imitating hormones, affecting the endocrine systems of living beings. This disturbance may result in modified hormone levels and stimulating or inhibiting hormone synthesis and metabolism. EDCs consist of a range of endocrine disruptors, such as phthalates, polybrominated compounds, polychlorinated biphenyls (PCBs), steroid sex hormones, pesticides, pharmaceutical goods, bisphenol A (BPA), alkylphenol ethoxylates, and alkylphenols. Exposure to EDCs such as BPA and phthalates during pregnancy might hinder the sexual development of children (Thambirajah et al. 2022). In addition, many PCPs, such as diethyltoluamide (DEET) insect repellents, ultraviolet (UV) screens, synthetic musk perfumes, and parabens, may also act as EDCs in water. The adverse effects of different categories of EPs are listed in Table 18.1 and illustrated in Fig. 18.2.

Table 18.1 Toxicity and impact of EPs

Category	Inference	References
Steroids and hormones	• Fish may experience estrogenic effects at low doses of 17-ethinylestradiol. Fish undergo feminization and lower egg fertilization due to changes in sexual traits and sex ratios • Glucocorticoids have a deleterious effect on reproductive and immune system development, whereas androgen hormones help fish become more masculine • During embryonic development, endocrine disruptors, such as phytoestrogens, may induce teratogenic, estrogenic, and physiological issues in fish and mammals	Richardson and Kimura (2020), Eustache et al. (2020)
Antiseptics	• Triclosan and other triclocarban-containing skincare and cosmetic products can potentially interfere with the body's endocrine or hormonal systems. These compounds adversely affect the embryos of fish, crabs, and algae • The reproductive axis and the balance of thyroid hormones may be disturbed by triclosan • Studies have shown that when used in certain quantities, triclosan may deleteriously affect phytoplankton accumulation in freshwater ecosystems. Vitellogenin production in fish may be induced by prolonged exposure to parabens, even at low concentrations	Awfa et al. (2018), Fu et al. (2020)
Plasticizers	• Studies have shown that males exposed to BPA had lower reproductive rates, sperm quality, sex hormone levels, and sexual function. Exposure to BPA in women has been associated with an increased risk of PCOS, breast cancer, miscarriage, endometrial problems, and preterm deliveries	Rochester (2013), Weber et al. (2015)
Flame retardants	• Research has linked low birth weights and body mass indexes, as well as cryptorchidism (undescended testicles) in newborn boys, to polybrominated diphenyl ethers (PBDEs) levels in breast milk • There may be comparable consequences in humans, as Dorman found that PBDE levels producing neurotoxicity in animal models imply • The lipophilicity of PBDEs causes them to bioaccumulate in adipose tissue. In animals, they have been associated with a variety of negative health outcomes, such as reduced sperm count, hormone disturbance, and fetal abnormalities	Collet et al. (2022), Dorman et al. (2018)

(continued)

Table 18.1 (continued)

Category	Inference	References
Pesticides	• Atrazine, chlordane, endosulfan, dieldrin, aldrin, and dichlorodiphenyltrichloroethane (DDT) are among the pesticides that may disrupt the endocrine system and cause hormonal abnormalities • Human malignancies, developmental delays in cognitive and motor skills, and an increased risk of genotoxicity have all been associated with organochlorine accumulation • Neurotoxic, cytotoxic, genotoxic, bactericidal, and ecotoxic describe nanoparticles in toxicological research. Anatase, zinc oxide, and nano-sized silicon dioxide are chemicals that may induce lung inflammation in both rats and humans • The discharge of silver nanoparticles into the environment can potentially disrupt ecological harmony	Souza et al. (2020), Du et al. (2018)
Disinfection by-products	• Water DBPs have been associated with several health problems, including congenital defects, bladder cancer, and premature miscarriage. Also, DBPs in pools could trigger asthma attacks or other respiratory problems • Whether inhaled, ingested, or come into direct skin contact with trihalomethanes, these have the potential for cancer. The research concluded that the largest cancer risk was associated with inhalation of chloroform and ingestion of bromodichloromethane	Gan et al. (2013)

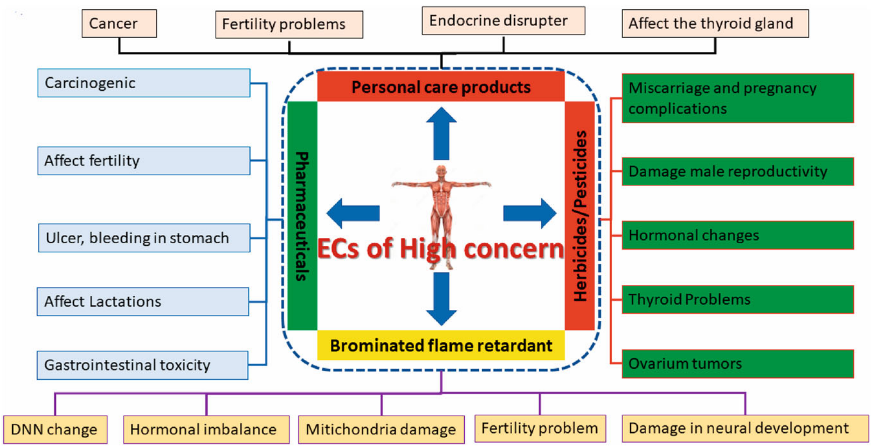

Fig. 18.2 Adverse impact of EPs on human health (Kumar et al. 2022a, b)

18.4 Treatment Technologies

Various treatment methods must be implemented for removing EPs because of their different chemical characteristics, variable potential to break down naturally, and the possibility of generating hazardous chemicals as an outcome. Each of these EPs has unique physicochemical properties that impact their effectiveness in treatment. Biological approaches are excellent for breaking down biodegradable chemicals, however persistent contaminants usually need sophisticated oxidation processes or adsorption techniques. In addition, the integration of treatment techniques may reduce operational difficulties, such as membrane fouling or excessive energy requirements, and enhance cost-efficiency. A complete strategy is necessary to guarantee the removal of pollutants and the provision of high-quality drinking water due to site-specific circumstances and strict regulatory regulations. The application of different treatment techniques biological treatments (activated sludge, trickling beds, utilization of enzymes and microbes), physicochemical treatments (coagulation-flocculation, electrocoagulation, adsorption), advanced treatments (photocatalysis, ozonation, Fenton, electrooxidation, membrane filtration), and hybrid treatments (membrane bioreactor, constructed wetlands, AOP-adsorption), have been discussed in details.

18.4.1 Biological Treatment

Anaerobic and aerobic processes are the two categories of biological treatment methods for wastewater. Activated sludge, membrane bioreactors, and sequencing batch reactors are examples of efficient aerobic treatments. Environmentally friendly anaerobic technologies include anaerobic sludge reactors and anaerobic film reactors. Bio-trickling filters have been used in WWTPs for many years to mitigate air pollution, remove biological and chemical oxygen demand (BOD and COD), manage odors, and remove pathogens. On the other hand, their use in removing EPs has not yet gained widespread acceptance. Although organic micropollutants may be removed by trickling filter beds, activated sludge treatment techniques are usually more successful. For example, for 55 PPCPs tested, trickling filter beds in a WWTP showed an average removal effectiveness of less than 70%, with half not being removed efficiently. On the other hand, activated sludge treatment has shown an average removal effectiveness of more than 85% for all 55 PPCPs examined (Kasprzyk-Hordern et al. 2009). PPCPs and EDCs have been successfully removed using anaerobic/anoxic/aerobic membrane bioreactors. With influent concentrations ranging from ng/L to mg/L, these techniques removed over 70% of the target EDCs and PPCPs. However, certain EPs are too toxic or resistant to microbial activity to degrade by biodegradation. When a growth substrate is necessary to promote microbial growth to biodegrade such pollutants, cometabolism is used.

The denitrification and nitrification procedures are typically ineffective in removing a wide spectrum of EPs. However, integrating these procedures with membrane bioreactors (MBRs) and other treatments may improve the effectiveness of removing EPs. Denitrification can effectively remove various EDCs and PPCPs at influent concentrations in the g/L range. These include EDCs such as estrone (E1), 17-ethinylestradiol (EE2), 17-estradiol (E2), estriol (E3), bisphenol A, 4-tert-butyl-phenol, and 4-tert-octylphenol, as well as PPCPs like benzophenone, galaxolide, oxybenzone, and salicylic acid. Denitrification is often used after ozonation to remove pollutants. Nevertheless, because of its effectiveness in removing nitrogen and organic carbon from water streams, it is also appropriate for use in a tertiary treatment process for water reclamation. The biological activated carbon approach has shown a 99% removal effectiveness for E1, while it is less successful in removing specific EDCs such as E3, octylphenol, and BPA (Gerrity et al. 2011). These results highlight the capacity of integrated biological treatment systems to reduce the presence of EPs in wastewater successfully.

The use of oxidoreductase enzymes, namely peroxidases, in the biological breakdown of contaminants is an emerging and promising field of study. Enzyme systems have been used to efficiently decompose various organic pollutants by oxidizing and degrading them into smaller intermediate compounds. Enzyme-based treatments provide many benefits, such as the ability to operate well in environments with high or low pollution levels, minimal energy consumption, decreased sludge generation, and the capability to treat a wide range of contaminant. Laccases and peroxidases are notable enzymes in bioremediation due to their exceptional ability to degrade a wide range of pollutants. These enzymes aid in the breakdown of a wide range of pollutants by oxidation and reduction processes. These pollutants include phenols, cresols, herbicides, chlorinated phenols, pesticides, synthetic textile dyes, dioxins, medicines, and PPCPs. Oxidoreductase enzymes, including peroxidases, oxidases, oxygenases, and dehydrogenases, are crucial in these activities (Bilal et al. 2018). Using these enzymes to treat polluted wastewater emphasizes their capacity for successful environmental rehabilitation, providing a sustainable and efficient method for reducing pollution.

Laccases, or Lac, are primarily present in various plants, bacteria, insects, and fungi. They are multi-copper oxidases. Microbial laccases, especially those generated from wood-decaying fungus, are particularly intriguing because of their capacity to oxidize a diverse array of chemicals and their wide substrate specificity. The microbial laccases have been successfully used to break down a wide range of EP and aromatic compounds. Research has shown that laccase can effectively degrade estrogen hormones, including E2, E1, and EE2, into substances with considerably lower or no estrogenic activity. Peroxidases are antioxidant proteins that include heme and are present in plants, fungi, bacteria, and mammals. They facilitate the oxidation of different chemical substrates by using H_2O_2 or organic hydroperoxides as co-substrates. Peroxidases are highly selective enzymes that help break down pollutants. Multiple investigations have emphasized the potential of peroxidases to remediate a wide range of EPs. Commonly used peroxidases for wastewater treatment include horseradish peroxidase, chloroperoxidase, manganese peroxidase, and soybean peroxidase. These enzymes have shown great effectiveness in breaking down various environmental pollutants, highlighting their usefulness in bioremediation endeavors (Morsi et al. 2020).

Microorganisms, including bacteria, algae, and fungi, used in biological wastewater treatment may efficiently and cost-effectively imitate the functionality of natural ecosystems to decrease water pollutants. Fungal bioreactors can eliminate a range of pharmaceuticals, such as beta-blockers, anticancer and gastroesophageal drugs, anti-inflammatory drugs, and antibiotics. Using an algae-based polishing pond treatment procedure, EPs such as E1, E2, and EE2 may be effectively eliminated by over 95% when present at a concentration of 1 g/L. While the activated sludge technique is often used to remove EPs globally, the amount of EPs removed by primary sedimentation, chemical precipitation, aeration volatilization, and sludge adsorption is negligible. Most of the EPs present in wastewater are eliminated by biodegradation, which is the primary approach for removing EPs. The activated sludge technique eliminates EDCs, achieving 75 and 100% removal rates (Rosal et al. 2010).

18.4.2 Physicochemical Treatments

Physicochemical treatments, such as coagulation-flocculation techniques, are typically ineffective in eliminating EDCs and PPCPs. Coagulation is a process in which colloidal particles undergo a chemical transformation, forming aggregates that eventually settle down. Research done by Westerhoff used a small-scale water treatment plant model and added 30 pharmaceuticals and 80 distinct EDCs to natural water samples. The study found no substantial reduction in these compounds except when activated carbon or chlorination and ozonation were employed for oxidation (Westerhoff et al. 2005). Adams discovered that metal salt coagulants, such as aluminum sulfate and ferric sulfate, did not eliminate carbadox, sulfadimethoxine, and trimethoprim (Adams et al. 2002). Additionally, Petrovic and Vieno showed similar results on the inefficacy of these treatments, eliminating diclofenac, carbamazepine, ibuprofen, and ketoprofen (Petrovic et al. 2003; Vieno et al. 2006). Huerta-Fontela discovered that adding aluminum sulfate to coagulation-flocculation and sand filtering effectively eliminated medications, including hydrochlorothiazide, warfarin, and betaxolol, resulting in an 80% removal rate (Huerta-Fontela et al. 2011). In addition, there were significant reductions in the levels of musk compounds, personal care items found in hospital wastewater. More precisely, celestolide, galaxolide, and tonalide showed removal rates of 83%, 79%, and 78%, respectively. Chemical processes such as coagulation, flocculation, and lime softening have shown little effectiveness in eliminating EDCs and PPCPs (Adams et al. 2002). Electrocoagulation is a process where an electrical current is applied to water, causing the anode materials, usually aluminum or iron, to undergo electrolytic oxidation and produce coagulant precursors. This method efficiently decreases pollution levels by producing these substances that cause coagulation. The research used an electrocoagulation device that included aluminum electrodes. The study aimed to remove six EDCs such as

E1, E2, E3, EE2, BPA, and nonylphenol. The investigation documented the removal efficiencies of E1, E2, E3, EE2, BPA, and NP was 62%, 60%, 68%, 53%, 42%, and 98%, respectively. Aluminum-based electrocoagulation effectively decreased EDC concentrations in the incoming and outgoing municipal wastewater streams (Cook et al. 2016).

Adsorption has shown to be more advantageous than the other techniques in terms of cost, design and operational flexibility, effectiveness, efficiency, and the generation of high-quality filtered output (Pal and Sen 2024). Activated carbon adsorption is a very efficient technique for removing various hydrophobic and charged medicines, EDCs, and PPCPs. This method exploits the hydrophobic interactions of activated carbon, specifically with non-polar chemicals (those with a log $K_{ow} > 2$), to eliminate most organic molecules from water. Schafer's study shows that powdered activated carbon (PAC) can eliminate as much as 90% of EDCs (Schäfer et al. 2011). In addition, Snyder conducted a study to determine the effectiveness of PAC in removing 66 distinct PPCPs at a concentration of 5 mg/L and a contact period of 5 h. The investigation revealed that out of these PPCPs, only nine were eliminated with an efficiency of less than 50% (Snyder et al. 2006). This demonstrates the diverse effectiveness of PAC in adsorbing various pollutants. The efficacy of removing trace pollutants is greatly affected by the interactions between particles and contaminants, competition for surface locations, and the closing of pores by other particles, all of which may diminish the effectiveness of activated carbon. Notwithstanding these difficulties, powdered activated carbon (PAC) continues to be the most efficient adsorbent, especially for pollutants comprising resistant organic and non-biodegradable chemicals. Comparative research conducted by Bodzek and Dudziak revealed that the process of sorption, specifically employing PAC and GAC, proved to be more effective than coagulation, even when combined with nanofiltration membranes in a hybrid system, for removing estrogens. This emphasizes the higher effectiveness of activated carbon in eliminating such impurities (Bodzek and Dudziak 2006).

18.4.3 Advanced Treatment Techniques

Ikehata's research on advanced oxidation processes (AOP) emphasised the generation of free radicals, namely hydroxyl radicals, that aid in the transformation of pollutants into less harmful and more easily decomposable substances (Ikehata et al. 2008). AOPs are very efficient methods for treating water and wastewater, since they possess the capability to break down and eliminate contaminants. Photocatalysis is a kind of AOP where a catalyst is activated by light to cause chemical changes by supplying the required energy for the reaction. Photocatalysts are often semiconductor metal oxides that possess a narrow energy band gap, rendering them well-suited for use in photocatalytic applications. Out of these options, titania is a well-researched kind of photocatalyst that is known for its ability to remain stable under light, its unreactive properties, and its affordability. Iron oxide nanoparticles, synthesized using various techniques (Kumar and Gangawane 2022a, b) have been used as photocatalysts for wastewater treatment (Kumar et al. 2022a, b). Moreover, the use of photocatalysis in conjunction with hydrogen peroxide has shown remarkable efficacy in eliminating a wide range of pesticides, such as aldrin, diazinon, and malathion, as well as some medicines like amoxicillin, ampicillin, and cloxacillin, with removal rates reaching as high as 99–100% (Prieto-Rodríguez et al. 2013).

When employed in isolation, ozone oxidation technology is often inadequate for the full breakdown of organic compounds owing to its relatively mild impact and the substantial quantity of ozone needed. Thus, it is often used in conjunction with other technologies. For example, the pairing of ozone with ultraviolet light (O_3/UV) increases the efficiency of eliminating intricate chemical substances. The UV/O_3 technique not only broadens the scope of degradable organic compounds but also enhances their disintegration rate. UV radiation promotes the generation of reactive oxygen species from O_3, hence intensifying the process of oxidation. Moreover, the integration of ultrasound and O_3 enhances the efficacy of ozone oxidation. Ultrasonic waves enhance the interaction between O_3 and liquid water, resulting in a greater surface area for contact and ultimately boosting the rate at which O_3 is transferred. This integrated method is both very effective and ecologically sustainable. Ozonation is a commonly used method in water and wastewater treatment for the removal of organic contaminants and the disinfection of water. In order to overcome the constraints of ozonation, catalysts may be used, or it can be integrated with other AOPs to boost its efficacy.

Fenton oxidation is a chemical process where the interaction between hydrogen peroxide and iron produces hydroxyl radicals. This approach is widely used for wastewater treatment because of its fast reaction rates and high effectiveness. The Electro-Fenton technique has been created as an improvement to the ordinary Fenton process. It has shown an efficiency of 88–93% in the removal of beta-blockers, including metoprolol tartrate, propranolol hydrochloride, and cendol (Isarain-Chávez et al. 2011). The solar photoelectron Fenton method is a novel approach that harnesses sun energy to enhance the process of pollutant degradation. Photo-Fenton reactions, using UV light to produce radicals via the interaction of hydrogen peroxide and iron, are extensively used for the elimination of EPs from wastewater. These approaches have shown significant clearance rates (95–100%) for a range of medicines, with the exception of penicillin G. Research suggests that UV-based photo-Fenton procedures are more efficient in removing beta-blockers and medicines compared to solar-based approaches. Gimeno's research on heterogeneous solar photocatalysis, which includes solar photo-Fenton, ozonation, and TiO_2, discovered that photocatalytic ozonation obtained superior degradation rates compared to photocatalytic oxidation. This difference in performance was attributable to the presence of oxygen (Gimeno et al. 2016). Electrooxidation, also known as anodic oxidation or electrochemical incineration, is a widely used Electro-Oxidative Advanced Oxidation Process for eliminating organic pollutants from wastewater. During this procedure, a varying electric current between 2 and 20 A is sent via two electrodes that are immersed in water. This leads to the production of hydrogen peroxide and hydroxyl radicals. These reactive species aid in the decomposition of organic contaminants. Electrooxidation is generally acknowledged as a very efficient electrochemical advanced oxidation technique for breaking down EPs in wastewater.

Reverse Osmosis (RO) and Nanofiltration (NF) have been more popular in recent years for their efficacy in reclaiming wastewater and treating drinking water. These membrane filtering methods are renowned for their capacity to eliminate a wide range of inorganic and organic contaminants. RO membranes have a greater ability to remove EPs compared to NF membranes, but they need more energy, which makes RO less preferable in terms of energy use. Multiple studies have shown that RO and NF membranes used in water treatment facilities may successfully eliminate EDCs and PPCPs, attaining removal rates of up to 95%. Moreover, NF membranes have shown their proficiency in eliminating pesticides such as simazine, atrazine, and diuron, together with atrazine metabolite, from water-based solutions (Musbah et al. 2013). NF membranes outperform conventional techniques such as particle coagulation-flocculation, dual medium filtration, and sedimentation. Among the tested substances, atrazine exhibits the greatest retention rate, while diuron shows the lowest. Moreover, NF membranes have effectively been used to eradicate organic chlorine pesticides, such as DDT, from potable water, attaining removal rates of up to 95%. These results highlight the capability of NF and RO membrane technologies to efficiently reduce the presence of different pollutants in water.

Acero subsequently demonstrated that ultrafiltration (UF) membranes were the most efficient in eliminating certain herbicides, independent of the water composition. Both NF and UF membranes exhibited a removal efficiency of over 90% for BPA in drinking water, with concentrations ranging from 60 to 600 μg/L (Acero et al. 2009). The synergistic adsorption of humic acid and BPA, driven by their hydrophobic properties, was determined to be a very efficient method for retaining BPA. Conventional filtering without pre-coagulation might be hard for removing nanoparticles due to their small size. Nevertheless, UF membranes were shown to eliminate over 99.6% of SiO_2 nanoparticles. Utilising membrane filtering as the last treatment method may improve the effectiveness of removing nanoparticles. Although membrane filtering techniques have some benefits, they are prone to fouling, resulting in a decrease in flux and higher operating expenses (Liu et al. 2014).

18.4.4 Hybrid Treatment Techniques

A major concern is that many conventional treatment approaches are fail to decrease the levels of EPs below the established regulatory limits. Therefore, there has been significant interest in recent years in investigating the use of hybrid treatment strategies. A hybrid treatment system combines many treatment approaches to improve the overall performance of the system. This allows the system to make use of the strengths of each treatment unit and overcome the limitations of individual procedures for removing EPs. Hybrid systems often integrate physical or chemical treatment techniques with biological processes. The choice of the hybrid treatment method is determined by the specific attributes of the incoming wastewater, the pace at which it flows, and the desired quality of the outgoing effluent. The main goal of hybrid systems is to purify wastewater to a level that enables its reuse. The present study assessed the performance of several hybrid systems in eliminating EPs and compared the resultant effluent concentrations from these treatment methods to statutory standards (Qin et al. 2018).

A Membrane Bioreactor (MBR) is a cohesive system that integrates conventional activated sludge processes (ASP) with membrane separation. MBRs have shown efficient effectiveness in eliminating conventional contaminants and nutrients from wastewater. In recent years, a multitude of studies have used MBR technology to address EPs, noting positive outcomes for certain categories of EPs (Dhangar and Kumar 2020). Nevertheless, MBRs have shown a restricted efficacy when it comes to physiologically persistent and hydrophobic substances. In order to overcome this constraint, researchers have combined MBRs with several treatment techniques, including ultrafiltration UF, RO, PAC, AOPs, and membrane distillation. This integration aims to improve the effectiveness of removing persistent EPs.

Luo recently conducted a study on the use of an osmotic MBR in conjunction with RO for the purpose of eliminating 31 specific EPs, consisting of 13 chemicals that resist water and 18 compounds that attract water. The research showed a clearance effectiveness of above 95% for the majority of EPs. Nevertheless, several pollutants, including carbamazepine, diclofenac, and atrazine, had reduced clearance rates of around 70%. The inclusion of electron-withdrawing groups such as chloride, amide, and nitrogen in the molecular structures of these molecules made them resistant to biological destruction. The resistance is ascribed to their low Kbio values (below 0.1 L/gMLSS d), which suggests a challenge in the biotransformation process during wastewater treatment. One major disadvantage of the osmotic MBR is the accumulation of saline, which has a negative impact on the biological stability and leads to membrane fouling (Luo et al. 2017).

Kovalova conducted a study on a MBR that included several treatment components, such as PAC at a concentration of 23 mg/L, O_3 at a concentration of 1.08 O_3/g of dissolved organic carbon, and UV radiation at a dosage of 2400 J/m^2. The purpose of this study was to treat hospital wastewater. The combination of MBR and ozonation demonstrated a high level of effectiveness (>95%) in removing pharmaceutical active chemicals, with an average concentration of 4800 ng/L. Nevertheless, the primary drawback of using ozonation and UV procedures is the geneartion of transformation products, which are often unidentified and possibly harmful. On the other hand, PAC does not face this issue since it undergoes elimination via an adsorption process rather than decomposition (Kovalova et al. 2013). In a separate investigation, Forrez used biogenic metal manganese oxides in a laboratory-scale membrane bioreactor to eliminate 13 EPs, with the highest initial concentration of carbamazepine being 1006 ng/L. The data demonstrated a clearance rate of over 90% for ibuprofen, naproxen, codeine, and diuron, but iohexol and iopromide exhibited lower removal rates of about 70%. The authors stated that chemical oxidation was the main process for removing diuron, whereas biological degradation was responsible for eliminating codeine, iohexol, and iopromide. MBR-based integrated systems have shown to be effective in eliminating EPs, but they encounter notable obstacles like as membrane fouling and high energy demands. Moreover, MBR systems incur significant operating and maintenance expenses as a result of using costly membranes, consuming large amounts of energy, and including intricate design intricacies (Forrez et al. 2011).

Constructed wetlands (CWs) are integrated structures that use processes such as plant absorption, substrate adsorption, and microbial decomposition to reduce water pollutants. These systems may be set up in several hydrologic configurations, such as horizontal flow, vertical flow, surface flow, or subsurface flow. Multiple research have investigated the combination of CWs with various treatment methods, including membrane distillation and ozonation. These studies have successfully achieved removal rates of over 90% for EPs. Lancheros conducted a recent study on a horizontal subsurface flow built wetland that was combined with ozonation to remove ibuprofen and naproxen from residence wastewater. The use of Cyperus ligularis macrophytes in the linked system resulted in improved removal efficiency compared to freestanding constructed wetland settings. The statistical analysis highlighted the crucial importance of the integrated system design in obtaining high clearance rates (>97%) for ibuprofen and naproxen (Lancheros et al. 2019). The dose of ozone, on the other hand, had a less significant influence. Although the removal of ibuprofen achieved 97%, the amounts of the substance in the effluent still beyond the legally established limits. This emphasises the need for more optimisation. In addition, the use of aerated lagoons has been investigated for the removal of EP, with the need for mechanical aeration to support biological oxidation in pond-like systems. These systems, categorised as aerobic or facultative, may achieve a maximum of 95% BOD elimination with different energy demands. Conkle conducted a study on the treatment of PPCPs in municipal wastewater. The study included the use of aerated lagoons, followed by surface flow constructed wetland and UV disinfection. The results showed that the treatment process achieved a removal rate of over 95% for most of the targeted EPs. Increased hydraulic retention time (HRT) in CW units was shown to be correlated with greater removal efficiency for certain EPs (Conkle et al. 2008). Although this integrated method successfully reduced the concentrations of some EPs in effluent to meet legal criteria, it is important to take into account problems related to land use and seasonal variations. Notwithstanding these difficulties, approaches based on chemical warfare provide economic viability and the possibility to be expanded for the treatment of huge amounts of wastewater, especially in regions where there is a shortage of land (Kivaisi 2001).

The use of AOPs in treating wastewater has attracted significant interest because of its effectiveness in removing pollutants and their fast response kinetics. AOPs produce diverse oxidising radicals that may break down pollutants found in water settings. Various strategies, including ozonation, Fenton oxidation, photocatalysis, and ultrasonic irradiation, have been combined with diverse biological treatment methods to enhance the removal of EPs. Nguyen used a combination of MBR technology and UV oxidation, specifically utilising UV lamps at a wavelength of 254 nm, in order to improve the elimination of hydrophilic and physiologically persistent chemical molecules. The combined strategy successfully achieved removal efficiencies ranging from 85 to 99% for all 22 chosen EPs. It is worth mentioning that chlorinated chemicals such as diclofenac, triclosan, and fenoprop showed a considerable increase in their elimination, which may be perhaps explained by the replacement of hydrogen atoms with halogen atoms and the subsequent breakdown of the compounds accelerated by the UV oxidation process (Nguyen et al. 2013).

Ding used laccase-mediated oxidation, a process enabled by the oxidoreductase enzyme laccase, which catalyses the oxidation of substances using oxygen as a terminal electron acceptor, together with soil adsorption (SA) to tackle the elimination of antibiotics. After 15 min, almost 75% of the response was eliminated when using a laccase dosage of 0.5 mg/L. Complete elimination was seen after 180 min. Tetracycline was shown to be removed via both laccase oxidation and SA among the antibiotics studied. However, laccase oxidation was the main route of removal in all cases. The concentration of tetracycline in the effluent, which was produced by the oxidation of tetracycline using the laccase-mediated oxidation along with SA hybrid system, met the recommended levels specified in the guidelines. However, this hybrid technique exhibited comparatively worse performance in comparison to the MBR along with ozonation system (Ding et al. 2016).

Surendra used a Ni-doped TiO_2 photocatalyst to degrade malathion, resulting in a maximum degradation rate of over 96%. The degradation efficiency of malathion exhibited a clear correlation with the pH value, reaching its maximum elimination efficiency at a pH of 11 (Surendra et al. 2020). Fetyan and Salem Attia conducted a research where they used a sonoelectro-Fenton hybrid system to break down herbicides, insecticides, and other persistent organic pollutants. The hybrid system facilitated the breakdown of organic pollutants by enhancing the movement of reactants towards the cathode, resulting in better mass transfer. The method also enabled the breakdown and transformation of organic compounds via radical and cavitation-induced mechanisms, respectively. Although ultrasonic procedures are efficient, their high energy needs limit their use on a broad scale (Fetyan and Salem Attia 2020). Mahamuni and Adewuyi performed a cost analysis on wastewater treatment using different hybrid ultrasound (US) systems. They found that ultrasound combined with AOPs can successfully remove organic pollutants. However, due to the high energy and chemical consumption, ultrasound-based AOPs are not suitable for scaling up the treatment process (Mahamuni and Adewuyi 2010). The majority of cutting-edge oxidation-based systems are quite effective, but they are expensive to operate and maintain. The primary expenses associated with Fenton-based processes are related to power and chemical reagent management. Significant expenses are associated with photocatalysis-based systems in terms of energy consumption, catalyst production, and handling and disposing of generated sludge. The energy-intensive nature of ozonation and ultrasound-based procedures adds to the expense of upkeep and operation (Majumder et al. 2021).

Several adsorbent materials, when combined with other treatment methods, have effectively been used to eliminate EPs. Sajjadi conducted a study on the breakdown of diazinon utilising a nanocomposite made of metal-organic framework. The degradation process was enhanced by exposing the nanocomposite to ultrasonic irradiation, resulting in degradation rates above 94%. Subsequent leaching studies demonstrated little leaching of iron and zinc compounds during degradation (Sajjadi et al. 2019). Shanmuganathan used a hybrid system consisting of submerged membrane-filtration and GAC adsorption to eliminate organic micropollutants. The research discovered that hydrophobic chemicals were efficiently eliminated by electrostatic adsorption onto negatively charged GAC, but hydrophilic compounds such as sulfamethoxazole had a lower removal rate of 76%. Nevertheless, prolonged response periods resulted in the elimination of more than 95% of all micropollutants, achieved by processes including electrostatic attraction, van der Waals forces, hydrogen bonding, and π–bonding (Shanmuganathan et al. 2017). Li synthesised a new adsorbent called nitrogen-doped carbon intercalated molybdenum disulfide nano-hybrid (NC–MoS_2) using a hydrothermal technique. This adsorbent was specifically designed for removing tetracycline from water solutions. Increasing the amount of adsorbent from 0.1 to 1.5 g/L increased the number of active adsorption sites and expanded the surface area available for interaction. As a consequence, the total removal effectiveness by NC–MoS_2 reached a maximum of 96.5% (Li et al. 2021). Although adsorption-based systems show potential and have lower operational costs compared to AOPs, there are several challenges that must be overcome before they can be widely used for removing EPs. These challenges include the risk of secondary pollution during disposal, the need to regenerate spent adsorbent, and the cost of adsorbent materials (Yadav et al. 2021).

18.5 Conclusions and Future Perspectives

The increasing prevalence of EPs in wastewater poses a significant challenge to environmental sustainability and human health. The long-term persistence and potential harm of pollutants need developing and implementing advanced treatment methods. This study has thoroughly examined the efficacy, durability, and incorporation of several modern treatment techniques, fully evaluating their abilities and constraints. AOPs are effective methods for breaking down persistent organic contaminants. Methods such as ozonation, photocatalysis, and Fenton reactions use very reactive chemicals to decompose complex organic compounds into less hazardous ones. The exceptional efficacy of AOPs in breaking down a wide range of contaminants, such as PPCPs, EDCs, flame retardants, and surfactants, has been extensively established. Nevertheless, the scalability of these systems to handle larger workloads and their high energy consumption present significant challenges. It is important to closely monitor and optimize AOPs to minimize the creation of secondary pollutants and prevent any negative consequences. Membrane filtration methods such as reverse osmosis, nanofiltration, and ultrafiltration provide excellent removal rates for a broad spectrum of EPs. These techniques use semi-permeable membranes to isolate contaminants from water physically. Membrane technologies are precise and reliable, making them well-suited for eliminating microplastics, nanoparticles, and specific organic pollutants. Despite their efficacy, membrane fouling and the high running costs linked to regular maintenance and energy consumption are still major problems. Progress in membrane materials and the development of anti-fouling coatings are crucial to improving the practicality of these technologies for widespread use.

Biological treatment techniques, including biofiltration, constructed wetlands, and microbial consortia, use the natural metabolic ability of microorganisms to break down contaminants. These ecologically sustainable methods may be incorporated into current wastewater treatment techniques. Constructed wetlands provide an economical and environmentally friendly method for eliminating several pollutants. Utilizing certain microbial strains that can break down pharmaceuticals and endocrine disruptors can improve biodegradation efficiency in these systems. Nevertheless, variations in microbial activity caused by external factors and the possible accumulation of contaminants in biomass need more investigation to enhance the efficiency of these processes. Integrating various treatment methods is becoming more widely acknowledged as an essential approach to thoroughly eliminating pollutants. Hybrid systems that integrate AOPs with biological treatments may effectively use the advantages of both methods. AOPs can pretreat wastewater by decomposing intricate contaminants into less complicated chemicals more easily susceptible to biological degradation. Implementing this consecutive approach may improve the overall effectiveness of removing pollutants and minimize the production of additional harmful substances. By integrating membrane filtration with biological processes, it is possible to overcome the limits of each approach and provide a strong solution for eliminating various pollutants. Preliminary trials and full-scale implementations of integrated systems have shown encouraging outcomes. For example, ozonation and biofiltration successfully eliminate medicines and personal care goods from municipal wastewater. Utilizing built wetlands as a post-treatment method after traditional treatment techniques may effectively decrease nutrient levels and remaining pollutants. These integrated methods not only boost the removal of pollutants but also improve the capacity of wastewater treatment systems to withstand and adapt to different levels of pollutants and environmental conditions.

Research endeavors have greatly enhanced our understanding of the environmental and human health hazards linked to EPs. Nevertheless, there still needs to be a significant improvement in our understanding of the enduring consequences of EPs. Our understanding of the effects of EPs on human health and aquatic life is currently limited and incomplete. This highlights the need for more extensive research and information gathering to comprehend their destiny and negative consequences fully. The rapid increase in EPs in the environment makes implementing cost-effective and sustainable measures for detecting, assessing the danger of, and remedying these compounds difficult. Therefore, tackling this dilemma requires multidisciplinary research efforts focused on understanding the mechanics of EP behavior, conducting extensive assessments of their possible hazards, and devising effective measures for their reduction and elimination.

EPs have emerged as a major problem in sustainable water management due to the combined effects of climate change and population expansion put additional pressure on water supplies. One major issue with these pollutants is that they are very small, making them difficult to remove using conventional water treatment procedures. WWTPs are crucial in removing pollutants before they are released into river systems. Nevertheless, some EPs have great persistence in water and offer difficulties in eliminating or fast biodegradation. Residual pollutants may spread into the air and pollute drinking water sources, making resolving environmental and public health problems associated with EP more difficult. In the future, upcoming research efforts should focus on contaminants that have the greatest influence on human health and the aquatic ecosystem. This method would enable the integration of research activities focused on reducing pollution inputs and maximizing resource use. Future research may successfully influence strategic responses to maintain environmental integrity and public health outcomes by prioritizing contaminants with the highest potential for damage.

Although effective procedures may not always be possible to implement source reduction measures and replace developing contaminants with less hazardous alternatives in all cases. Consequently, research on the removal of new contaminants must give top priority to the development of strong remediation procedures based on sustainable concepts. To facilitate compliance with regulatory requirements, such procedures should be carefully developed to guarantee alignment between the characteristics of pollutants and the effectiveness of integrated removal approaches. Future technical developments must provide environmentally friendly treatment options targeting many EPs with the least energy and capital expense. Provisions for the recovery of treated water are also necessary, as is the capacity of treatment effectiveness to adjust to changing concentrations of newly emerging contaminants in the aquatic environment. This all-encompassing strategy for remediation projects promotes a harmonic equilibrium between human well-being and environmental preservation.

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S. Dey and M. P. Shah (eds.), *Biotechnological Removal of Emerging Pollutants from Wastewater Systems*, Advances in Wastewater Research,
https://doi.org/10.1007/978-981-96-3945-8