

Nancy George · Vagish Dwibedi ·
Santosh Kumar Rath ·
Prakram Singh Chauhan *Editors*

Management and Mitigation of Emerging Pollutants

 Springer

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Preface

The endeavour of the book entitled “Management and Mitigation of Emerging Pollutants” is to present details of the cutting-edge research in the field of origin and fate of the emerging pollutants along with mechanisms underlining the functional applications of microbes, nanomaterials and other advanced strategy for management of these pollutants. With over 90% of waste openly dumped or burned in low-income countries, poorly managed waste is contaminating the world’s oceans, clogging drains and causing flooding, transmitting diseases, increasing respiratory problems from burning, harming animals that consume waste unknowingly, and affecting economic development. In addition, poor waste management is leading to release of broad range of emerging pollutants which have recently been identified as threat to the environment and human health. Emerging pollutants include wide array of synthetic chemicals generated from human activities. There is rising level of concern linked to these emerging pollutants, mainly because the adverse impact of these pollutants on environment and general population is largely unknown. Thus, it is the need of hour to investigate advanced and sustainable strategies for mitigation and remediation of these emerging pollutants.

Environmental biotechnology-based approaches have the potential to endow with sustainable solutions to remediate the emerging pollutants generated by growing commercialization and population. To accomplish this, there is need of an extensive understanding of occurrence and fate of these emerging pollutants, their potential impact on ecosystem along with the exploration of ecofriendly and sustainable remediation approaches to mitigate this problem of great concern. Investigating advanced strategies such as unifying the role of nanoparticles, bio-adsorbents, electrode-ionization systems, microbial and enzyme technology, agriculture-based approach, recycling and reuse of emerging pollutants, their life cycle and techno-economical analysis will not only enrich our existing knowledge but also guide the researchers for development of multidisciplinary and sustainable approaches to safeguard the environment from these emerging contaminants.

This book provides some exciting and remarkable information in a structured manner to the scientists, researchers, students, entrepreneurs and policy/decision

makers working in the field of waste management, pollution management, microbial biotechnology, and nano-biotechnology. This book unifies the cutting-edge multidisciplinary research to address these environmental issues. This collective work is distinct because of our focus on diverse emerging technologies which are high-throughput, scalable and applicable to different countries regardless of their socio-economic conditions. We believe this book represents a sincere attempt to promote the underutilized potential of advanced technologies in addressing issues that are dynamic in the field of sustainable management and emissions reduction. We are firmly hopeful that this book will be helpful for all biotechnologists, academicians, and industrialists.

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Acknowledgments

Environmental biotechnology offers promising avenues for developing sustainable solutions to address the remediation of emerging pollutants. The effective implementation of such solutions requires a comprehensive understanding of the occurrence and fate of these emerging pollutants, as well as their potential impact on ecosystems. Furthermore, there is a critical need to explore eco-friendly and sustainable remediation approaches that can effectively mitigate this concern. The edited book presented here serves as a valuable resource, providing up-to-date knowledge to researchers in this field. Compiling diverse studies within a single publication poses a considerable challenge, but it offers an opportunity to consolidate and disseminate important information in the related field. First of all, we would like to acknowledge all the contributor authors of chapters in this book for bringing such an exhaustive compilation for a wider readership. All the editors gratefully acknowledge their parent organization for all the support and encouragement rendered. Thanks are also due to all those researchers whose original work has made the basis of this compilation, without the endless efforts of the researchers, science and society could not progress. We are also thankful to the team Springer for bringing this compilation to the scientific fraternity.

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Dr. Vagish Dwibedi did his B.Sc. from Lucknow University, Lucknow, Uttar Pradesh, and Ph.D. from Thapar Institute of Engineering and Technology, Patiala, India. Dr. Dwibedi is an academician and researcher with more than 8 years of experience in biotech research and development. He has carried out research projects and consultancy work in the areas of plant–microbe interaction/bioassay-guided drug-discovery and development, food security/sustainable agriculture and wastewater treatment. Presently, he is working as Assistant Professor at University Institute of Biotechnology, Chandigarh University, Gharuan Mohali, Punjab. Formerly, he was worked as Research Scientist at Agpharm Bioinnovations LLP incubated at Thapar Institute of Engineering & Technology, Patiala, India. He was also Winner in Down select competition-DST-Lockheed Martin-Tata Trust _IIGP 2.0 (2k18) (India Innovation Growth Programme 2.0) Innovation ID: IIGPUIBSUNB (The award carries financial support up to 11 Lac INR.). Dr. Dwibedi’s work is directed towards the development of screening platforms for different biological activities such as anti-microbial, anti-oxidant, anti-cancer, or finding novel molecules that interfere in the mechanism of development of diseases such as Alzheimer dementia (AD), Parkinson disease (PD), obesity, anti-gout (arthritis) and type 2 diabetes. He is also interested in food security, which predominantly involves the exploitation of plant–microbe interaction to combat abiotic stress and post-harvest preservation to enhance the shelf life of fresh crop/horticulture produces. He has published more than 15 research papers in various national and international journals and published 1 Indian patent.



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Dr. Santosh Kumar Rath is a medicinal and natural product chemist with more than 10 years of experience in research, academia, and industry. Dr. Rath received his doctorate from AcSIR at CSIR-Institute of Minerals and Materials Technology (CSIR-IMMT), Bhubaneswar, India. Presently, he is working as Assistant Professor at Department of SoPPHI, Faculty of Pharmacy, DIT University, Dehradun, Uttarakhand, India. Formerly, he worked as an Associate Professor and Research Head at the Department of Pharmaceutical Chemistry, Danteshwari College of Pharmacy, Jagdalpur, Chhattisgarh, India. He also worked as Research Associate (CSIR-RA) in the School of Chemistry & Biochemistry at Thapar Institute of Engineering & Technology, Patiala, India. Dr. Rath has received Research Associateship from CSIR and Senior Research Fellowship (ICMR-SRF) from ICMR, New Delhi, India. He did research at CSIR-Indian Institute of Integrative Medicine (CSIR-IIIM), Jammu, India. Dr. Rath has many publications to his credit, published more than 27 research papers in highly reputed international journals, 4 book chapters and 1 Indian patent. His area of research are Natural Product Chemistry and Organic Synthesis, in which he has expertise in isolation, identification and characterization of bioactive secondary metabolites, structural modification of major chemical constituents from plants as well as fungal sources. He is acquainted with various chromatographic techniques such as column, Preparative TLC, and HPLC for separating and purifying compounds. Dr. Rath is well aware of the interpretation of spectroscopic data viz., 1D and 2DNMR, MASS, IR, etc. His research areas involve multistep synthesis of biologically active synthetic and/or natural product-based hybrid scaffolds for lead identification in special targets to neurological disease, cancer, HIV, Covid-19 and infectious diseases. His research is mainly focused on the synthesis of novel P-gp and bacterial efflux pump inhibitors, besides synthetic modifications of the bioactive natural products for better activity/minimize toxicity profiles. Currently, he is developing new synthetic

methodologies for C-H functionalization of heterocycles and other medicinally relevant molecules. He contributed substantially to many research projects and is also having collaborative research work with many other research groups. The contributions, dedication, and brilliance of Dr. Rath in the area of natural product drug discovery and organic synthesis are truly commendable. His contributions aim to serve as an inspiration to all scientific fraternity and inculcate scientific temperament to others to think innovatively.



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Dr. Prakram Singh Chauhan is a Molecular Microbiologist, who obtained his master's degree in Biotechnology from Maharshi Dayanand Saraswati University, Ajmer, Rajasthan with first rank in university campus. He received his Ph.D. in Microbiology from the Panjab University, Chandigarh in 2015. He is life member of numerous scientific/professional societies including American Society for Microbiology (ASM), Association of Microbiologists of India (AMI). He is enlisted two times (2020, 2021) in top 2% scientist of world ranking, data compiled by Stanford University, USA. He is a recipient of several international awards/grants including prestigious Australian Endeavour Research award, Planning and Budget Committee (PBC) grant by Israel Council of Higher Education, Technion-Guangdong grant, INSO International Scientist Award-2022 on engineering, science and medicine, Young Scientist Award (Industrial Microbiology)-2019 by AMI-New Delhi, and ICOBM-2014, Penang, Malaysia, European Project "Nano2Clinic" best poster and trainee award in Trieste, Italy, CSIR-Senior Research Fellowship, etc. Dr. Chauhan has published 5 international patents, 38 research articles in various high impact journals of international repute with h-index of 22 and presented his research in many countries in the world. He worked in Monash University, Melbourne, Australia in the field of Nano-biotechnology. Currently, he is working as a research scientist in Faculty of

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List of Abbreviations

Abbreviations	Full form
2,4-D	2,4-dichlorophenoxyacetic acid
ACF	Activated carbon filtration
ACNR	Abiotic chemical nitrate reduction
Ag NPs	Silver nanoparticles
ARG	Antibiotic resistance genes
CAPS	Chemically assisted primary sedimentation
CEPT	Chemically enhanced primary treatment
CFCs	Chlorofluorocarbon
CNTs	Carbon nanotubes
DWDS	Drinking water distribution systems
ECL	Electrochemiluminescence
EDCs	Endocrine disrupting chemicals
EPs	Emerging pollutant
HBCD	Hexabromocyclododecane
IPM	Integrated pest management
LAS	Linear alkyl benzene sulphonate
LCA	Lifecycle assessment
LOD	Limit of detection
MBRs	Membrane bioreactors
MECs	Microbial electro-deionization cells
MFC	Microbial Fuel Cell
MFC-PC	Microbial fuel cell-photocatalytic
MOB	Methane-oxidizing bacteria
MOFs	Metal-organic frameworks
MPLC	Medium Pressure Liquid Chromatography
NIH	National Institute of Health, USA
NSAIDs	Non-Steroidal Anti-Inflammatory Drugs
NWT	Natural wastewater treatment
OD	Optical Density

PAHs	Polycyclic aromatic hydrocarbons
PCBs	Polychlorinated biphenyls
PDMS	Polydimethylsiloxane
PhACs	Pharmaceutically active chemicals
PM	Particulate matter
PMSF	Phenylmethane sulfonyl fluoride
POPs	Persistent organic pollutants
PPCPs	Pharmaceuticals and personal care products
rGO	Reduced graphene oxide
SCFC	Sugarcane filter cake
SDS–PAGE	Sodium dodecyl sulphate–Polyacrylamide gel electrophoresis
SSF	Slow sand filtration
SSRIs	Selective serotonin reuptake inhibitors
TAE	Tris acetate EDTA
TCA	Trichloro acetic acid
TiO ₂	Titanium oxides
TMDs	Transition metal dichalcogenides
TPCK	Tosyl phenylalanyl chloromethyl ketone
TPU	Thermoplastic polyurethane
UHPLC	Ultra-high-performance liquid chromatography
USFDA	United States Food and Drug Administrations
VOCs	Volatile organic compounds
WHO	World Health Organization

Emerging Pollutants in the Environment and Ecological Risks



Tarun Sharma, Akashdeep Singh, Naveen Kumar, Garima Chauhan, Davinder Paul Singh, Arjun Singh, and Bharat Bhushan Rana

Abstract The burgeoning population combined with industrialization and urbanization has been the stepping stone to pollutants, either natural or synthetic, affecting the ecosystem around the globe. These emerging pollutants across the ecosystems may persist for a significant duration or may be mobile across air, water, and land. Although yet not checked, these pollutants pose a serious threat to human health and environmental sustainability. Ongoing research advancements have made the detection and analysis of trace elements or micropollutants easy, but the continued emergence of new compounds or chemicals makes refinement and development in diagnostic techniques a necessity for the detection of pollutants in the environment. The pollutants are classified into various categories according to their source of origin such as pharmaceutical, cosmetic, and farming-based pollutants. This chapter elaborates on the fate, movement, and environmental and ecological risks associated with their intake or movement across the ecosystems as direct or metabolized pollutants. The fate of pollutants across the ecosystems such as freshwater or marine water bodies from different sources influences the risks they pose to the sustainability of the environment. Emerging micropollutants from industries or other sources have been discussed in detail. The chapter describes the potential strategies to control pollutants as well as the bioremediation techniques based on vegetation, microorganisms, and engineered structures for the purpose.

Keywords Bioremediation · Bio removal · Environmental risks · Phytoremediation · Micropollutants

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1 Introduction

Over the decades, the dependence on synthetic pesticides has increased because of industrialization, mushrooming population, and growing food demand. “Emerging pollutants” (EPs) refer to all compounds with potentially hazardous effects that are not currently regulated or that have emerging regulatory standards under national or international law (MacAfee 2017). The pollutants pose a tremendous threat to the ecosystem and human health (Khan et al. 2021a, b). These pollutants are often synthetic or naturally occurring substances that were not previously of significant concern such as pharmaceuticals, personal care products, industrial chemicals, and their by-products (Khalidi-Idrissi et al. 2023). The emergence of these pollutants is a result of various factors, including advances in scientific detection methods, increased awareness of environmental issues, and changes in human activities. These pollutants enter the environment through various pathways, such as industrial discharges, agricultural runoff, improper waste disposal, and atmospheric deposition (Khalidi-Idrissi et al. 2023). Their origin can be traced back to waste resulting from anthropogenic activities such as the decomposition of organic compounds leading to the accumulation of persistent metabolites (Sørensen et al. 2007). Increased concentration of biological pollutants during the distribution of drinking water may be affected by numerous factors such as a change in human demographic behavior and a shift toward intensive farming practices (Houtman 2010). Soil micropollutants such as chemicals from pharmaceutical industries, hormones, endocrine disruptors, and other biological pollutants are all examples of emerging pollutants (Archer et al. 2021; Devault et al. 2021; Khalidi-Idrissi et al. 2023). Even after being banned and replaced by environmentally friendly substitutes, pesticide residues prevail on the surface and in groundwater (Stuart et al. 2012; Santos et al. 2019; Chaturvedi et al. 2021; Sahani et al. 2022). It was stated at the World Water Forum in Kyoto, Japan, that since 2002, annually 2 million tons of pollutants are released into the water from various sources such as industries, urban discharges, or agricultural activities (Moya et al. 2011; Vasilachi et al. 2021).

Due to their persistence, EPs spread throughout the different environmental matrices via water and air (Pavel et al. 2013). The presence of pollutants from the areas where they were not previously reported is rapidly emerging. Globally, the annual production of contaminants has reportedly increased from 1 million to 500 million tons (Thomaidis et al. 2012). Although the concentration of pollutants has increased, but it may vary from one place to other, primarily depending on the conditions such as dosage of pesticides, treatment efficiency, and persistence. (Ranjan et al. 2022). Ultimately, these pollutants find their way to the ecosystem through water either system or air. Different levels of PPCPs pollution were detected in two Indian rivers after sampling. Although the concentration of various pharmaceuticals (PCs) varied depending on the location, the river *Netravathi* basin had a higher human population and higher PC pollution levels (Joshua et al. 2020). Many cosmetics and other beauty products require microplastics as an integral component. It was found that beaches in Mexico had microplastic concentrations ranging from

31.7 to 545.8 MP/m² (Alvarez-Zeferino et al. 2020). In other words, emerging pollutants do not come from somewhere; they already exist in detectable quantities here and have a permanent negative impact on both the environment and human health (Pal et al. 2010).

2 Characteristics and Functioning of Emerging Pollutants

In general, EPs originate mainly from urban areas, and industries, or from diffuse which consists of agriculture pollution (Farré et al. 2010; Geissen et al. 2010). The movement of these EPs from their source to the water bodies mainly depends on the properties of the pollutants which may include the persistence of the pollutants, volatility, polarity, and absorption properties. The pollutants produced by various wastewater treatment plants are directly dumped in the rivers and other water bodies which raises a major concern for marine life (Fig. 1) and the people consume the water regularly for household purposes (Liang et al. 2013). The pollutants can undergo various biodegradation and transformations and impact the groundwater (Hernandez et al. 2012). The biodegradation of pollutants mainly depends on the presence of various organisms which are capable of transforming the pollutants through metabolic networks (Xie et al. 2013). In rural areas, EPs spread and are transported by the action of air and runoff erosion until the pollutants reach a water

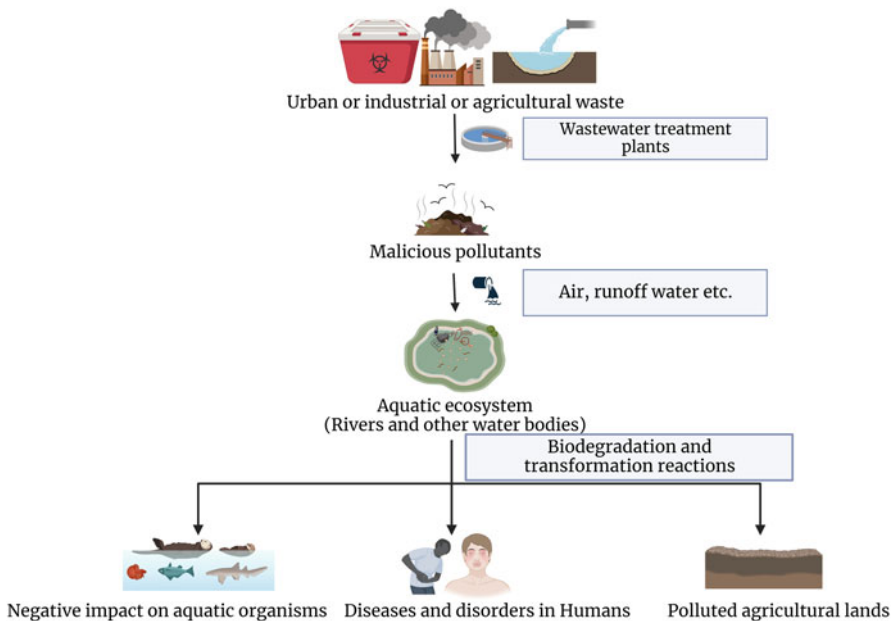


Fig. 1 Fate and movement of pollutants in the ecosystem

body (Kasel et al. 2013). The existence of manure in agricultural fields also contributes to the persistence of pollutants in the soil (Monteiro and Boxall 2009).

3 Emerging Pollutants with Their Related Ecological and Environmental Risks

3.1 *Pharmaceutical-Based Emerging Pollutants*

Pharmaceutical-based emerging pollutants encompass a group of contaminants that originate from the use, production, and disposal of pharmaceutical drugs (Svensson Grape et al. 2023). The residues of pharmaceuticals are highly stable, which makes it difficult for animals and humans to fully assimilate post-use (Yan et al. 2017). According to studies, about 90% of pharmaceutically active chemicals (PhACs) made their way into residential water through the city municipal drainage system. Due to their inadequate treatment, these metabolites may reach the environment through wastewater treatment facilities (Samal et al. 2022). Over 3000 chemicals, including impotence medications, painkillers, antibiotics, antidiabetics, beta-blockers, antidepressants, X-ray contrast media, contraceptives, and lipid regulators, were employed as pharmaceutical components (Campanha et al. 2015; Diamond et al. 2015). Some medications, primarily cotinine, caffeine, and acetaminophen, are the primary sources of PhACs found in drinking water ingested through groundwater or surface water (Stackelberg et al. 2004; Park and Oh 2020; Khoshvaght et al. 2021). Here, are some examples of pharmaceutical-based emerging pollutants and their related risks:

1. **Antibiotics:** Antibiotics are widely used in human and veterinary medicine and are often detected in the environment. They can enter aquatic systems through wastewater treatment plant effluents, agricultural runoff, and direct disposal. Antibiotics can have ecological consequences by disrupting microbial communities in aquatic environments, leading to the development of antibiotic resistance (Szymańska et al. 2019; Kovalakova et al. 2020; Valdez-Carrillo et al. 2020). Additionally, their presence in the environment can affect natural bacterial populations and disrupt ecological processes.
2. **Hormones:** Hormones, such as those used in contraceptive pills and hormone replacement therapy, can be released into the environment through human excretion and improper disposal of unused medications. These hormones can disrupt the endocrine systems of aquatic organisms, leading to reproductive abnormalities and behavioral changes (Ramírez-Sánchez et al. 2015; Valdez-Carrillo et al. 2020). They can also affect the reproductive success of fish and other aquatic species, potentially leading to population declines (Vieira et al. 2020).
3. **Non-steroidal anti-inflammatory drugs (NSAIDs):** NSAIDs, including ibuprofen and diclofenac, are widely used for pain relief and inflammation (Duarte et al. 2023). They are often found in wastewater effluents due to incomplete removal

during conventional water treatment processes. NSAIDs can have adverse effects on aquatic organisms, such as inhibiting the growth of algae and affecting the behavior and reproduction of fish and invertebrates (Evgenidou et al. 2015; Świacka et al. 2021; Ortúzar et al. 2022).

4. Antidepressants: Antidepressants, such as selective serotonin reuptake inhibitors (SSRIs), are frequently prescribed medications. They can enter the environment through sewage systems and greywater treatment plants. Antidepressants have been found to affect the behavior and physiology of aquatic organisms, including fish, by altering neurotransmitter levels (Brodin et al. 2013). Changes in fish behavior, such as increased boldness or reduced predator avoidance, can have ecological implications in natural ecosystems.
5. Chemotherapeutic drugs: Chemotherapeutic drugs used in cancer treatment can enter the environment through excretion and improper disposal. These drugs are designed to be toxic to cancer cells but can also be harmful to non-target organisms in aquatic ecosystems. Chemotherapeutic drugs can affect the growth and reproduction of aquatic organisms, potentially leading to population imbalances and ecological disruptions.

The ecological and environmental risks associated with pharmaceutical-based emerging pollutants highlight the need for proper management strategies. Many of these have been described as acutely poisonous to marine life. Health hazards associated with certain PhACs, such as estrogenic and chronic toxicity, have been reported by some health organizations, but we currently lack the expertise to prevent these negative effects (Liu et al. 2015). Improved wastewater treatment processes, public education on proper medication disposal, and the development of environmentally friendly pharmaceuticals are essential to mitigate the impact of these pollutants on ecosystems and protect the environment.

3.2 Pesticides-Based Emerging Pollutants

Pesticides-based emerging pollutants include varied chemicals used in agriculture, horticulture, and pest control. The usage of antibiotics, biocides, and pesticides is heavily influenced by the type of bacteria present, their level of resistance, and their ability to degrade plant material in the area where agriculture is practiced (Zhang et al. 2015). As the world progresses, the demand for fertilizers, biocides, and pesticides rises along with the expansion of agriculture. These substances can have ecological and environmental risks when they enter the environment through various pathways. Due to the improper drainage system, the kind of soil, and the local geography, these pesticides and biocides are easily released into the water through runoff or drainage (Leu et al. 2004).

1. Organophosphate pesticides: Organophosphate pesticides, such as chlorpyrifos and diazinon, have been widely used for insect control (Rashid et al. 2010). These pesticides can contaminate soil, water bodies, and vegetation through agricultural

runoff and spray drift. Organophosphates are highly lethal to non-target organisms, including beneficial insects, birds, fish, and amphibians (Nicolopoulou-Stamati et al. 2016). They can disrupt the nervous system, inhibit enzyme activity, and lead to population declines and ecological imbalances (Sharma et al. 2019).

2. **Neonicotinoid pesticides:** Neonicotinoids, including imidacloprid and clothianidin, are systemic pesticides commonly used in agriculture and horticulture. They are particularly concerning due to their impact on pollinators, such as bees and butterflies. Neonicotinoids can contaminate nectar and pollen, leading to adverse effects on pollinators' behavior, reproduction, and immune systems (Nicolopoulou-Stamati et al. 2016). The decline of pollinator populations can have cascading effects on ecosystems and agricultural productivity.
3. **Pyrethroid pesticides:** Pyrethroids, such as cypermethrin and deltamethrin, are widely used insecticides in agriculture, public health, and residential settings. They can enter water bodies through runoff and drift, affecting aquatic organisms. Pyrethroids are toxic to fish, amphibians, and crustaceans, disrupting their nervous systems and impairing reproduction and behavior. They can also harm non-target terrestrial insects, leading to disruptions in food webs.
4. **Herbicides:** Herbicides, including glyphosate (found in products like Roundup), are used to control weeds in agriculture, landscaping, and forestry (Nicolopoulou-Stamati et al. 2016). These chemicals can contaminate soil, surface water, and groundwater through runoff and leaching. Herbicides can have detrimental effects on non-target plants, affecting biodiversity and ecosystem composition (Arman et al. 2021). They can also enter aquatic systems, impacting algae, macrophytes, and associated organisms, disrupting aquatic habitats and food chains.
5. **Fungicides:** Fungicides are used to control fungal diseases in agriculture, forestry, and horticulture. Common fungicides, such as azoxystrobin and chlorothalonil, can leach into groundwater or enter surface water through runoff. Fungicides can harm non-target fungi, affecting the balance of fungal communities and disrupting nutrient cycling processes (Pathak et al. 2022). They can also be toxic to aquatic organisms, including fish and amphibians, causing reproductive and developmental abnormalities.

The ecological and environmental risks associated with pesticides-based emerging pollutants emphasize the need for sustainable pest management practices. Integrated pest management (IPM) approaches that prioritize biological controls, crop rotation, and reduced pesticide use can help minimize the impact on non-target organisms and promote ecosystem health. Strict regulation, proper application techniques, and education on pesticide handling and disposal are crucial for mitigating the environmental risks associated with these emerging pollutants.

3.3 *Personal Care Products Based on Emerging Pollutants*

Personal care products based on emerging pollutants refer to a group of substances found in various cosmetics, skincare products, fragrances, and hygiene items. These products often contain synthetic chemicals that can have ecological and environmental risks when they are washed off and enter the environment through wastewater. Leaching is a common method of introducing toxins into water sources, easily discovered in urban water reserves (Margot et al. 2015). Parabens are the first of these and are typically utilized as preservatives in food, medications, and cosmetics at concentrations ranging from 30 to 20 g/L. Secondly, temperature/time control for safety (TCS) is the most widely used bactericide in personal care items such as toothpaste, shampoo, soap, mouthwash, skin care lotions, cosmetics, and deodorants. Thirdly, *N, N*-dimethyl-meta-toluamide (DEET) is the component most frequently used in the production of insect repellent. The majority of these self-care items are made for external users and can be washed without undergoing any chemical changes to their structure or characteristics (Campanha et al. 2015). Due to urban runoff, they are now substantially more prevalent in groundwater reserves. Some instances of personal care products-based emerging pollutants are discussed below.

1. **Microplastics:** Microplastics are tiny plastic particles found in exfoliating scrubs, toothpaste, and other personal care products. These particles are typically made of polyethylene or polypropylene and can be harmful when they enter aquatic ecosystems. Microplastics can accumulate in the environment, affecting aquatic organisms such as fish, mollusks, and filter-feeding organisms (Silva et al. 2021). They can cause physical harm, ingestion-related issues, and disruption of normal biological functions.
2. **UV filters:** Ultraviolet (UV) filters, such as oxybenzone and octinoxate, are commonly used in sunscreens and other personal care products to protect the skin from UV radiation. However, these chemicals can pose risks to aquatic environments when they wash off during swimming or enter water systems through wastewater. UV filters have been found to be toxic to coral reefs, contributing to coral bleaching and impairing the growth and reproduction of marine organisms.
3. **Fragrance chemicals:** Fragrance chemicals, including phthalates and synthetic musks, are used in perfumes, colognes, and other scented personal care products. These chemicals can be released into the environment through product use and wastewater. Phthalates have been associated with endocrine disruption and reproductive toxicity in aquatic organisms (Dueñas-Muñoz et al. 2022). Synthetic musks can accumulate in sediments and aquatic organisms, posing long-term risks to ecosystems.
4. **Triclosan:** Triclosan is an antimicrobial agent commonly found in antibacterial soaps, hand sanitizers, and other personal care products. It can be released into wastewater and enter aquatic systems. Triclosan has been shown to have toxic effects on algae and aquatic plants, disrupting their growth and survival (Ebele

et al. 2017; Juliano and Magrini 2017). There are also concerns about the potential of triclosan to contribute to the development of antibiotic resistance in bacteria.

5. Silicones: Silicones, such as cyclotetrasiloxane (D4) and cyclopentasiloxane (D5), are used in various personal care products, including hair conditioners and skincare products, to provide a smooth texture. These compounds can be released into the environment during product use and can persist in aquatic systems. Some silicones have been found to be toxic to aquatic organisms, such as fish and invertebrates, affecting their reproduction and development.

To address the ecological and environmental risks associated with personal care products-based emerging pollutants, there is a growing focus on developing and promoting more sustainable and environmentally friendly alternatives. This includes the use of natural and biodegradable ingredients, avoiding microplastics, and adopting eco-friendly manufacturing and packaging practices. Additionally, proper disposal of personal care products and wastewater treatment are crucial in preventing these pollutants from entering and harming the environment.

3.4 Micropollutants-Based Emerging Pollutants

Micropollutants-based emerging pollutants are a group of contaminants that are present in low concentrations but have the potential to adversely affect ecosystem and the environment. These pollutants are diverse in nature and include various substances, such as pharmaceuticals, pesticides, industrial chemicals, personal care products, and their metabolites. Many chemical and microbiological agents travel long distance because of their high stability and transportability properties. These biological pollutants are readily detectable in drinking water (Kolpin et al. 2002). Leaching, due to the overuse of fertilizers in agricultural practices, leads to an increase in pollutants in water resources and subsequent health issues. Due to the abundance of biological and chemical micropollutants, wastewater treatment plants are also one of the main sources of these contaminants. After being separated from wastewater, these toxins are disposed of via burning or washed away by the freshwater sources, which explains the connectedness between sources and receptors as volatilization, dispersion, and sorption from one environment to another. These micropollutants are difficult to eliminate since they are present in such small quantities, and have negative impacts on human health, such as chronic poisoning and endocrine disruption (Rosal et al. 2010). Here are some examples of micropollutants-based emerging pollutants and their related ecological and environmental risks:

1. Pharmaceuticals and personal care products (PPCPs): PPCPs, including prescription drugs, over-the-counter medications, and personal care products, are widely used by humans and can enter the environment through wastewater discharge and improper disposal. PPCPs can accumulate in surface water, groundwater, and

soil. They can have adverse effects on aquatic organisms, such as fish and invertebrates, by disrupting their endocrine systems, impairing reproduction, and causing behavioral changes. Some PPCPs have also been linked to the development of antibiotic resistance in bacteria (Ebele et al. 2017).

2. **Pesticides:** Pesticides, including insecticides, herbicides, and fungicides, are commonly used in agricultural and urban settings. These chemicals can enter the environment through runoff, drift, and improper disposal (Pathak et al. 2022). Even at low concentrations, pesticides can have detrimental effects on non-target organisms, such as pollinators, birds, fish, and aquatic invertebrates (Rashid et al. 2010; Haddaoui and Mateo-Sagasta 2021). They can disrupt ecosystems, alter food chains, and lead to population declines of sensitive species.
3. **Industrial chemicals:** Industrial chemicals, such as flame retardants, plasticizers, and surfactants, can be released into the environment through manufacturing processes, industrial discharges, and improper waste management. These chemicals can persist in the environment, bioaccumulate in organisms, and pose risks to wildlife. For example, polybrominated diphenyl ethers (PBDEs), used as flame retardants, can be toxic to aquatic organisms and have been associated with adverse effects on neurological development in animals.
4. **Heavy metals:** Heavy metals, including lead, mercury, cadmium, and arsenic, are naturally occurring elements that can enter the environment through various human activities, such as mining, industrial processes, and improper disposal of electronic waste (Ramírez-Malule et al. 2020). Heavy metals can accumulate in soils, sediments, and water bodies, posing risks to organisms and ecosystems (Lodeiro et al. 2019). They can be toxic to aquatic life, impair reproductive success, and lead to long-term ecological imbalances (Wei et al. 2013).
5. **Microplastics:** Microplastics are small plastic particles (<5 mm) that come from the breakdown of larger plastic items, as well as from microbeads in personal care products. Microplastics can be found in marine and freshwater environments, affecting aquatic organisms. They can be ingested by organisms, leading to physical damage, blockage of digestive systems, and the potential for the transfer of contaminants associated with microplastics through the food chain.

The ecological and environmental risks associated with micropollutants-based emerging pollutants necessitate proactive measures to minimize their release and impact. Strategies include improving wastewater treatment systems to remove micropollutants, promoting proper disposal and recycling practices, developing greener alternatives for chemicals, and implementing sustainable agricultural practices. Additionally, monitoring programs and research efforts are essential to understand the potential risks and inform appropriate management strategies to protect ecosystems and the environment from the harmful effects of micropollutants.

3.5 *Dioxins and Polychlorinated Biphenyls (PCBs)*

Dioxins and polychlorinated biphenyls (PCBs) are two groups of persistent organic pollutants (POPs) that have been recognized as significant environmental contaminants. They are highly toxic and can have severe ecological and environmental risks. Dioxins are a family of toxic chemical compounds that are unintentional by-products of certain industrial processes, such as waste incineration, paper and pulp manufacturing, and chemical production (Zubair and Adrees 2019). They are formed during incomplete combustion and can persist in the environment for a long time. Dioxins are known to be highly toxic and can cause a range of adverse effects on both wildlife and humans. PCBs are a group of synthetic chemicals that were widely used in electrical equipment, such as transformers and capacitors, as well as in industrial processes before their production was banned in many countries (Montuori et al. 2020; Saktrakulkla et al. 2022). PCBs are persistent, meaning they do not easily break down in the environment, and can still be found in soils, sediments, and aquatic systems (Cui et al. 2020).

1. **Bioaccumulation and biomagnification:** Dioxins have a high affinity for fatty tissues and can bioaccumulate in organisms. They tend to accumulate in higher concentrations as they move up the food chain through a process called biomagnification. This poses a risk to organisms at higher trophic levels, such as top predators, as they can experience higher levels of dioxin exposure (Gouin et al. 2004; Cui et al. 2020; Battisti et al. 2022).
2. **Reproductive and developmental effects:** Dioxins can disrupt reproductive processes in wildlife, leading to reduced fertility, impaired reproduction, and birth defects. They can affect hormone levels and interfere with reproductive organs and the development of offspring (Kirkok et al. 2020; Battisti et al. 2022; Driesen et al. 2022).
3. **Immune system and health effects:** Dioxins can suppress the immune system in both animals and humans, making organisms more susceptible to infections and diseases. Exposure to dioxins has been associated with various health issues, including cancer, hormonal disruptions, and neurological effects (Battisti et al. 2022; Driesen et al. 2022).
4. **Toxicity and accumulation:** Like dioxins, PCBs are highly lipophilic, meaning they have an affinity for fats and can accumulate in organisms (Kirkok et al. 2020). They can accumulate in the fatty tissues of animals, leading to long-term exposure and potential toxicity.
5. **Disruption of hormonal systems:** PCBs are known to have endocrine-disrupting properties, interfering with hormone signaling and regulation. This can lead to reproductive impairments, developmental abnormalities, and disruptions in the growth and behavior of organisms (Kirkok et al. 2020).
6. **Impact on wildlife and biodiversity:** PCBs have been linked to negative impacts on wildlife populations and biodiversity. They can cause population declines, reduced reproductive success, and altered behavior in various species, including birds, fish, and mammals.

7. Persistence and long-range transport: PCBs are highly persistent in the environment, meaning they can remain in ecosystems for long periods. They can also undergo long-range transport, being transported over long distances through air and water currents, potentially affecting ecosystems far from their original source.

The risks associated with dioxins and PCBs highlight the importance of strict regulations, proper disposal of waste containing these chemicals, and remediation efforts to reduce their presence in the environment. Ongoing monitoring and research are crucial to understand their persistence, exposure pathways, and potential impacts, allowing for effective management strategies to protect ecosystems and human health from these hazardous pollutants.

3.6 Polycyclic Aromatic Hydrocarbons (PAHs)

Polycyclic aromatic hydrocarbons (PAHs) are those organic compounds formed by the fusion of two or more aromatic rings. They are formed naturally during incomplete combustion processes, such as burning fossil fuels, as well as through human activities such as industrial processes, vehicle emissions, and the burning of biomass and waste (Abdel-Shafy and Mansour 2016; Mojiri et al. 2019; Patel et al. 2020). PAHs are persistent organic pollutants that can pose ecological and environmental risks (Liu et al. 2020). Although a wide variety of PACs have been examined throughout the years, the United States Environmental Protection Agency (USEPA) listed a small number of PACs (approximately 16) as pollutants. PACs influence human health when they are ingested or through cutaneous contact, smoking, and inhalation. The studies revealed that 50% of PACs are carcinogenic and pose other health issues such as infertility, diabetes, inadequate fetal development, oxidative stress, cardiovascular disease, and inflammation (Jomova et al. 2012; Wang et al. 2015). Besides, PACs have certain immediate side effects, including nausea, eye irritation, vomiting, DNA damage, gene mutations in proteins, and skin irritation. The related risks associated with polycyclic aromatic hydrocarbons (PAHs) are discussed below.

1. Toxicity to aquatic organisms: PAHs are toxic to a wide range of aquatic organisms, including fish, invertebrates, and amphibians (Honda and Suzuki 2020; Adeniji et al. 2019). They can have acute and chronic effects on these organisms, such as reduced survival, impaired reproduction, developmental abnormalities, and behavioral changes. PAHs can also affect fish and amphibian populations by disrupting their endocrine systems and altering their growth and development (Patel et al. 2020).
2. Bioaccumulation and biomagnification: PAHs have the potential to bioaccumulate in organisms (Patel et al. 2020). They can be absorbed by aquatic organisms through ingestion, respiration, and dermal contact (Ke et al. 2010). PAHs can accumulate in fatty tissues and organs, leading to higher concentrations in organisms higher up the food chain through biomagnification. This poses risks

to top predators, such as birds and marine mammals, which can experience high levels of PAH exposure.

3. **Carcinogenicity:** Several PAHs, including benzo[a]pyrene, are classified as carcinogens (Honda and Suzuki 2020). Prolonged exposure to high levels of PAHs can increase the risk of cancer in humans and wildlife (Låg et al. 2020; Patel et al. 2020). PAHs can cause DNA damage, gene mutations, and disruption of normal cellular processes, leading to the development of tumors.
4. **Soil and sediment contamination:** PAHs have low water solubility and tend to bind to soil and sediment particles. This can lead to the accumulation of PAHs in terrestrial ecosystems, especially in areas close to pollution sources. PAH-contaminated soil and sediments can negatively impact soil microorganisms, plants, and invertebrates, affecting ecosystem functioning and biodiversity (Liu et al. 2020).
5. **Air pollution and human health risks:** PAHs are released into the atmosphere through the burning of fossil fuels, industrial processes, and other combustion sources. Inhalation of PAHs through air pollution can pose risks to human health, especially for individuals living in urban areas or near industrial sites (Låg et al. 2020). PAH exposure has been associated with respiratory problems, cardiovascular effects, and an increased risk of certain cancers in humans.

Efforts to mitigate the risks associated with PAHs include implementing emission controls, promoting cleaner combustion technologies, and reducing industrial and vehicular emissions. Proper waste management, remediation of contaminated sites, and monitoring programs are also important in minimizing PAH contamination in soil, water, and air. Additionally, public awareness, education, and regulatory measures can help reduce human exposure to PAHs and protect both ecosystems and human health from their adverse effects.

4 Strategies to Control Environmental Pollutants

Activated carbon has demonstrated its ability to remove a wide range of chemicals (emerging pollutants) in a considerable capacity (more than 90%) for instance ciprofloxacin can be eliminated by adding activated carbon, which lowers the overall concentration quickly below the detection limit (Carabineiro et al. 2011). Biochar has recently been extensively used in research on the adsorption of emerging pollutants (Oliveira et al. 2017). The pyrolysis parameters used throughout the biochar synthesis process determine how well-emerging pollutants are adsorbed on biochar (Tan et al. 2015). Without thermal activating biochar helps in adsorption of 35% sulfamethoxazole, whereas when heat activated, it loses its adsorption capacity resulting in adsorption of merely 16% sulfamethoxazole (Zheng et al. 2013).

The surface-modified clays can be used as effective adsorbents to remove larger concentrations of emerging pollutants since they possess special physiochemical properties that native clays are unable to exhibit on their own. Two pharmaceutically

based ECs, namely tramadol and doxepin, have been adsorbed using sodium-exchanged smectite clay mineral (Mt) which acted as a geo-sorbent (Thiebault et al. 2015). Activated sludge and anaerobic granular sludge are widely employed in wastewater treatment to remove emerging pollutants (EPs). Various types of sludges are utilized in these treatments, including pure strains, aerobic sludge, anaerobic sludge, and genetically modified bacteria. Activated sludge processes involve the use of a diverse microbial community that degrades EPs through aerobic conditions. The sludge serves as a carrier for the microorganisms, facilitating the breakdown of pollutants. Anaerobic granular sludge, on the other hand, operates under oxygen-depleted conditions, utilizing anaerobic microorganisms to convert EPs into less harmful substances. These sludge-based treatments offer efficient and sustainable solutions for the removal of EPs from wastewater, contributing to the protection of aquatic ecosystems and human health (Wang and Wang 2018).

4.1 Approaches in Bioremediation of Pollutants

Bioremediation is a versatile approach that harnesses the power of living organisms to mitigate and clean up pollutants in the environment (Bala et al. 2022). Several approaches are commonly employed in bioremediation, each tailored to specific pollutants and site conditions. Biostimulation is one approach that focuses on enhancing the activity and growth of indigenous microorganisms capable of degrading pollutants (Sharma et al. 2020). This is achieved by providing nutrients, such as nitrogen and phosphorus, or other growth-promoting factors to the contaminated site. By stimulating the existing microbial population, biostimulation can accelerate the natural degradation of pollutants. It is particularly useful when the native microorganisms possess the necessary metabolic capabilities but are limited by the availability of essential nutrients. Bioaugmentation, on the other hand, involves the introduction of exogenous microorganisms into the contaminated site (Akubude et al. 2020; Sharma et al. 2020). These microorganisms, such as bacteria or fungi, are carefully selected for their ability to efficiently degrade the target pollutants (Ahumada-Rudolph et al. 2021; Ortúzar et al. 2022). By adding the specialized degraders, bioaugmentation enhances the overall microbial diversity and metabolic capacity, leading to a more effective breakdown of pollutants. This approach is often employed when the native microbial population lacks the required capabilities or when rapid cleanup is required.

Phytoremediation utilizes the natural abilities of plants to uptake, transform, and stabilize pollutants (Kurade et al. 2021). Through various mechanisms such as rhizodegradation, phytoextraction, and rhizofiltration, plants can effectively remove or degrade contaminants from soil, water, or air (Odoh et al. 2019; Capuana 2020; Wei et al. 2021). Phytoremediation is particularly well suited for organic contaminants, heavy metals, and certain metalloids. It is a sustainable and aesthetically pleasing approach that can be used in a range of environments, including industrial sites, brownfields, and wastewater treatment systems (Kaloudas et al. 2021).

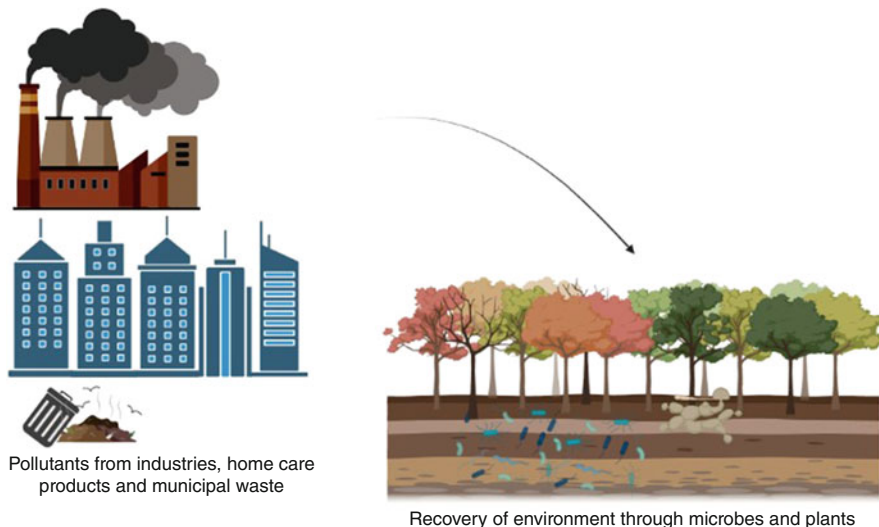


Fig. 2 Bioremediation of the pollutants using microbes and plants

Mycoremediation is a specialized form of bioremediation that utilizes fungi to degrade or transform pollutants (Vaksmaa et al. 2023). Fungi, especially white-rot fungi, produce enzymes that can break down a wide range of organic pollutants, including complex compounds such as polycyclic aromatic hydrocarbons (PAHs) and chlorinated compounds. Mycoremediation can be employed in soil, in water, or within closed systems such as bioreactors (Wang et al. 2014; Akhtar and Mannan 2020). The fungi efficiently degrade the pollutants, converting them into harmless by-products. Rhizoremediation exploits the interactions between plants and root-associated microorganisms to promote the degradation or immobilization of pollutants. Plants release compounds such as organic acids and enzymes into the rhizosphere, the soil region influenced by their roots, creating a favorable environment for microbial degradation. The combined action of the plants and associated microorganisms enhances the breakdown of pollutants and their subsequent removal from the environment. Rhizoremediation is effective for both organic and inorganic contaminants and is often used in conjunction with phytoremediation (Fig. 2).

Constructed wetlands are engineered systems that utilize the combination of plants, microbes, and the physical properties of wetland soils to treat and remove pollutants from wastewater or contaminated surface water (Herath and Vithanage 2015; Wang et al. 2022). Wetland plants and the associated microbial communities play a crucial role in the treatment process. They uptake, transform, and immobilize pollutants, removing them from the water column. Constructed wetlands are effective in treating a wide range of contaminants, including organic compounds, heavy metals, and nutrients (Ravikumar et al. 2022; Sánchez et al. 2022). The choice of bioremediation approach depends on various factors such as the type of pollutants, site characteristics, and specific environmental conditions. In many cases, a

combination of approaches may be employed to achieve effective and sustainable cleanup. Continuous monitoring and optimization of the bioremediation process are critical to ensure its success and to minimize any potential risks associated with the contaminants. Bioremediation offers a promising and environmentally friendly solution for the cleanup of polluted sites, promoting the restoration and protection of ecosystems and human health.

5 Conclusion

There is an ongoing concern for human safety and health as well as the ecosystem due to the existence of a large group of chemicals classified as emerging pollutants. Human activities in industries, households, and agriculture release emerging contaminants into the environment. They are difficult to eliminate from the environment due to their intricate structure and exceptionally stable properties. Risks are created for the ecosystem and the population as a whole. Because of their tiny size, very advanced equipment is required to remove these toxins from the environment. They will continue to appear if they are not stopped promptly, becoming the primary causal agents of disease in living things as well as a menace to the environment. The biological approaches are superior to other approaches in their ability to combat these developing contaminants.

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Origin and Management of Inorganic and Organic Contaminants



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Abstract This summary discusses the mitigation and management of inorganic and organic contaminants through colorimetric and fluorometric methods, adsorption processes, and bioremediation techniques. Colorimetric and fluorometric methods utilize specific dyes or fluorescent probes to detect contaminants based on their color or fluorescence. These techniques are simple, cost-effective, and suitable for on-site analysis. Adsorption processes involve the use of materials like activated carbon and zeolites to remove contaminants by adsorbing them onto their surfaces. This method offers high removal efficiencies and versatility. Bioremediation utilizes microorganisms or plants to degrade or transform contaminants. Microorganisms can break down organic contaminants, while plants can accumulate and immobilize them. Bioremediation is a sustainable and environmentally friendly approach with benefits like natural attenuation and low cost. Overall, the integration of colorimetric and fluorometric methods, adsorption processes, and bioremediation techniques provides a comprehensive approach to mitigate and manage inorganic and organic contaminants. These methods offer valuable tools for contaminant detection, removal, and remediation, contributing to environmental preservation and human health protection. Continued research and technological advancements in these areas will further enhance our ability to address the challenges posed by contaminants in our ecosystems.

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1 Introduction

Environmental contaminants refer to substances or pollutants that are introduced into the environment as a result of human activities, thereby causing adverse effects on ecosystems and potential risks to human health (Noguera-Oviedo and Aga 2016). These contaminants exist in various forms, including chemical compounds, heavy metals, pesticides, and biological agents. The ubiquitous presence of environmental contaminants has become a matter of global concern due to their deleterious impact on atmospheric, aquatic, and terrestrial systems, as well as their potential implications for human well-being (Thompson and Darwish 2019; Manciocco et al. 2014). For instance, air pollution resulting from the emission of noxious gases and particulate matter from anthropogenic sources, such as factories and transportation, contributes to respiratory ailments and premature mortality (McCawley 2015). Water contamination, often caused by industrial discharges or inadequate sewage management, poses significant hazards to aquatic ecosystems and the availability of potable water (Bove et al. 2002; López-Pacheco et al. 2019). Exposure to these contaminants through contaminated food, air, or water can engender a plethora of health issues, including respiratory disorders, cardiovascular diseases, neurologic impairments, and even carcinogenesis (Kraybill 1978; Kjellstrom et al. 2006; Manisalidis et al. 2020).

Addressing the predicament of environmental contaminants necessitates a multifaceted approach, encompassing governmental regulations, industrial practices, and individual accountability. Endeavors are underway to develop cleaner technologies, enhance waste management systems, and promote sustainable practices aimed at minimizing the release of contaminants into the environment (Kumar et al. 2022). Moreover, fostering awareness and providing education play pivotal roles in cultivating a sense of responsibility toward the environment. By comprehending the sources, impacts, and mitigation strategies associated with environmental contaminants, individuals can make informed decisions and actively contribute to a healthier and more sustainable future (Marsalek and Chocat 2002; Edzwald 2011).

These contaminants are broadly classified as inorganic and organic contaminants (discussed in detail below). Their entry into the environment can occur through industrial processes, agricultural practices, improper waste disposal, and accidental releases (discussed in detail). Once released, these contaminants often exhibit persistence, remaining in the environment for extended periods and exerting long-term effects. Thus, concerted efforts by society are imperative to mitigate the release of contaminants and adopt sustainable practices, ultimately ensuring a cleaner and safer environment for future generations.

1.1 Organic and Inorganic Contaminants

Inorganic and organic contamination is a widespread environmental issue that refers to substances that can negatively impact the environment and human health. Contamination refers to the presence of substances in various environmental media, including water, soil, air, and biota. Inorganic contaminants are elements or compounds that do not contain carbon atoms, while organic contaminants are substances that contain carbon atoms bonded with other elements such as hydrogen, oxygen, and nitrogen (Mohammed et al. 2011). Heavy metals, such as lead (Pb), mercury (Hg), cadmium (Cd), arsenic (As), and chromium (Cr), are among the most common and toxic inorganic contaminants. Metalloids, including arsenic (As), selenium (Se), and antimony (Sb), exhibit properties of both metals and nonmetals. They are naturally present in the Earth's crust but can also be released through human activities, particularly mining and industrial processes (Duruibe et al. 2007; Wen et al. 2017; Mohammed et al. 2011; Ratier et al. 2018; Lin et al. 2017).

1.1.1 Sources of Contamination

Inorganic and organic contaminants can originate from various sources, including natural processes and human activities. Here are common sources of inorganic and organic contaminants:

- (a) **Industrial activities:** Industries such as manufacturing, mining, and power generation are significant sources of both inorganic and organic contaminants. These include heavy metals, such as lead, mercury, and cadmium, released from manufacturing processes and mining activities. Organic contaminants like organophosphate compounds, polychlorinated biphenyls (PCBs), volatile organic compounds (VOCs), and industrial solvents can also be emitted from industrial operations.
- (b) **Agriculture and pesticides:** Agricultural practices contribute to the presence of inorganic and organic contaminants in the environment. Inorganic fertilizers and pesticides containing chemicals like nitrates, phosphates, and chlorinated pesticides can enter water bodies through runoff or leaching from agricultural fields. Livestock farming can also result in the release of organic contaminants such as antibiotics and hormones.
- (c) **Landfills and waste disposal:** Improper waste management, including landfill sites and inadequate disposal practices, can lead to the release of inorganic and organic contaminants. Leachate from landfills can contaminate groundwater with inorganic substances, including heavy metals and toxic ions. Organic contaminants can be generated from the decomposition of organic waste, including landfill gas emissions that contain methane and volatile organic compounds.
- (d) **Urban runoff and sewage:** Urban areas contribute to the release of inorganic and organic contaminants through stormwater runoff and sewage systems. Runoff from roads, rooftops, and industrial areas can carry pollutants such as heavy

metals, motor oil, pesticides, and fertilizers into water bodies. Sewage treatment plants can release organic contaminants like pharmaceuticals and personal care products into receiving waters if not adequately treated.

- (e) **Atmospheric emissions:** Atmospheric emissions from various sources, including vehicles, power plants, and industrial smokestacks, can lead to the deposition of inorganic and organic contaminants onto land and water surfaces. Airborne particles containing heavy metals, such as lead and mercury, can settle on soil and water bodies. Volatile organic compounds, including benzene and formaldehyde, can be released into the air and contribute to air pollution.
- (f) **Construction and demolition:** Construction and demolition activities can generate inorganic and organic contaminants. Dust and particulate matter containing heavy metals, asbestos, and other harmful substances can be released during construction and demolition processes. Organic contaminants, such as polycyclic aromatic hydrocarbons (PAHs) and volatile organic compounds (VOCs), can be emitted from paints, solvents, and building materials.
- (g) **Natural sources:** Some inorganic and organic contaminants occur naturally in the environment. For example, geological processes can release naturally occurring heavy metals like arsenic and uranium into water sources. Organic contaminants such as toxins produced by certain algae or naturally occurring radon gas can also be present in the environment.

Understanding these sources is crucial for implementing effective pollution control measures, developing appropriate remediation strategies, and promoting sustainable practices to reduce the release and spread of inorganic and organic contaminants.

1.1.2 Environmental Implications

Organic and inorganic contaminants pose significant environmental implications due to their potential adverse effects on ecosystems, biodiversity, and human health (Lin et al. 2017; Akram et al. 2018; Borah et al. 2020). Here are some key environmental implications associated with these contaminants:

- (a) **Water pollution:** Both organic and inorganic contaminants can contaminate water bodies, leading to water pollution. Inorganic contaminants, such as heavy metals and toxic ions, can accumulate in aquatic ecosystems, disrupting the balance of the ecosystem and posing risks to aquatic organisms. Organic contaminants, including pesticides, herbicides, and industrial chemicals, can have toxic effects on aquatic life and disrupt the reproductive and physiological processes of organisms.
- (b) **Soil contamination:** Organic and inorganic contaminants can contaminate soil, affecting soil quality and agricultural productivity. Inorganic contaminants, like heavy metals and metalloids, can persist in soil for extended periods, posing risks to plants, animals, and microorganisms. Organic contaminants, such as

persistent organic pollutants (POPs), can accumulate in the soil, leading to long-term environmental impacts and potential bioaccumulation in the food chain.

- (c) Air pollution: Some organic contaminants, known as volatile organic compounds (VOCs), can contribute to air pollution. These compounds are released from various sources, including industrial emissions, vehicle exhaust, and solvents. VOCs can react in the atmosphere, leading to the formation of secondary pollutants like ozone and particulate matter, which have detrimental effects on air quality and human health.
- (d) Ecological disruption: Organic and inorganic contaminants can disrupt ecological balance and biodiversity. They can accumulate in organisms, affecting their growth, reproduction, and survival. Contaminants may also bioaccumulate in the food chain, with potential impacts on higher trophic levels. The loss of key species and disruptions in food webs can lead to cascading effects on ecosystem functioning and overall ecosystem health.
- (e) Habitat degradation: Contaminants can result in the degradation and loss of habitats. Inorganic contaminants, such as mining waste and industrial discharges, can lead to the destruction of aquatic and terrestrial habitats, impairing the ability of species to survive and thrive. Organic contaminants, such as oil spills, can have severe impacts on coastal and marine habitats, affecting sensitive ecosystems like coral reefs and mangroves.
- (f) Human health risks: Exposure to organic and inorganic contaminants can pose risks to human health. Inorganic contaminants, such as lead, mercury, and arsenic, can enter the food chain and accumulate in edible plants and animals, potentially causing adverse health effects upon consumption. Organic contaminants, including pesticides, industrial chemicals, and pollutants like dioxins and polychlorinated biphenyls (PCBs), can have toxicological effects on humans, leading to various health issues such as neurological disorders, hormonal imbalances, and increased cancer risks.
- (g) Environmental persistence: Certain organic and inorganic contaminants are persistent in the environment, meaning they resist degradation and can persist for long periods. This persistence can lead to long-term environmental contamination and an increased potential for bioaccumulation and biomagnification in the food chain, amplifying the environmental and health risks associated with these contaminants.
- (h) Addressing the environmental implications of organic and inorganic contaminants requires comprehensive pollution control measures, effective remediation strategies, and sustainable practices. It is crucial to minimize the release of contaminants, promote proper waste management, and implement regulations and policies to protect ecosystems and human health from the detrimental effects of these contaminants.

1.1.3 Management of Inorganic and Organic Contaminants

The management of both inorganic and organic contaminants involves comprehensive strategies and practices aimed at preventing, controlling, and mitigating the release and adverse effects of these pollutants on the environment and human health. Here are key aspects of managing inorganic and organic contaminants:

- (a) **Source identification and characterization:** Identifying and characterizing the sources of contaminants is crucial for effective management. Thorough investigations and assessments should be conducted to determine potential contamination sources, analyze their composition, and assess associated risks. This information is essential for developing targeted management approaches.
- (b) **Risk assessment and prioritization:** Conducting risk assessments helps prioritize management actions. Evaluating the toxicity, persistence, mobility, and potential exposure pathways of contaminants assists in determining the urgency and severity of contamination sites. This prioritization enables the efficient allocation of resources for mitigation efforts.
- (c) **Prevention and reduction:** Emphasizing pollution prevention and reduction measures is a fundamental aspect of managing contaminants. Best management practices should be implemented in industrial processes and agricultural practices to minimize the release of contaminants into the environment. Promoting sustainable production methods, implementing proper waste management practices, and advocating for the use of safer alternatives to hazardous substances are essential prevention strategies.
- (d) **Regulatory frameworks:** Governments and environmental agencies play a critical role in managing contaminants by establishing and enforcing stringent regulations and standards. These regulations limit the release of contaminants into the environment, set emission and discharge limits, and mandate proper waste management practices. Compliance with these regulations is crucial for preventing and controlling contamination (Puri et al. 2023).
- (e) **Monitoring and surveillance:** Regular monitoring and surveillance programs are essential for assessing the effectiveness of management strategies and tracking changes in contamination levels. Monitoring activities involve sampling and analyzing environmental media, such as air, water, and soil, to accurately detect and measure the presence of contaminants.
- (f) **Remediation and restoration:** When contamination occurs, implementing remediation measures becomes necessary. Remediation techniques, including physical, chemical, and biological methods, should be employed based on the specific contaminants, site conditions, and remediation objectives. Restoration efforts aim to rehabilitate contaminated areas, restore ecological balance, and ensure long-term sustainability.
- (g) **Stakeholder engagement and education:** Engaging stakeholders, including local communities, industries, and relevant organizations, is crucial for the effective management of contaminants. Stakeholders should be encouraged to participate in contamination prevention, management, and remediation efforts. Providing

information on risks and promoting responsible practices through education and awareness campaigns are essential.

- (h) **Research and innovation:** Continual research and innovation are vital for improving management strategies and developing new technologies to address contaminants. Ongoing efforts should focus on advancing analytical techniques for accurate detection, exploring novel remediation approaches, and assessing the long-term impacts of contaminants on ecosystems and human health.

By implementing these management measures, it is possible to minimize the release of contaminants, mitigate their impacts, and ensure sustainable management practices. Effective management of both inorganic and organic contaminants requires collaboration among stakeholders, long-term commitment, and adaptable strategies to address evolving challenges in this field.

Prevention of Organic and Inorganic Contamination

Preventing organic and inorganic contamination is crucial for safeguarding the environment and protecting human health. Here are key preventive measures for minimizing the release and spread of these contaminants:

- (a) **Pollution prevention:** Implementing pollution prevention practices is essential for reducing the generation and release of organic and inorganic contaminants. This includes adopting cleaner production technologies, promoting sustainable practices in industries and agriculture, and minimizing the use of hazardous substances through the substitution of safer alternatives.
- (b) **Proper waste management:** Establishing proper waste management systems is vital for preventing contamination. This involves implementing segregation, recycling, and proper disposal of organic and inorganic waste materials. Encouraging responsible waste management practices among industries, households, and communities is crucial for minimizing the risk of contamination.
- (c) **Regulatory measures:** Governments and regulatory bodies play a pivotal role in preventing contamination by enforcing regulations and standards. These regulations set limits on the release of contaminants, impose restrictions on the use of hazardous substances, and establish guidelines for waste management and disposal practices. Compliance with these regulations is crucial to prevent contamination at its source.
- (d) **Sustainable agriculture practices:** Promoting sustainable agricultural practices helps prevent both organic and inorganic contamination. This includes minimizing the use of chemical fertilizers and pesticides, implementing integrated pest management techniques, adopting organic farming practices, and promoting soil conservation methods. These practices reduce the potential for contaminant runoff and leaching into water sources.
- (e) **Control of industrial emissions:** Industries should implement measures to control and reduce emissions of organic and inorganic contaminants. This includes installing pollution control technologies, employing efficient production

processes, and monitoring emissions regularly. Regular maintenance and inspection of equipment are essential to ensure optimal performance and minimize the risk of contamination.

- (f) **Spill prevention and preparedness:** Implementing spill prevention measures is crucial for preventing accidental release of contaminants into the environment. Industries and transportation sectors should have proper spill response plans in place, including spill containment systems, staff training, and equipment maintenance. A quick and effective response to spills can significantly reduce the potential for contamination.
- (g) **Public awareness and education:** Creating awareness among the public about the impacts of organic and inorganic contamination is vital for prevention. Educating individuals about proper waste management practices, responsible chemical usage, and the importance of sustainable living can promote behavioral changes that contribute to contamination prevention.
- (h) **Research and development:** Continued research and development efforts are necessary to develop innovative technologies and solutions for preventing contamination. This includes advancements in pollution prevention techniques, eco-friendly alternatives to hazardous substances, and improved monitoring and detection methods.

By implementing these preventive measures, it is possible to significantly reduce the release and impact of organic and inorganic contaminants. Collaboration among governments, industries, communities, and individuals is essential for creating a culture of contamination prevention and ensuring a cleaner and healthier environment for future generations.

Monitoring and Assessment of Inorganic and Organic Contaminants

Monitoring and assessment of inorganic and organic contaminants play a critical role in understanding their presence, distribution, and potential risks to the environment and human health. Here are key aspects of monitoring and assessment:

- (a) **Sampling and analysis:** Monitoring programs involve the collection of samples from various environmental media, including air, water, soil, sediment, and biota. These samples are then analyzed using appropriate analytical techniques to determine the concentrations and types of inorganic and organic contaminants present. Analytical methods can range from simple field tests to sophisticated laboratory analyses, depending on the contaminants and their concentrations (Saleh 2020).
- (b) **Environmental monitoring:** Environmental monitoring involves the systematic and regular collection of samples to track changes in contaminant levels over time. This includes establishing monitoring stations or networks at specific locations to capture variations in contaminant concentrations. Continuous monitoring instruments and automated sampling techniques can be employed to obtain real-time data, especially for pollutants with short-term fluctuations.

- (c) **Ecological assessment:** Ecological assessments focus on evaluating the impacts of inorganic and organic contaminants on ecosystems. This involves studying the responses of organisms, such as plants, animals, and microorganisms, to contamination through field surveys, laboratory experiments, and ecological modeling. Assessments can determine the effects on biodiversity, food webs, and ecosystem functions, providing insights into the overall health and resilience of ecosystems.
- (d) **Human health risk assessment:** Human health risk assessments evaluate the potential risks posed by inorganic and organic contaminants to human populations. This involves assessing exposure pathways, such as ingestion, inhalation, and dermal contact, and estimating the potential health effects based on toxicological data. Risk assessments consider factors like exposure duration, sensitive populations, and the cumulative effects of multiple contaminants to inform decisions on remediation and risk management.
- (e) **Data management and analysis:** Effective monitoring and assessment programs rely on robust data management and analysis. This includes maintaining accurate records of sampling locations, methods, and results. Advanced statistical techniques and data visualization tools are employed to analyze the collected data, identify trends, and determine the effectiveness of pollution control measures.
- (f) **Compliance monitoring:** Compliance monitoring ensures that regulatory standards and guidelines for inorganic and organic contaminants are met. Regulatory agencies perform regular inspections and monitoring of industries, wastewater treatment plants, and other sources to ensure compliance with emission limits and discharge regulations. Non-compliance may result in penalties and enforcement actions to prevent further contamination.
- (g) **Research and innovation:** Ongoing research and innovation are crucial for enhancing monitoring and assessment capabilities. This includes developing new analytical techniques, biomonitoring methods, and remote sensing technologies to improve the detection and quantification of contaminants. Research efforts also focus on understanding the fate and transport of contaminants in different environmental compartments and identifying emerging contaminants of concern.

By conducting comprehensive monitoring and assessments, policymakers, environmental agencies, and industries can make informed decisions to protect the environment and human health. Regular monitoring provides valuable data for designing effective pollution control measures, evaluating the success of remediation efforts, and implementing proactive strategies to prevent further contamination.

Remediation of Organic and Inorganic Contaminants

Remediation refers to the process of removing or reducing the presence of organic and inorganic contaminants from the environment. Here are key approaches for the remediation of these contaminants:

- (a) **Physical remediation:** Physical remediation techniques involve the physical removal or containment of contaminants. This includes methods such as excavation and removal of contaminated soil or sediments, containment using barriers or liners to prevent further spread, and dredging of contaminated water bodies.
- (b) **Chemical remediation:** Chemical remediation involves the use of chemicals to transform or degrade contaminants into less harmful substances. Examples include chemical oxidation, which uses powerful oxidizing agents to break down organic contaminants, and chemical precipitation, which involves adding chemicals to form insoluble compounds that can be removed through sedimentation or filtration.
- (c) **Biological remediation:** Biological remediation, also known as bioremediation, utilizes microorganisms or plants to degrade or transform contaminants. Bioremediation can be accomplished through processes such as bio-augmentation, where specific microorganisms are introduced to enhance contaminant degradation, or phytoremediation, which involves the use of plants to absorb, metabolize, or stabilize contaminants.
- (d) **Thermal remediation:** Thermal remediation methods involve the application of heat to facilitate the removal or destruction of contaminants. Examples include thermal desorption, where elevated temperatures vaporize organic contaminants for subsequent capture and treatment, and thermal destruction, which involves incineration or high-temperature treatment to break down contaminants.
- (e) **Electrochemical remediation:** Electrochemical methods use electrical currents to remove or transform contaminants. Electrokinetic remediation involves the application of an electric field to enhance the migration of contaminants from soil or groundwater toward electrodes for subsequent treatment. Electrocoagulation is another technique that uses electrically generated metal ions to destabilize and remove contaminants through coagulation and precipitation.
- (f) **Nanotechnology-based remediation:** Nanotechnology offers innovative approaches for remediating organic and inorganic contaminants. Nanoscale materials, such as nanoparticles, can be used for targeted delivery of chemicals, enhanced adsorption, or catalytic degradation of contaminants. However, careful consideration of the potential risks associated with the use of nanomaterials is necessary.
- (g) **Pump-and-treat systems:** Pump-and-treat systems involve the extraction of contaminated groundwater using wells or pumps, followed by treatment through various techniques such as filtration, chemical precipitation, or activated carbon adsorption. The treated water can then be reintroduced into the environment or used for other purposes.
- (h) **Natural attenuation:** In some cases, natural processes can contribute to the remediation of contaminants. Natural attenuation relies on the inherent capabilities of natural systems to degrade or immobilize contaminants over time. This approach may involve factors such as microbial activity, hydrolysis, dilution, or natural sorption processes.

It is important to note that the selection of remediation techniques depends on factors such as the type and extent of contamination, site conditions, regulatory requirements, and cost-effectiveness. Often, a combination of different remediation approaches is employed to achieve the most effective and sustainable remediation outcome. Site-specific assessments and ongoing monitoring are crucial to ensure the success of remediation efforts and the restoration of the affected environment.

In the management of inorganic and organic contaminants, various techniques are employed, including colorimetric and fluorometric methods, adsorption, and bioremediation. Colorimetric and fluorometric techniques involve the use of specific dyes or fluorescent probes to detect and quantify contaminants based on their characteristic color or fluorescence signals. Adsorption processes utilize materials such as activated carbon or zeolites to remove contaminants from water or air by adsorbing them onto their surfaces. Bioremediation employs microorganisms or plants to degrade or transform contaminants into less harmful substances. These techniques play vital roles in the detection, removal, and remediation of inorganic and organic contaminants, contributing to environmental protection and human health preservation. We have discussed these approaches as case studies below.

2 Case Studies: Inorganic and Organic Contamination

2.1 Heavy Metals (Hg, Cr, Pb, Cd, As) Contamination

Heavy metal ion contamination is a rising environmental concern. Heavy metals—elements with atomic numbers larger than 20 and atomic densities more than 5 g/cm³—threaten ecosystems and human health due to their toxicity and persistence in the environment; these include Cd, Pb, Hg, Cr, As, and U. Contamination with heavy metals can occur for many different reasons such as in the modern chemical industry, fertilizer production, metal plating facilities, battery manufacture, pesticide and paper production, fossil fuel extraction, tanneries, and the production and manufacturing use of various plastics (Mohammed et al. 2011). Other metals such as Cu, Fe, Ni, Co, Zn, Mo, and Mn are all examples of micronutrients that are necessary for trace amounts but can have deleterious effects in higher concentrations, including stunted plant growth, chlorosis, senescence, and an imbalance in the plant's water balance as well as acute or chronic poisoning in humans (Vardhan et al. 2019). In addition, these metals can inhibit glycolysis, leading to an overall decrease in ATP synthesis. These contaminants accumulate in soils, sediments, and aquatic systems by atmospheric deposition, surface runoff, and leaching into water bodies. Discharges of heavy metals into the environment are harmful to both human health and ecosystems. They can cause harm to physiological issues, stunted growth and reproduction, and even death in plants, animals, and bacteria. Chronic health problems including organ damage, neurological malfunction, and cancer are also linked to the ingestion of contaminated food and water. The most dangerous heavy metals, such as lead and arsenic, can enter the water supply through plumbing materials

corrosion and industrial waste, and drinking lead-contaminated water is the major source of lead poisoning in animals. Water with lead can cause major health issues, especially in children where brain and nerve system diseases can result from its exposure. Mercury is another heavy metal found in nature and is also a well-known toxin for renal organs and neurologic systems. It can contaminate water bodies, and a potential source of its contamination includes industrial wastes, production units of wiring devices, switches, fossil fuels, and dental works. Further study and monitoring are needed to understand heavy metal pollution's origins, behavior, and effects. To solve this serious environmental issue, this understanding will help build effective mitigation measures and solid environmental regulations.

2.1.1 Adsorption Techniques for Heavy Metals (Hg, Cr, Pb, Cd, As)

Toxic metals, especially heavy metals, can be removed from polluted water using several different methods that have been developed as a result of technical breakthroughs. Precipitation, electrochemical removal, ion exchange, coagulation, and flocculation are all examples of these techniques (Fu and Wang 2011). Nonetheless, there are limitations to each of these approaches. For instance, the precipitation technique results in hazardous waste that must be treated further; however, flocculation and coagulation produce similar sludge. The primary drawbacks of the membrane filtering technology are its high initial cost, the difficulty of dealing with leftover materials, and their potential for pollution. The ion exchange process is advantageous except that it cannot be recycled. Though efficient, electrodialysis requires a lot of power and is expensive to run (Qasem et al. 2021). Adsorption is one of these methods that is both effective and economical. The molecules of one phase attach to a two-dimensional matrix at the phase boundaries in a process known as adsorption.

Adsorption-Based Separation

Both the adsorbent material and the heavy metal ions present have physical and chemical properties that influence the efficacy of the adsorption process in wastewater treatment. Other factors include the operating conditions, which include the temperature, adsorbent amount, pH value, adsorption time, and the initial concentration of metal ions. Heavy metal ions are often bound to the adsorbent's surface while regeneration of adsorbed metal ions is a crucial step in the adsorption process that has been acknowledged for its low cost, high efficiency, and easy operation. There are two kinds of adsorption processes identified according to the nature of interaction among adsorbates and adsorbents: physisorption (adsorbate and the adsorbent must link via the van der Waals force) and chemisorption (adsorbate molecules chemically connect to the adsorbent surface). Adsorption quality is tied to adsorption capacity, which is determined by the nature of the adsorbent surface and its interactions with the target contaminants. Reactivity with contaminants can

also be affected by factors such as surface charge, surface area, and functional groups.

Types of Adsorbents Employed for Heavy Metal Ions

Based on the composition and origin, there are broadly the following categories of adsorbents that are employed in the adsorption of heavy metal ions:

(a) Carbon-based heavy metal adsorbents

The efficacy of various carbon-based adsorbents in extracting heavy metal ions from wastewater has been the subject of substantial research. When it comes to adsorption, activated carbon (AC) is a popular choice because of its large surface area, porosity, and excellent adsorption ability. It has remarkable adsorption efficiency for several heavy metal ions. Activated carbon due to its very high surface area and large number of micro- and mesopore volume are suitable substrates for heavy metal adsorption. A large number of reports related to AC have emerged in the current decades (Raninga et al. 2023; Mariana et al. 2021; Deliyanni et al. 2015; Wang et al. 2023). Due to the depletion of natural resources, commercial availability of coal-based AC declined and now additives and AC composites could be suitable options for adsorptive. There are several alternative additives such as alginate (Guo et al. 2020), citric acid (Xie et al. 2021), surfactants (Bade and Lee 2011), and tannic acid (Ma et al. 2021); modified AC adsorbents are reported in recent literature. There are also some concerns of exploring new carbon sources which are abundant and inexpensive. Chen et al. (2011) reviewed the thermal and chemical treatment of rice husk to produce activated carbon. The cost consideration of conversion of abundant carbon sources into AC is also a major concern.

There is a lot of room for innovation in adsorption processes thanks to the recent surge in nanotechnology. Another category of carbon-based adsorbents includes the use of carbon nanotubes (CNTs) in heavy metal removal. Because of their peculiar structural features, which increase their adsorption capabilities, CNTs are another appealing adsorbent. CNTs are variously reported in the literature for the selective removal of heavy metals from contaminated water. With their exceptional chemical and physical characteristics, CNTs have gained prominence as effective adsorbents. However, the adsorption capabilities of bare CNTs are not very high, but the selectivity and sensitivity of CNTs could be enhanced by the addition of new functional groups to their surfaces. Wang et al. (2021) reported the fabrication of CNTs with magnetic nanoparticles. Experimental results show the composite has a maximum adsorption capacity of 215.05 mg/g for Pb(II). Functionalizing CNTs with acids to oxidize them is the most common technique. Similar work was reported to remediate the arsenic problem by oxidizing CNTs using HNO₃ and H₂SO₄ using sonication (Veličković et al. 2013). Other functionalized nanohybrids of CNTs using Fe (III) oxide ethylene diamine coating (Veličković et al. 2012), zirconia (Ntim and

Mitra 2012), and graphene oxide (Li et al. 2021) are also reported for the As removal. The incorporation of sulfur and also coating of MnO_2 enhanced the adsorption of Hg with CNTs-based adsorbents (Moghaddam and Pakizeh 2015). Similar adsorptive removal of Hg using CNTs functionalized with amino thiol is reported in the literature (Bandaru et al. 2013).

(b) Graphene oxide (GO)-based adsorbents

GO is another type of carbonaceous material that is widely utilized in the adsorption of heavy metal ions due to its high affinity for adsorbing diverse metal ions, huge surface area, high mechanical strength, and remarkable adsorption properties. Graphene is a honeycomb lattice constructed from a single sheet of carbon atoms. The affinity of GO for Cu(II) , Zn(II) , Cd(II) , and Pb(II) is $\text{Pb(II)} > \text{Cu(II)} > \text{Cd(II)} > \text{Zn(II)}$. This arrangement is consistent with the electronegativity of the metal ions and the initial stability constant of the respective metal hydroxides (Sitko et al. 2013). The stronger the attraction of heavy metal ions to the negatively charged surface of GO, the greater their electronegativity. In addition, the adsorption process may entail the complexation of heavy metal species with oxygen-containing surface functional groups, such as hydroxyl ($-\text{OH}$) and carboxyl ($-\text{COOH}$) ($-\text{COOH}$). Stability constants associated with these complexation events affect the speciation of heavy metal ions.

(c) Zeolites and MOF-based heavy metal adsorbents

It is very crucial to find out which adsorbent is suitable for pilot as well as industrial scale. The adsorption of heavy metal ions using natural zeolites is well explored in nature (Velarde et al. 2023). They are more popularized due to a variety of different structures, chemical compositions, and selective adsorption of contaminants. Just like CNTs, zeolite treatment with acid, base, and salt creates more adsorption sites, and activates zeolites for the adsorption of heavy metal ions. The acid pretreatment is crucial in the case of zeolites which replace cations with H^+ ions and also tailor the adsorption capacities for heavy metal ions. Similarly, base treatment can dissolve Si in zeolites and decrease Si/Al ratio against acid treatment (Shi et al. 2018). The common salts such as NaOH , NaCl , and Na_2CO_3 used in the salt treatment where Na ions were incorporated into the structure by replacing other cations lead to increased surface area and better ion exchange capacity (Lin et al. 2015). Modification of zeolites with other metallic elements such as the formation of magnetic zeolites also led to better adsorption capacities due to the presence of abundant adsorption sites (Yuan et al. 2018). The magnetic incorporation also does not hinder the previously present zeolite's adsorption sites. The mechanism of metal adsorption onto zeolite includes ion exchange, electrostatic attraction, surface complexation, and intrapore adsorption. However, most reported mechanisms involve ion exchange and electrostatic interaction (Anari-Anaraki and Nezamzadeh-Ejhih 2015).

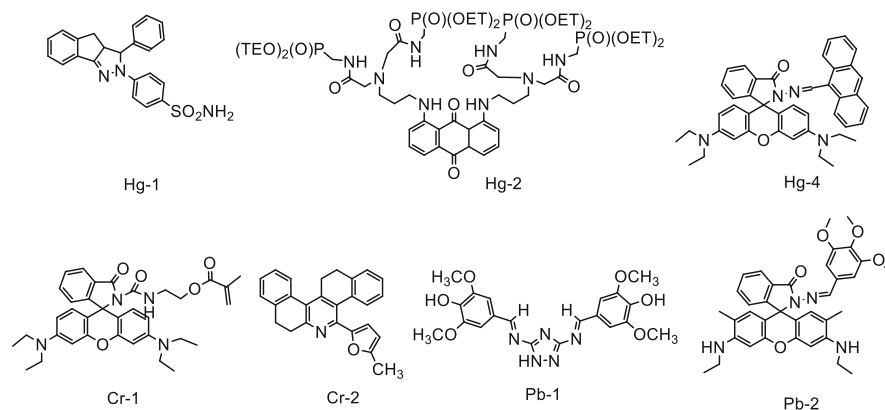
Metal-organic frameworks (MOFs) are an additional category of metal-based adsorbents used to remove hazardous heavy metals. MOFs are a unique type of three-dimensional organic-inorganic compounds with very porous nanostructures made of metal ions or clusters and organic linkers. These

materials offer several benefits, such as a large surface area, a variety of shapes and topologies, a flexible topology, chemical stability, and ordered-column configurations. MOFs are flexible in applications such as gas storage, separation, energy storage and conversion, metal ion sensing, drug delivery, catalysis, and sensors because of their excellent porosity, customizable pore sizes, ease of functionalization, and increased number of exposed chelating sites. The metal nodes, organic linkers, and functional groups linked to the surface of the MOF can all form stable complexes by chelating heavy metal ions. Given these advantages, MOFs have garnered substantial attention and are considered a highly promising adsorbent for various heavy metal ions.

Modification of MOFs with suitable linkers on the surface could enhance the selective adsorption of some heavy metal ions. Similar work has been reported by Wang et al. (2020) where they prepared a single-layered 2D MOF nanosheet possessing ultrahigh sulfur content. The thiocyanate anchored on both surfaces has a greater ability to capture Hg ions in aqueous media. Also, to combat the problem of agglomeration of nanoadsorbents, they can immobilize onto some substrates. Similar work has been reported by Hua et al. (2019) where using the colloid-electrospinning process, PAN/Uio-66-(COOH)₂ nanofibrous membranes are manufactured. The hierarchically organized nanofibrous membranes with high adsorption capacities for Tb³⁺ and Eu³⁺ ions and good photoluminescence characteristics with color-tunable luminescence were investigated. Pre- and post-modification of MOF composites for efficient adsorption have also been thoroughly investigated in the literature. Literature reports the post-modification of Uio-66-NH₂ with resorcylic aldehyde for the selective removal of Pb(II) from aqueous environments by forming double/quadracoordinate metal complexes. The highest adsorption quantity of Uio-66-RSA was 189.8 mg/g at an ideal pH of 4, and the adsorption isotherm and kinetics were accurately represented by the Langmuir/Dubinin-Radushkevich and pseudosecond-order models, respectively (Fu et al. 2019).

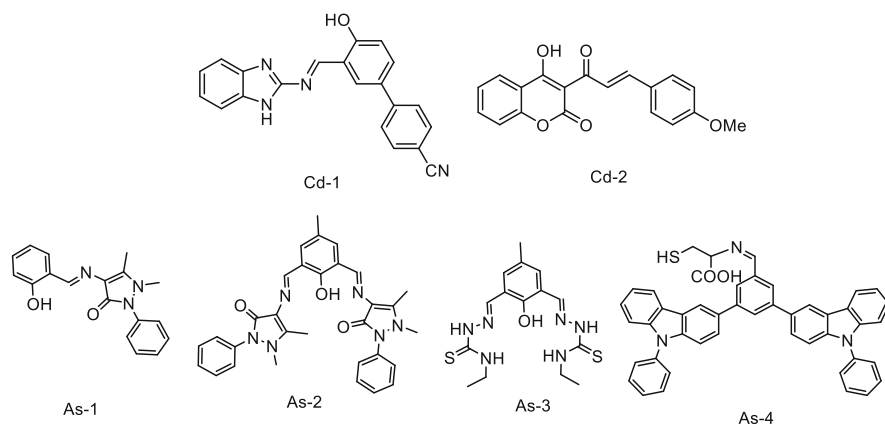
2.1.2 Colorimetric/Fluorometric Monitoring

Colorimetric and fluorometric based methods are valuable tools for recognition and quantification of heavy metal ions. Colorimetric techniques involve the use of specific reagents that undergo a color change with target analyte, allowing for visual detection. Fluorometric methods utilize fluorescent probes that emit a characteristic fluorescence signal upon binding to the heavy metal ions, enabling sensitive and selective detection. These monitoring methods offer advantages such as simplicity, rapidity, and cost-effectiveness. They can be applied in various environmental, industrial, and biomedical settings to assess heavy metal contamination levels and ensure compliance with regulatory standards. Continued research and development in this field will further enhance the sensitivity and applicability of colorimetric and fluorometric monitoring methods for effective heavy metal ion detection (Alam et al. 2021; De Acha et al. 2019; Yan et al. 2022).



Gul and co-workers explained the pyrazoline-based chemosensor Hg-1 for recognition of Hg^{2+} . The probe Hg-1 showed a decrease in emission intensity in the presence of Hg^{2+} with fluorescent color change from blue to non-fluorescent. The job plot analysis showed 2:1 complexation between the Hg-1 and Hg^{2+} . The limit of detection and association constant were calculated to be $0.16 \mu\text{M}$ and $4.69 \times 10^5 \text{M}^{-2}$, respectively (Bozkurt and Gul 2020). Lemeune and co-workers explained the colorimetric chemosensor Hg-2 for sensitive and selective recognition of Hg^{2+} in water. The probe Hg-2 shows blue color in water with strong absorption maxima at 561 nm due to intramolecular charge transfer. The gradual addition of Hg^{2+} displayed change in fluorescent color from blue to pink, with a hypochromic shift in absorption maxima from 561 to 509 nm. Detection limit was found to be 4 ppm (Ermakova et al. 2013). Bakir and co-workers reported the complex of fluorescein and thiourea (1:1) as probe Hg-3 for colorimetric detection of Hg^{2+} in water. The complex of fluorescein and thiourea with Hg^{2+} showed visible color change from yellow color to red by naked eyes. The complex Hg-3 with Hg^{2+} showed decrease in emission intensity with change in fluorescent color from green to non-fluorescent. The LOD was estimated to be 0.24nmol/l by absorption titrations (Bakir et al. 2022). Wei and co-workers synthesized fluorescent probe Hg-4 for recognition of Hg^{2+} in 7:3 DMSO- H_2O . Hg-4 with 6.6 equiv. of Hg^{2+} displayed the increase in emission intensity at 578 nm due to spirolactam ring opening with fluorescent color change from non-fluorescent to pink under 365 nm light. Hg-4 displayed the formation of 2:1 complexation by mass spectroscopy and could detect as low as 9.99 nM by fluorescence titration (Hu et al. 2023). Yao and co-workers reported the rhodamine-urea methacrylate-based chemosensor Cr-1 for recognition of Cr^{3+} in 9:1 $\text{CH}_3\text{CN}-\text{H}_2\text{O}$. The UV-vis spectra of probe Cr-1 with Cr^{3+} exhibited a 71-fold increase in absorption intensity with visible color change to pink. The probe Cr-1 (ex-520 nm) with Cr^{3+} showed the enhancement in fluorescence intensity at 584 nm with color change from non-fluorescent to red under 365 nm. Cr-1 showed the formation of 1:1 stoichiometry and detected as low as $5.5 \times 10^{-8} \text{M}$ (Liu et al. 2014). Lyer et al. explained the furan-based chemosensor Cr-2 for detection of Cr^{3+} in 9:1 CH_3CN and water. The absorption spectrum of the probe with Cr^{3+} displayed

the ratiometric change in which there is a decrease at 333 nm and a simultaneous increase at 375 nm with color change from colorless to yellow. The Cr-2 with Cr^{3+} upon excitation at 340 nm displayed the increase in fluorescence intensity at 405 nm with fluorescence color change from weak blue to intense blue. The probe Cr-2-loaded paper strips detect Cr^{3+} with color change to dark blue (Seenan et al. 2021). Patra and co-workers reported the triazole-based chemosensor Pb-1 for the recognition of Pb^{2+} in 1:1 CH_3OH -tris buffer. Upon addition of 3 equiv. Pb^{2+} , the absorption spectrum of the probe displayed a decrease at 330 nm and a simultaneous appearance of new bathochromic maxima at 400 nm with isosbestic point at 355 nm. The lowest limit of detection was calculated to be 1.2 μM with visible color change from colorless to yellow. The solution of Pb-1 (ex-340 nm) displayed the 17-fold enhancement in intensity at 440 nm due to restriction of PET process. Pb-1 showed the formation of 1:2 complexation and association constant $1.43 \times 10^{11} \text{ M}^{-2}$ (Rout et al. 2019). Shivaraman and co-workers reported the rhodamine 6G hydrazone-based chemosensor Pb-2 for recognition of Pb^{2+} in HEPES buffer. The addition of Pb^{2+} in the solution of Pb-2 exhibited the appearance of new absorption maxima at 530 nm. The emission spectra of Pb-2 in the presence of Pb^{2+} showed 100-fold enhancement in fluorescence intensity at 552 nm due to the opening of spirocyclic ring with detection limit 0.015 μM . The probe Pb-2 displayed 1:1 stoichiometry between Pb-2 and Pb^{2+} with binding constant $3.432 \times 10^2 \text{ M}^{-1}$ (Sunnapu et al. 2015).



Shuang and co-workers reported Schiff base probe Cd-1 for detection of Cd^{2+} in the binary mixture of CH_3CN and water (3:2). The probe in the presence of Cd^{2+} displayed the reduction in absorption intensity at 297 and 382 nm and a simultaneous appearance of red-shifted maxima at 500 nm with visible color changed to yellow due to interaction of Cd-1 with Cd^{2+} via O-H and N heteroatoms. The addition of Cd^{2+} to the solution of Cd-1 exhibited the 13 times increase in emission intensity at 547 nm. Cd-1 showed the 1:1 stoichiometry between Cd-1 and Cd^{2+} with binding constant $1.70 \times 10^4 \text{ M}^{-1}$ and LOD $1.05 \times 10^{-8} \text{ M}$ (Yang et al. 2022). Ahmed and co-workers reported the coumarin-chalcone hybrid-based chemosensor Cd-2

for detection of Cd^{2+} in 3:7 $\text{CH}_3\text{CN}:\text{H}_2\text{O}$. The UV-vis spectra of Cd-2 with Cd^{2+} exhibited the formation of higher energy maxima from 387 to 370 nm with visible color change from colorless to yellow. The probe Cd-2 (ex-387 nm) with Cd^{2+} exhibited enhancement of emission intensity at 497 nm with change in quantum yield from 0.11 to 0.88 due to chelation-enhanced fluorescence. The probe Cd-2 exhibited 1:1 complexation between Cd-2 and Cd^{2+} with association constant $9.56 \times 10^5 \text{ M}^{-1}$. The limit of detection was calculated to be $5.84 \times 10^{-8} \text{ M}$. The Cd-2-loaded paper strips detect Cd^{2+} by change in visible color from yellowish to colorless and non-fluorescent to white (Kumar and Ahmed 2017). Das and co-workers explained an antipyrine-based chemosensor As-1 for recognition of arsenate (H_2AsO_4^-) in 1:4 MeOH / H_2O . The probe As-1 with H_2AsO_4^- displayed the enhancement in emission intensity at 498 nm ($\phi = 0.196$) compared to other anions. The enhancement in fluorescence intensity of As-1 with arsenate occurred due to hydrogen bonding. The LOD and association constant were determined to be 3 μM and $8.9 \times 10^3 \text{ M}^{-1}$, respectively (Lohar et al. 2013). Chattopadhyay and co-workers reported an antipyrine-based chemosensor As-2 for the recognition of AsO_3^{3-} ion. The addition of arsenate to As-2 displayed ratiometric change in absorption spectra in which there is a decrease at 356 nm and a simultaneous increase at 428 nm. As-2 in the presence of arsenate exhibited ninefold enhancement in fluorescence intensity with change in emission color from colorless to green under 365 nm light. The formation of hydrogen bonding between As-2 and arsenate inhibited PET. The analysis of Job's plot showed 1:1 complexation between As-2 and AsO_3^{3-} and association constant was estimated to be $2.53 \times 10^5 \text{ M}^{-1}$. The probe could detect as low as 4.12 ppb by fluorescence titration. As-2 was used to detect arsenite ions from the water samples (Lohar et al. 2014). Sinha and co-workers reported colorimetric and fluorometric probe As-3 for detection of AsO_3^{3-} in the binary mixture of acetonitrile and water. The addition of AsO_3^{3-} to As-3 showed a decrease at 312 and 368 nm and a simultaneous increase at 458 nm with visible color change from colorless to dark yellow. As-3 exhibited 35-fold time change in fluorescence intensity at 560 nm with yellow fluorescence due to hydrogen bonding between the AsO_3^{3-} ion and $-\text{NH}/-\text{OH}$ group. Job's plot and mass spectrum analysis showed formation of 1:1 complex between As-3 and AsO_3^{3-} . The LOD and association constant were determined 15 nM and $1.0 \times 10^5 \text{ M}^{-1}$. This As-3 was able to detect AsO_3^{3-} ion from the groundwater samples (Purkait et al. 2018). Tian and co-workers reported the carbazole-based chemosensor As-4 for recognition of As^{3+} in the binary of mixture of THF and water (3:7). The plot of fluorescence intensity of As-4 with As^{3+} displayed a linear increase between 0 and 120 ppb and LOD 1.32 ppb. The As-4 showed enhancement in fluorescence intensity due to interaction between As^{3+} and $-\text{SH}$ group of cysteine. The Job's plot displayed the formation 1:3 complexation between As-4 and As^{3+} . The As-4 was used to detect As^{3+} from water samples (Tian et al. 2017).

2.1.3 Bioremediation Techniques

Due to the progressive increase in industrialization, globalization and unsafe agricultural practices across the world adding an array of different heavy metals into the environment (water/soil) cause environmental pollution. Heavy metals such as Cr, Hg, Cd, Pb, and As are generally released into wastewater of different industrial units involved. The release of excessive heavy metals beyond permissible limits into the environment poses a threat to natural flora/fauna, human health, and the ecosystem. These heavy metals can remain longer in the environment as they do not degrade easily and tend to bioaccumulate. Similarly, metalloids or semi-metals are widely used and released into the environment by various industrial units (Kumar and Saini 2019).

Conventionally, a variety of remediation technologies are used to treat heavy metals, including physical and chemical methods. However, the use of chemicals and components can lead to high capital costs and may also result in the production of toxic sludge, which may need to be properly disposed of in sanitary landfills. In contrast, bioremediation using biological agents such as bacteria, plants, fungi, and yeast can be an environmentally friendly and green approach (Wróbel et al. 2023). Further, there is a need to screen and select suitable adapted microbial diversity from polluted sites whose metabolic potential could be exploited to achieve cleanup of heavy metals from polluted sites.

Different physical and chemical techniques, including the addition of coagulants/lime, membrane separation, ion-exchangers, reverse osmosis, adsorption, solvent precipitation, electro dialysis, evaporation, and incineration, are traditionally used to treat heavy metals; however, these techniques use costly chemicals, consume more electricity, result in incomplete removal, and produce toxic sludge. In contrast, bioremediation approach for the removal of heavy metals is a green, cost-efficient, and environmentally friendly alternative for rectification of wastewater and polluted sites (Kumar and Saini 2019). Bioremediation is a complex process involving addition of bacteria, plants, fungi, and yeast to achieve detoxification/biotransformation of pollutants such as heavy metals. Also, the supplement of nutrients such as carbon and energy sources, electron sources, and other potential microbes can gradually enhance the bioremediation process (Pratish et al. 2018). Using microorganisms, pollutants can be reduced to non-toxic forms and sometimes even to undetectable levels within the limits of regulatory bodies.

Microbes use various detoxification and resistance mechanisms to counter toxicity caused by heavy metals. This includes bio-reduction using enzymes, production of exopolysaccharides, extrusion, and use of metallothioneins (Wu et al. 2010; Dixit et al. 2015). Toxicity of heavy metals can be reduced by microorganisms by various mechanisms such as biotransformation, bioaccumulation, bio-sorption, bio-precipitation, and bioleaching (Rahman and Singh 2020). The phenomenon of biotransformation mainly includes reduction, oxidation, methylation, and demethylation of heavy metals, for example, the conversion of Cr (VI) form to Cr (III) by reduction process leading to reduction in toxicity (Kumar and Saini 2019). When the

rate of contaminant absorption is higher than the rate of loss, the phenomenon called bioaccumulation takes place. Thus, it leads to the accumulation of toxic chemicals such as heavy metals into the organism (Huang et al. 2023). Microbes can resist the toxicity of heavy metals to a certain extent; exceeding this limit of tolerance can have detrimental effects on the genetic material, cell membrane, and cell organelles affecting the survival of microbes. The sensitivity of microorganisms generally depends on the toxicity of chemicals as well as the type of the organism involved in bioremediation process (Ramzan et al. 2023; Mishra and Malik 2013). The microbes capable of bioaccumulating heavy metals generally have high tolerance and biotransformation capability. The basic mechanism behind bioaccumulation is import-storage system which can transport heavy metals across the cell membrane to cytoplasm via transporter proteins. Once inside the cytoplasm, these heavy metals can form insoluble precipitates by binding to proteins or peptide ligands or lipids. Hence, microbes can bioaccumulate heavy metals in the cytoplasm or cell wall/membrane (da Silva et al. 2023). Similarly, microbes are reported for their bio-sorption capabilities due to surface adsorption or linking of heavy metals to extracellular polymers (Priya et al. 2022). Bio-precipitation is the result of microbial activity leading to the formation of precipitates of heavy metals into insoluble form. Cilliers et al. (2022) reported bio-precipitation of lead (Pb) by dissimilatory metal reduction carried out by microbial consortium under anaerobic conditions. The method of bioleaching is based on the transformation of heavy metals into sparingly soluble substances/form which can be easily recovered from solutions. Tapia et al. (2022) carried out bioleaching of heavy metals such as gold, silver, tin, copper, zinc, and lead from printed circuit board residues (PCBs) using acidophilic iron-oxidizing bacterial consortium composed of *Tissierella*, *Acidiphilium*, and *Leptospirillum*.

Chromium (Cr) can exist in a variety of redox states, primarily as Cr (VI) and Cr (III). Because of its high aqueous phase solubility, Cr (VI) is 100 times more hazardous and 1000 times more mutagenic than Cr (III) (Kumar and Saini 2019). Enzymatic reduction is typically used by microorganisms converting Cr (VI) to Cr (III), which resulted in extracellular or intracellular precipitation. In literature, many of the bacterial genera are reported for the transformation of chromium such as *Bacillus* spp., *Pseudomonas* spp., *Microbacterium* spp., and *Serratia* spp. and among fungi *Candida*, *Trichoderma*, and *Aspergillus* genus are reported (Rahman and Singh 2020).

Heavy metals such as cadmium are known for its toxicity and severe hazardous effect. Currently, a number of procedures are being employed to remove cadmium pollution from polluted places. Bioremediation using bacteria mainly includes efflux system, enzymatic conversion into less toxic forms, proteins causing binding of metal, and metal ion sequestration. Sharma et al. (2000) reported *Klebsiella planticola* strain (Cd-1) for the precipitation of Cd ions as insoluble precipitates due to the production of hydrogen sulfide from thiosulfate under anaerobic conditions. Huang et al. (2014) reported extracellular accumulation of cadmium in *Bacillus cereus* due to bio-sorption. Heavy metals bioaccumulation of chromium, cadmium, and lead is seen in many of the bacterial genera such as *Pseudomonas* spp., *Alcaligenes* spp., *Enterobacter* sp., *Microbacterium* sp. *Comamonas* spp.,

Bacillus spp., *Lactobacillus* spp., *Ralstonia* spp., *Lactobacillus plantarum*, *Serratia* spp., *Klebsiella* spp., and *Stenotrophomonas* sp. (Amoozegar et al. 2012; Kumar and Saini 2019).

Zhang et al. (2023) reported the involvement of exopolysaccharide (EPS) released by anaerobic methylating microbes for the dissolution process of cinnabar (α -HgS) minerals. Sevak et al. (2023) reported *Acinetobacter junii* strain b2w capable of reducing 98.24% of 10 ppm Cr (VI) to Cr (III). They suggested the role of reduction, bioaccumulation, and efflux mechanism adopted by *Acinetobacter junii* strain b2w to survive in the presence of Cr. Wróbel et al. (2023) reported the involvement of genus *Bacillus* in EPS-mediated bio-sorption, bioaccumulation, and bio-precipitation of lead, cadmium, mercury, chromium, arsenic or nickel in the environment.

Metalloids or semi-metals are a group of elements comprising intermediate properties of both metals and nonmetals. This mainly includes silicon (Si), boron (B), antimony (Sb), germanium (Ge), arsenic (As), and tellurium (Te). They generally have a metallic appearance and moderate conductors of electricity (Presentato et al. 2020). Bacteria can be used for the removal of arsenic (As) from the contaminated sites as environmentally friendly and low-cost option in comparison to other methods. For instance, Dey et al. (2016) reported 51.99 and 53.29% removal of arsenite and arsenate by the use of gram-positive bacteria. Similarly, Sher et al. (2022) reported *Microbacterium* sp. strain 1S1 which was able to tolerate arsenite and arsenate up to 75 and 520 mM concentration. They reported uptake and surface adsorption of arsenite by scanning electron microscope (SEM), energy dispersive X-ray (EDX), and Fourier-transform infrared spectroscopy (FTIR) analysis in *Microbacterium* sp. strain 1S1. In literature, many of the bacterial genera are reported for the removal of As from contaminated sites such as *Bacillus* spp., *Alcaligenes* spp., *Pseudomonas* spp., *Flavobacterium* spp., *Enterobacter* spp., *Klebsiella* sp., *Acinetobacter* spp., and *Microbacterium* spp. (Sher et al. 2022). Table 1 contains few reports of heavy metal ions using bioremediation techniques.

For the possible remediation approaches, conventional methods were traditionally used for the removal of heavy metals; however, they have their drawbacks. In contrast, bioremediation can be used as an alternative to conventional methods as it is a more environmentally friendly and cost-effective method. Bioremediation approaches have many different methods wherein different microorganisms can use a variety of mechanisms such as reduction or metal sequestration. For achieving this, bio-prospecting of novel microbes for carrying out bioremediation can be used as a potent tool.

Table 1 A list of microorganisms involved in the removal of heavy metals/metalloids

S. N.	Name of microorganism	Target metal	Conditions (Temperature/pH/substrate concentration/mechanism)	Incubation time	Removal (%)	Reference
1.	<i>Acinetobacter junii</i> Pb1	Pb (II)	30 °C/pH 7.0/100 mg/l (Adsorption and accumulation)	48 h	100	Kushwaha et al. (2017), Bandala et al. (2006)
2.	<i>Arthrobacter viscosus</i>	Cr (VI)	26 °C/pH 1.0/100 mg/l (Reduction)	72 h	100	Hlihor et al. (2017)
3.	<i>Microbacterium</i> sp. M5	Cr (VI)	30 °C/pH 9.0/400 mg/l (Reduction)	48 h	100	Kumar and Saini (2019)
4.	<i>Ochrobactrum</i> sp. GDOS	Cd (II)	30 °C/pH 7.0/50–350 mg/l (Bio-sorption)	16 h	83.33 mg/g	Khadvinia et al. (2014), Xiao et al. (2011)
5.	<i>Pseudomonas aeruginosa</i> PA1	Hg (II)	25 °C/pH 7.0/1.0 mM (Adsorption)	30 min	297.2 µmol/g	Yin et al. (2016), Xiao et al. (2011)
6.	<i>Pseudomonas aeruginosa</i> N6P6	Pb (II)	37 °C/pH 7.0/800 mg/l (able to grow and tolerant)	24 h	NA	Kumari and Das (2019)
7.	<i>Shewanella putrefaciens</i>	Cd (II)	25 °C/pH 5.0/20 mg/l (Adsorption)	4 days	86.54	Yuan et al. (2019)
8.	<i>Pseudomonas stutzeri</i>	As (III) and As (V)	30 °C/pH 4.0/10 mg/l (Adsorption)	50–80 min	99	Manirethan et al. (2020)
9.	<i>Pseudomonas aeruginosa</i>	Hg (II)	37 °C/pH 7.0/5 mg/l (Reduction)	24 h	99.7	Imron et al. (2019)
10.	<i>Exiguobacterium</i> sp. As-9	As (III) and As (V)	30 °C/pH 8.0/100 mg/l each of As (III) and As (V) (Accumulation)	168 h	90 and 99%, respectively	Pandey and Bhatt (2016)

2.2 *Volatile Organic Compounds (VOCs), Chlorinated Compounds, Pesticides, Organophosphorus Compounds (OPs)*

2.2.1 Adsorption Techniques

Unlike carbon monoxide, carbon dioxide, metallic carbides, and others, according to the US Environmental Protection Agency, atmospheric photochemical processes are aided by volatile organic compounds (VOCs). According to the US Environmental Protection Agency, atmospheric photochemical processes are aided by volatile organic compounds (VOCs). VOCs' toxicity contributes to the greenhouse effect, photochemical haze, and stratospheric ozone depletion. VOC elimination research has increased in recent years. Carbon materials as VOC adsorbents are a cost-effective way to reduce VOC emissions. Many studies have examined VOC adsorption onto carbon materials, including novel carbonaceous adsorbents (Dai et al. 2018).

The chemical structures and characteristics of VOCs have a significant impact on the efficacy of VOC removal. During the elimination or breakdown of volatile organic compounds (VOCs), interactions such as π -interactions and electron donor–acceptor interactions are possible because of the electron-rich environment created by the aromatic ring. Nonpolar VOCs like benzene typically undergo interactions such π -interactions, π -complexation, and electrostatic attraction during the removal or degradation of aromatic VOCs. Hydrogen bonding, polar–polar interactions, electron donor–acceptor interactions, and acid–base interactions are just some of the interactions that VOCs can participate in thanks to the polar functionalities that originate from heteroatoms like functional groups containing halogen, oxygen, sulfur, or nitrogen.

There has been a rise in the use of adsorption techniques that employ AC for the removal of VOCs. Adsorption is affected by the AC's surface area, pore size, pore volume, and chemical functional groups, as well as the VOCs' molecular size and polarity. The adsorption capacity is also influenced by the ambient temperature and humidity. Bedane et al. (2019) synthesized activated carbon from peanut shells via chemical activation with ZnCl_2 and evaluated its ability to absorb volatile organic compounds. At different temperatures, the adsorption behavior of ethyl benzene, toluene, and xylene vapors on the produced AC was analyzed. N_2 adsorption isotherm measurements were used to assess the surface parameters of the activated carbon, revealing a BET surface area of $1025 \text{ m}^2/\text{g}$, a pore size of 0.70 nm , and a micropore volume of $0.37 \text{ cm}^3/\text{g}$, showing a narrow pore size distribution. By combining semiconducting catalysts with biochar/ACs and utilizing a photocatalytic method, destructive VOC reductions may also be accomplished (Ahmad et al. 2023).

Due to its limitations, activated carbon has been largely replaced by other carbon-based nanomaterials for the adsorption and removal of VOCs. These include CNTs, graphene, and composites of CNTs. These materials are ideal for interacting with

VOCs due to the presence of a variety of polar groups on their surfaces (Bao et al. 2016).

Aromatic volatile organic compounds, such as benzene, toluene, and xylene, tend to adsorb on hydrophobic surfaces rather than hydrophilic ones. Graphene oxide (GO), reduced graphene oxide (rGO), and their composites have all been studied for their potential in the adsorption-based elimination of aromatic VOCs. Because of the oxygen functions on its surface, GO is less hydrophobic than rGO. When initially loaded with 50 ppm benzene in a continuous flow reactor, the adsorption capacities of GO and rGO are reported in the literature to be 216.2 and 276.4 mg/g, respectively (Yu et al. 2018). Because of its hydrophobic character and increased propensity to form π -bonds, rGO is superior to GO in improving the adsorption capacity of aromatic VOCs. Additionally, it was hypothesized that rGO's larger surface area compared to GO's contributed to its superior adsorptive ability. The adsorption capabilities of modified GO with other adsorbing materials may be improved. Elimination capacity of 251 mg/g was reported in the literature for cases where MOF was manufactured with GO for the removal of benzene. Despite the MOF's great porosity, they failed to retain small molecules at room temperature and pressure because of the weak and non-specific adsorption forces between the small molecules and MOFs (Liu et al. 2015). Similar examples were also reported using the combination of GO and Cu-BTC (Li et al. 2016) for toluene adsorption where adsorption capacity was 46% higher than pristine Cu-BTC reported. Relative humidity also affects the adsorption capacity of GO composites with ZIF-8 for toluene (Chu et al. 2018).

CNTs are a cylindrical form of graphene sheets comprising sp^2 hybrid carbon atoms and show excellent properties in adsorption processes. Yang et al. (2017) investigated the adsorption behavior of CNTs for indoor formaldehyde at a low concentration of 1.50 mg/m^3 , and the adsorption capacity was found to be 62.49 mg/g . The study demonstrated that the surface of CNTs exhibited favorable hydrophobicity and consistency, enabling strong interactions with organic compounds and making them a promising adsorbent. A similar study on MWCNTs chemical modification leads to enhanced adsorption of polar VOCs (Hussain et al. 2009). The introduction of polar functionalities on the MWCNT surface significantly altered their sorption characteristics, extending the breakthrough time from 12 to 35 min for ethanol in continuous flow column.

Adsorption with Zeolites and MOF

Zeolite has several desirable characteristics that set it apart from other materials, including its hydrophobicity, huge surface area (between 250 and $800 \text{ m}^2/\text{g}$), and adjustable porosities. It is often used as a catalyst, adsorbent, and filter in the chemical industry. Zeolite's Si/Al ratio may be changed to alter its textural features, providing even more scope for adsorption of VOCs. Carbon-based materials, in contrast, have issues with combustibility and regeneration. However, zeolite is an

excellent substitute since it is hydrothermally and chemically stable (Jafari et al. 2018).

Several zeolite types, such as silicalite-1, beta, SSZ-23, and chabazite, have been identified as promising adsorbents for VOCs adsorption (Cosserson et al. 2013). Jafari et al. (2018) demonstrated the use of ZIF-8 for the adsorptive removal of toluene and CCl_4 in a fixed-bed reactor. There was an influence of thermal activation of adsorbent on adsorption capacity. It shows higher adsorption capacity than others when thermal activation was done from 200 to 300 °C. Si/Al ratio of zeolite also affects the adsorption of VOCs. Similar observations were reported by Kang et al. (2018) where different zeolites (FAU and MFI) with different Si/Al ratios were analyzed for the adsorption of dichloromethane vapors. They concluded that MFI zeolites with highest Si/Al ratio exhibited maximum adsorption capacity.

In terms of adsorption ability for VOCs, zeolite is on par with activated carbon attributed to its tunable specific surface area and pore structure. Zeolite's silicon (Si) content, which is modifiable during synthesis, determines its resistance to water. Because of its high adsorption capacity, great thermal stability, and simplicity of reproducibility, zeolite is viewed as a traditional adsorbent for VOCs. However, tetraethyl orthosilicate, cetyltrimethyl ammonium bromide, and other ingredients in zeolite production might add up to be more expensive than AC, and the process can take a long time.

MOFs have been extensively studied because of their potentially enormous applications in fields such as gas storage, heterogeneous catalysis, separations, and sensing. Open metal sites on the pore surfaces of MOFs are accessible for boosting the adsorption of a variety of VOCs. After regeneration, MOF retains its permanent structure and crystalline order, unlike conventional adsorbents. Various types of metal-organic frameworks (MOFs), including MIL series, UiO series, and ZIF series, have been synthesized for the treatment of VOCs. Studies comparing different MOFs have shown variations in adsorption capacities. For example, ZIF-67 exhibited the highest adsorption capacity for toluene, followed by MOF-199, UiO-66, and MIL-101 (Vellingiri et al. 2017). The high adsorption capacity of ZIF-67 can be attributed to its large surface area. MIL-101 outperforms more common adsorbents when it comes to soaking up various volatile organic compounds. Competitive adsorption with water molecules lowers MIL-101's adsorption capabilities under humid circumstances. Scientists have experimented with a wide range of alterations to maximize the hydrophobicity and adsorptive selectivity of MOFs (Zhu et al. 2017).

Adsorption of Pesticides

Pesticides have increased agricultural production and fought insect-borne diseases, improving human health. If misused or overused, pesticides can harm humans. Pesticides are a varied collection of biologically active compounds with varying toxicity used to control pest populations. Because they can linger in the environment and build up in organisms, they constitute a health risk (Tang et al. 2021). Acute and

chronic pesticide poisoning exists. Long-term pesticide exposure may induce chronic illness, whereas high-dose exposure causes illness quickly. Persistent pesticide exposure has been related to birth defects, prenatal toxicity, genetic changes, and blood, nerve, and organ illnesses. Pesticide exposure has been related to chronic neurological, renal, reproductive, and respiratory and cardiovascular diseases in humans.

Insecticides, rodenticides, molluscicides, herbicides fungicides, algicides, and bactericides are the principal pesticide classes. They are organochlorines, organophosphorus compounds, carbamates, and pyrethrins/pyrethroids. Phenoxyacetic acid herbicides (2,4-D and others) and bipyridyls supplement these classes (e.g., paraquat and diquat). Inorganic insecticides including sulfur, copper, mercury, lead, and arsenic form a subgroup with these pesticides. Pervasiveness and soil contamination limit their use (Anju et al. 2010).

Eliminating pesticides and their by-products is a global environmental issue. Pesticide removal might be biological, chemical, or physical. Since nature breaks down organic molecules into innocuous substances, biological methods are cheap and safe. Chemical remediation uses specific chemicals to convert pesticides into safer by-products. Combining chemical treatment with physical activities can boost remediation efficiency, but it is expensive and context-dependent. Adsorption is the foundation of physical remediation and the best water filtration method due to its high capacity, efficiency, and application.

(a) Carbon-based material for pesticide adsorption:

There are several reports in the literature about activated carbon's use for the adsorption of different pesticides chemicals (Hgeig et al. 2019; Wang et al. 2019; Rolph et al. 2018). Spaltro et al. (2018) tested two commercial activated carbons, GAB and CBP, for the adsorption of 2,4-D and 4-chloro-2-methylphenoxyacetic acid (MCPA) from aqueous solutions. GAB, which had a greater microporous surface area and pore volume than CBP, displayed a greater pesticide adsorption capability. The adsorption rate was affected by the solution's ionic strength and pH, with a higher ionic strength promoting the adsorption of 2,4-D and MCPA. The adsorption capacity of both pesticides reduced when pH increased beyond the point of zero charge (pHPZC) of the activated carbons and as the pKa values of the pesticides increased. This indicates that electrostatic interactions between the activated carbon surface and the pesticides played an important part in the adsorption mechanism. Similarly the modified ACs with H_3PO_4 were utilized for the fixed-bed column and batch adsorption of diazinon pesticide by some other researchers (Bayat et al. 2018).

The use of graphene-based materials in the pesticide removal has also been reported in the literature. In similar studies, Lazarević-Pašti et al. (2018) documented the elimination of chlorpyrifos and dimethoate using graphene-based structures. The results demonstrated that the sorbent and sorbate properties had a substantial impact on pesticide adsorption onto graphene-based adsorbents and that surface area was not the most important element in determining removal performance. The hydrophilic oxidized graphene surfaces were more susceptible

to aliphatic dimethoate adsorption, but the graphene basal plane, which contains an electron system and strong structural order, removed chlorpyrifos preferentially due to its aromatic moiety. The graphene-based adsorbent's surface had a low concentration of oxygen functional groups, which facilitated the removal of chlorpyrifos and dimethoate. In another study reported by Yan et al. (2020), GO nanoplatelets were used for the adsorption of chloridazon and its degradation metabolites methyl-desphenylchloridazon (MDC) and (desphenyl-chloridazon (DC)) from aqueous solutions. The results showed that GO has a high adsorption capacity for chloridazon (67.18 mg/g), MDC (36.85 mg/g), and DC (34.30 mg/g), demonstrating its efficacy for efficient remediation. The adsorption mechanism was linked to hydrophobic interactions which also include hydrogen bonding and π -interactions between the GO surface and the pesticides and their metabolites.

CNTs are also used for the adsorption-based remediation of various pesticides. Al-Shaalan et al. (2019) in a study used low-cost multi-walled CNTs synthesized using Ni/MgO compounds with particle sizes ranging from 10.0 to 40.0 nm with a high surface area. The synthesized MWCNTs exhibited efficient removal of diuron from water, achieving a removal efficiency of 90.5% under optimized conditions. The adsorption of diuron onto MWCNTs was found to be prompt and endothermic, as confirmed by statistical adsorption data. The adsorption mechanism was characterized by the formation of supra-molecular adsorption complexes, involving interactions such as π - π stacking, π -alkyl bonds, and π -donor hydrogen bonds between MWCNTs and diuron. These interactions resulted in diuron physisorption and the formation of a diuron-MWCNT composite via sixteen hydrophobic connections and two hydrogen bonds. Another study reported that MWCNTs produced from Ni/MgO were used for the adsorption of fenuron from water. To develop a mechanistic understanding of the adsorption process, simulation studies were carried out. The results revealed that fenuron underwent physisorption onto the synthesized MWCNTs, involving interactions such as π - π T-shaped bonds, π - π stacking, π -alkyl bonds, and π - σ hydrophobic interactions between adsorbate and adsorbent. These findings provided valuable information about the adsorption mechanism of fenuron onto MWCNTs (Ali et al. 2019).

In another study conducted by Hue et al. (2018), the adsorption of 2,4-D from aqueous solutions onto CNTs with a specific surface area of 267 m²/g was investigated using batch technique. The adsorption process was found to be exothermic, with a maximum adsorption capacity (q_{\max}) of 84.03 mg/g achieved under desired adsorption conditions (initial concentration $C_0 = 102$ mg/l, contact time $t = 50$ min, and temperature $T = 283$ K). Similar studies of 2,4-D adsorption in fixed-bed adsorption column were also reported where various factors on the adsorption of 2,4-D, including flow rate, initial concentration, bed depth, and pH, were investigated (Bahrami et al. 2018).

(b) Zeolites and MOF for pesticide adsorption:

Yonli et al. (2012) reported a study on the utilization of HY zeolites and steaming HBEA zeolites as endosulfan adsorbents in water treatment. They

discovered that as the bronsted acidity of the zeolite declined, the endosulfan removal effectiveness increased. This effect was more noticeable in HY zeolites than in HBEA zeolites. The elimination of bronsted acid sites also resulted in an increase in hydrophobicity, hence restricting the water adsorption. The HY (40) zeolite was shown to be the most efficient adsorbent due to its lower acidity, which prevented the immobilization of pesticide molecules on bronsted acid sites, and the selective adsorption of water molecules. On HBEA zeolites, the immobilization of endosulfan was limited by the preferential adsorption of water on bronsted sites. Modification of zeolites using organic and inorganic compounds is an effective method to enhance their adsorption properties. Zeolite HY, with a high Si/Al mole ratio of around 100, has been modified in various ways, including hexadecyltrimethylammonium chloride (HDTMA) and sodium dodecyl sulfate (SDS) surfactants. These modified zeolites were tested for their adsorption capacity of paraquat and 2,4-D pesticides. The adsorption ability of the zeolites was influenced by the functionalization with surfactants and the formation of micelles on the zeolite surface. The adsorption of paraquat increased when zeolites were modified with SDS surfactant, but excessive amounts of HDTMA led to a decrease in adsorption efficiency. In contrast, for 2,4-D, zeolites modified with higher amounts of HDTMA and SDS were more effective (Pukcothanung et al. 2018).

Chen et al. (2020) reported a study on the removal of imidacloprid and carbendazim using five different zeolites. FeNaY zeolite was synthesized by impregnating NaY zeolite with 3.5% Fe, the NTY sample by dealumination, and FeY zeolite by ion exchange. The results showed that the NTY sample, which had reduced hydrophilicity and an elevated Si/Al ratio due to dealumination, had much greater carbendazim adsorption capacity than the NaY zeolite. MCM-22 zeolite demonstrated outstanding carbendazim adsorption capacity (100%), most likely due to structural properties such as a high Si/Al ratio of 10 that suppresses competing adsorption of water molecules and its unique pore shape that restricts pesticide migration.

Despite its low toxicity, scientists have expressed concern about the immobilization of nicosulfuron, a routinely used insecticide. Researchers synthesized composites of zeolite BEA and silver tungstophosphate using three different methods: ion exchange, two-step impregnation, and physical mixing in a study. They also made composites with varying zeolite and AgPW mass ratios (2:1, 4:1, and 10:1). The study's goal was to look at the influence of adsorbent quantity on nicosulfuron immobilization. Various observations obtained following adsorption include samples made by physical mixing having the lowest adsorption capacity, even lower than pure zeolite, but those obtained through two-step impregnation had higher pesticide adsorption rates as AgPW content increased. Hydrogen bonding is involved in the adsorption mechanism. The two-step impregnation procedure permitted the growth of AgPW salt as the dominant form on the adsorbent surface, resulting in significantly higher adsorption compared to the ion exchange process (Janićijević et al. 2020).

Pesticide chemicals are also removed through various MOF and MOF composites (Mirsoleimani-azizi et al. 2018; Jung et al. 2013). Akpınar et al. (2019) investigated several Zr₆-based MOFs and discovered that NU-1000(Zr) had the maximum efficiency in eliminating atrazine pesticide in 5 min. The structure of the linker in the MOFs influenced their adsorption capabilities significantly. MOF linkers with more carboxylic acid groups and aromatic rings performed better. A pyrene-based linker in NU-1000(Zr) allowed efficient adsorption via π -interactions. Furthermore, the researchers revealed that NU-1000(Zr) could be regenerated three times without substantial loss of performance. Similar study was reported on elimination of OPPs (organophosphorus pesticides) such as metrifonate and dichlorvos using two Zr-based MOFs (UiO-67(Zr) and UiO-66 (Zr)). UiO-67(Zr) adsorbs more (571 mg/g for dichlorvos and 379 mg/g for metrifonate) than UiO-66(Zr) (Jamali et al. 2019). The functionalization of UiO-66 (Zr) with cationic sites also evaluated for the adsorption of 2,4-D pesticide (Wu et al. 2020).

Abdelhameed et al. (2016) provided Cu-BTC@cotton composite for the removal of ethion from water samples. The MOF composite's 182 mg/g adsorption capacity removed 97% of ethion from aqueous solutions. The composite performed well for five cycles after the Langmuir model adsorption process. The composite's performance was due to two factors: hydrogen bonding from cellulose functional groups and a coordination link between the MOF's Cu atom and ethion's S atom. In another study, cotton@UiO-66 (Zr) composite adsorbent was utilized in a packed column to selectively adsorb herbicides such as 2,4-D, 4-chlorophenoxyacetic acid and 2-(2,4-dichlorophenoxy) propionic acid (Su et al. 2020).

2.2.2 Colorimetric/Fluorometric Monitoring of Organophosphorus Compounds

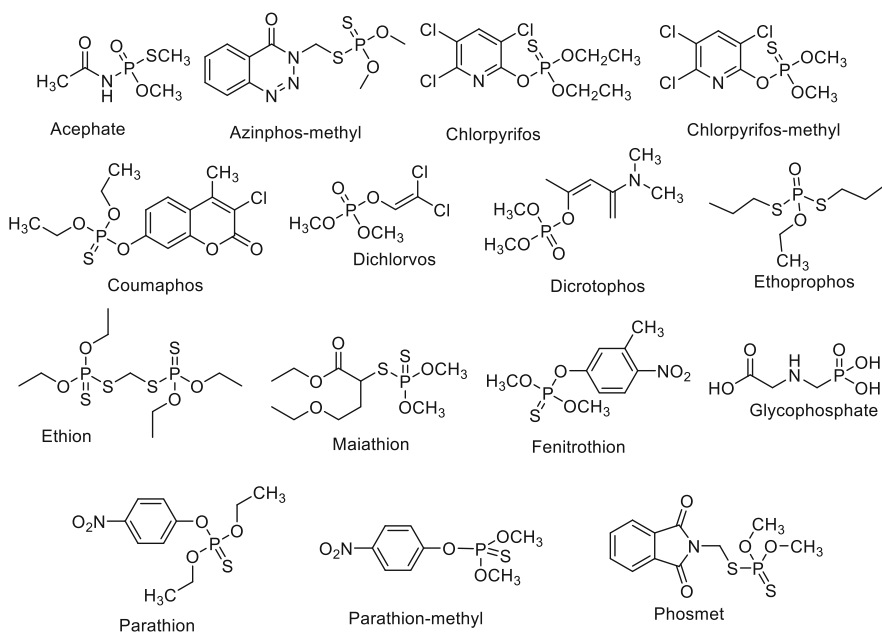
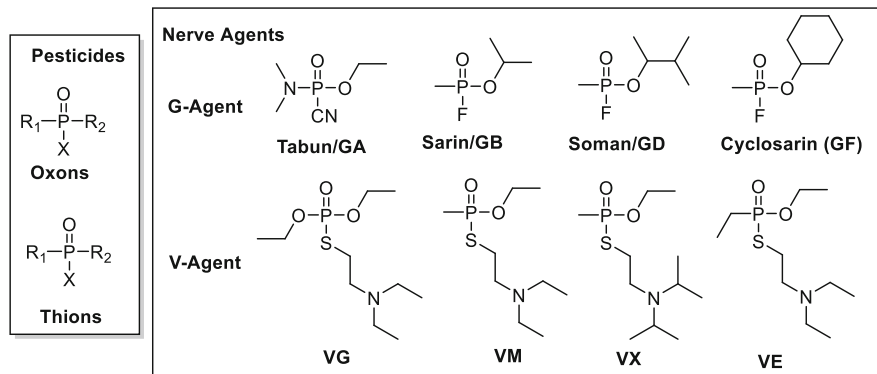
Organophosphorus (OP) compounds constitute a diverse group of chemical compounds characterized by the presence of carbon–phosphorus bonds. Within this category, nerve agents represent an especially hazardous subgroup, posing significant risks to human health. These agents function by inhibiting the enzyme acetylcholinesterase, resulting in the accumulation of acetylcholine neurotransmitters and the subsequent overstimulation of the nervous system. Inhalation, ingestion, or contact with nerve agents can lead to severe symptoms like muscle twitching, respiratory distress, blurred vision, convulsions, and paralysis. Primarily developed for warfare purposes, nerve agents are classified as chemical weapons due to their extreme toxicity. The production, stockpiling, and utilization of these agents are stringently regulated by international agreements such as the Chemical Weapons Convention. Continuous efforts are underway to prevent the associated risks by implementing preventive measures and preparedness protocols specifically designed for nerve agents and other toxic organophosphorus compounds.

In addition to nerve agents, the class of organophosphates encompasses both natural and synthetic compounds. Natural organophosphates are synthesized by plants and microorganisms and serve various functions, including signaling and defense mechanisms. On the other hand, synthetic organophosphates are artificially produced in laboratory and industrial settings and have been widely employed as pesticides, insecticides, and other applications in agriculture and public health programs. However, concerns have arisen regarding their potential toxicity and environmental impact. Consequently, there has been an emphasis on developing safer alternatives and implementing regulations to mitigate the associated risks.

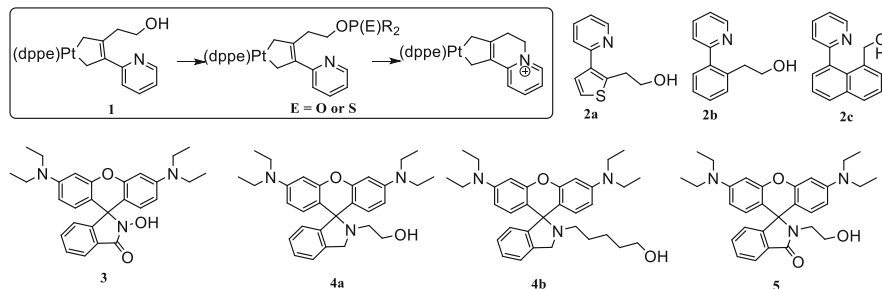
Chromo-fluorescent sensors have been developed to facilitate the detection and measurement of organophosphate compounds. These sensors utilize specific chemical compounds, referred to as sensor molecules, which undergo distinct color or fluorescence changes in the presence of organophosphates. Sensor molecules typically consist of a receptor component responsible for recognizing and binding to organophosphates, along with a chromophore or fluorophore component that generates the observable color or fluorescence alteration. The interaction between the sensor molecule and organophosphates triggers a chemical reaction or a structural change, leading to modifications in the optical properties of the sensor. This change can be visually observed as a color variation or quantified using specialized instruments that measure fluorescence intensity. By comparing the obtained signal with known standards, the concentration of organophosphates in a sample can be determined.

Chromo-fluorescent sensors for organophosphates offer significant potential for various applications. They can be utilized in environmental monitoring to detect the presence of organophosphate residues in water, soil, or food samples. Furthermore, these sensors are valuable in industrial settings to ensure the safety of individuals handling organophosphate-containing compounds. They provide advantages such as high sensitivity, selectivity, and real-time monitoring capabilities. Ongoing research aims to improve sensor designs, enhance their detection limits, and expand their applicability to encompass a wider range of organophosphate compounds. It is crucial to note that while chromo-fluorescent sensors are valuable tools for organophosphate detection, they should be employed in conjunction with other analytical methods to validate results and ensure accurate measurements.

Organophosphorus pesticides are phosphoric, phosphorothioic, or phosphonothioic acid esters, amides, or thiol derivatives. There are currently over a hundred OP compounds on the market, each with a unique set of chemical, physical, and biological properties. Pesticides are classified as oxon ($P=O$) or thione ($P=S$) based on the linkage of phosphorus to oxygen and sulfur atoms. Nerve agents, on the other hand, are organophosphorus compounds of two types: G-agent and V-agent (shown below).

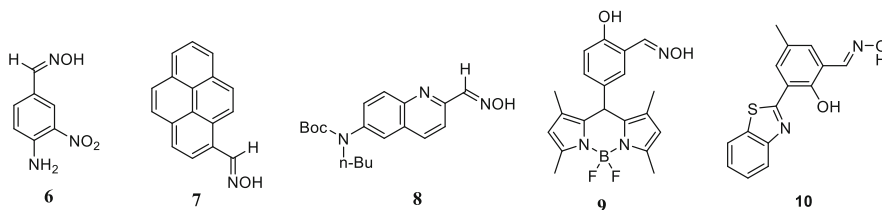


Van Houten et al. reported the first fluorescent chemosensor platinum 1, 2-dienethiolate complexes with an appended primary alcohol for detecting OP analytes (Van Houten et al. 1998). The interaction of the OP analytes with the complex's hydroxy unit further forms a fluorescent cyclic product via intramolecular reaction. The resulting cyclic product induced the intramolecular charge transfer emission at 605 and 710 nm on excitation at 450 nm. This method was effective in OP analyte detection.



To develop novel chemosensors, a very similar technique was used on other chromophores/fluorophores units (**2a–2c**) (Guo et al. 2014; Hu et al. 2015; Han et al. 2010; Wu et al. 2011). The compounds **2a** and **2b** had absorption peaks at 314 nm and 273 nm, respectively, which were shifted to 353 nm and 290 nm after interaction with the diethyl chlorophosphate (DCP) and diethyl fluorophosphate (DFP).

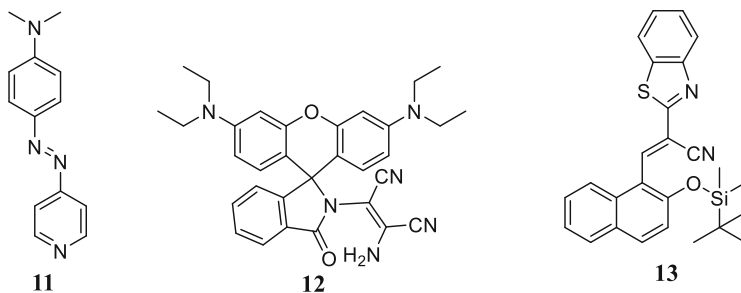
Furthermore, utilizing controllable equilibrium between non-fluorescent spirolactam and strong fluorescent ring-opened form, Han and co-workers developed rhodamine-deoxylactam-based compound **3**, which showed high emission in the presence of DCP with detection limit of 25 ppm. Utilizing a similar approach, two new fluorescent chemosensors as improvement were synthesized as **4a** and **4b**. Wu and colleagues created rhodamine-based compound **5**, which demonstrated ratiometric emission enhancement at 590 nm due to spirolactam opening followed by cyclization to oxazoline product (Wu et al. 2012).



Another approach of detection involved the interaction of oximate to the OP analytes (Dale and Rebek Jr 2009; Kerkines et al. 2010; Kim et al. 2017). Because oximate is highly nucleophilic, it quickly interacts with compound **6**, DCP, and DFP, resulting in a shift in absorption from 461 to 410 nm (Wallace et al. 2005). This approach was expanded to develop novel sensors using different chromo-fluorogenic units (**7–9**). When compound **7** interacts with phosphonyl moieties in GB or GD nerve agents, a color change from blue to strong green occurs (by Lee and co-workers). Furthermore, compound **8**'s paper test strips showed potential for detecting DCP vapor by undergoing a fluorescent color change from blue to yellow (Cai et al. 2017). Additionally, compound **9**, developed by Churchill et al., exhibited reduced emission intensity upon interaction with DCP and DEMP (Jang et al. 2014). Chen et al. synthesized compound **10**, based on ESIPT fluorescence, as a mimic for the nerve gas diethyl cyanophosphonate (DECP) in both solution and gas phases.

Compound **10** demonstrated a distinct color change and a 60-fold increase in emission in the presence of DECP, with a detection limit of 1.3 nM (Chen et al. 2018).

Another category of chemosensors for the detection of nerve agents involves the attack of nitrogen-containing bases. Pyridine-based compounds were used as a sensor for different analytes (Guha et al. 2000; Pipko et al. 2008; Yao et al. 2016; Huang et al. 2016). Compound **11** displayed an absorption peak at 475 nm and a shoulder peak at 553 nm. In the presence of DCP, compound **11** showed three convoluted absorption peaks at 475, 551, and 575 nm (Royo et al. 2011).



Goswami and coworkers have synthesized rhodamine-based compound **12**, which opens up the spirolactam ring upon interaction with DCP and thus displayed the bright colorimetric response with the appearance of the absorption peak at 558 nm and bright emission at 582 nm (Goswami et al. 2014). Furthermore, Das and co-workers have demonstrated naphthalene-based compound **13** for the detection of DCP and DECP through relay recognition technique. Compound **13** contained the silyl unit, which allows dual and relay sensing (Das et al. 2016).

2.2.3 Bioremediation of Pesticides

Pesticides can be defined as any chemical/biological entity which is used to control the foreign intruders such as insects, pests, weeds, rodents, and fungi or any infections caused by microbes (Hassaan and El Nemr 2020). The reckless use of pesticides, viz. insecticides, herbicides, fungicides, and rodenticides, in agricultural practices can cause its accumulation in the soil environment, drains, and rivers. Additionally, the use of this water for ferti-irrigation can cause accumulation of these pesticides in agricultural soil and direct exposure of the human population consuming produces from such sites (Song et al. 2017). The pollution related to the presence of pesticides residues poses threat to food safety, flora/fauna, and environment (soil/water) (Kumar et al. 2020). Pesticides can also enter the food chain leading to biomagnification in higher organisms. Currently, the use of pesticides is increasing consistently in order to meet and fulfill food commodities as per the demand of ever-increasing world population. Hence, in order to control the damage to agricultural crops, pesticides can be used to control the insect, weeds, and rodents' population

harming agricultural produce. Pesticides are generally xenobiotic, toxic in nature, and reported to have high persistence in the environment (Wang et al. 2022). Different physicochemical methods can be used for the treatment of pesticides, viz. extraction, coagulation/flocculation, adsorption, ultraviolet (UV)-Fenton, nano-filtration, and reverse osmosis (Giri et al. 2021). But these methods are costly, can cause inefficient breakdown of pesticides, and generate secondary pollution and toxic sludge. In contrast, bioremediation can be used as an environmentally friendly and green approach for the remediation of pesticides polluted sites (Kumar et al. 2020).

Bioremediation using indigenous/adapted microbes residing/surviving at polluted sites can be one of the options for the treatment of these toxic, persistent pollutants. Pesticides have been reported for their complex structures as well as presence of multiple halogen groups making them resistant to degradation. Hence, for achieving the degradation of these complex molecules microbes might require the supply of growth factors and carbon sources in order to support their growth as well as energy for transforming pesticides into less toxic compounds (Jaiswal et al. 2019). Microorganisms possess an array of different enzymes capable of degrading pesticides. However, the mere presence of enzymes does not guarantee that breakdown will take place. There are several ecological, biochemical, physiological, and molecular factors, in addition to the enzymes, that are crucial for the biodegradation and biotransformation of pesticides (Sehrawat et al. 2021). The degradation of pesticides by microbes generally depends on the type of pesticide used and activity of pesticide consuming microbial population. As a result, latest biotechnological tools/methods are required for the isolation/selection of potential microbial populations capable of transforming/detoxify complex pesticides (More et al. 2022).

The bioremediation of pesticides can be carried out by bio-augmentation and bio-stimulation process. The bio-stimulation includes the addition of organic/inorganic nutrients, viz. carbon/energy sources, electron donors, oxygen, and vitamins, to stimulate the activity of indigenous microorganisms present at polluted sites (Lopes et al. 2022). In the literature, Aislabie and Lloyd-Jones (1995) carried out complete biodegradation of 2,4-D due to the addition of oxygen and dissolved organic carbon (DOC) in microcosm after an incubation of 42 days. Gibert et al. (2022) reported the increased removal of dieldrin, lindane pesticide residues, and nitrate from groundwater due to the addition of denitrifiers inoculum by the process of heterotrophic denitrification (HDN) or acetate and injection of zero-valent iron nanoparticles by the process of abiotic chemical nitrate reduction (ACNR). On the other hand, bio-augmentation involves the addition of exogenous microorganisms to the polluted site in order to achieve the bioremediation of target pollutants. Bio-augmentation approach can be used on-site or off-site for the elimination of target pesticides. In the literature, Raimondo et al. (2020) carried out the enhanced degradation of lindane-contaminated soil due to bio-augmentation of actinobacteria consortium and sugarcane filter cake (SCFC) providing organic matter/nutrients for enhancing microbial growth and activity. Some of the bacterial cultures such as *Dehalococcoides* are reported to utilize chlorinated compounds as their final terminal electron acceptors and also gain energy by the process of reductive

dechlorination (Dutta et al. 2022). Pesticides such as DDT, lindane, dieldrin, aldrin, heptachlor, and endosulfan have been reported to be degraded by different fungal and bacterial strains indicating the microbial potential of POPs degradation (Sakthivel et al. 2022). Microbial population such as algae, bacteria, and fungi can bio-transform these pesticides due to the production enzymes such as dechlorinases, oxidases, catechol 1,2-dioxygenase, and catechol 2,3-dioxygenase that can act on different organic contaminants efficiently (Sun et al. 2022).

Among pesticide classes, organophosphate pesticides are widely used for controlling the spread of nematodes and insects of agricultural crops. Microbes such as bacteria are most explored for bioremediation of pesticides. In the literature, several organophosphate-degrading bacteria such as *Serratia marcescens* (Cycoń et al. 2013), *Rhodococcus* sp. (Huang et al. 2022), *Pseudomonas* (Jiang et al. 2022), *Microbacterium* spp. (Cabrera et al. 2010; Logeshwaran et al. 2022), *Brevibacterium* sp. (Sidhu et al. 2019), and *Sphingomonas* spp. (Parthasarathi et al. 2022) have been reported. Similarly, biodegradation of different types of pesticides has been reported by many of the bacterial isolates such as *Alcaligenes*, *Flavobacterium*, *Rhodococcus*, *Klebsiella* sp., and *Bacillus subtilis* (Aislabie and Lloyd-Jones 1995; Huang et al. 2018).

In the previous literature, Elshikh et al. (2022) reported 70% degradation of chlorpyrifos (200–300 mg/l) by bacteria viz. *Bacillus cereus* CP6 and *Klebsiella pneumoniae* CP19 which were isolated from sediment sample collected from a municipal soil. Zhao et al. (2022) reported 12.5 mg/l/h of atrazine by a novel *Paenarthrobacter ureafaciens* ZY bacterium isolated from agricultural soil. They also reported the presence of three novel atrazine-degrading genes named as *trzN*, *atzB*, and *atzC* in *Paenarthrobacter ureafaciens* ZY. Fang et al. (2023) reported 88.82% degradation of 20 mg/l profenofos by *Cupriavidus nantongensis* X1^T. They also reported the presence of organophosphorus hydrolase (OpdB) by RT-qPCR responsible for the degradation of profenofos by *Cupriavidus nantongensis* X1^T. Sakthivel et al. (2022) reported 98% degradation of endosulfan by *Pseudomonas* sp. MSCAS BT01 as confirmed by GC-MS analysis.

Aside from bacteria, many of the fungal species such as *Phanerochaete chrysosporium*, *Aspergillus* spp., *Penicillium* spp., *Cladosporium* spp., *Trichoderma* spp., and white-rot fungi are some of the widely known pesticide degraders (Maqbool et al. 2016; Huang et al. 2018). The fungal species are preferred for the bioremediation of pesticides as they can utilize organic pollutants as growth substrates, substantially produce enzymes, and are capable of absorbing pesticides due to the formation of mycelial networks (Maqbool et al. 2016). In the literature, Ibrahim et al. (2014) reported 91% degradation of organophosphorus compound malathion by filamentous cyanobacteria *Nostoc muscorum*. Hu et al. (2022) reported the degradation of 1 mg/l of malathion by a white-rot fungus named *Trametes versicolor* after an incubation of 48 h. Nguyen et al. (2022) reported the degradation of 2,4-dichlorophenoxyacetic acid (2,4-D) and 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) by white-rot fungus named *Rigidoporus* sp. FMD21. Magnoli et al. (2023) reported 50% degradation of 2,4-D by *Penicillium crustosum* strains (RCP4 and RCP13) after 7 days of incubation in synthetic wastewater.

Algae can also be utilized in the bioremediation of pesticides as they are reported for utilizing organic pollutants as carbon and energy sources. There are several algae genera reported for the degradation of pesticides such as *Chlorella*, *Scenedesmus*, and *Stichococcus* and among cyanobacteria include *Anabaena*, *Oscillatoria*, and *Nostoc* (Cáceres et al. 2008). In the previous literature, Kabra et al. (2014) reported microalgae *Chlamydomonas mexicana* which was able to degrade atrazine. Kurade et al. (2016) reported 94% degradation of 20 mg/l diazinon by *Chlorella vulgaris*. Xu and Huang (2017) reported the bioaccumulation of fungicide triadimefon by a green algal species *Scenedesmus obliquus*. Hussein et al. (2017) reported 98 and 99% degradation of pendimethalin (10 mg/l) and carbofuran (20 mg/l), respectively, by *Chlorella vulgaris*. Wan et al. (2020) reported 100% and 51.3% degradation of 100 and 200 mg/l of trichlorfon (TCF) by freshwater algae *Chlamydomonas reinhardtii*.

In summary, the management of organic and inorganic contaminants can be effectively addressed through various methods such as adsorption, colorimetric and fluorometric techniques, and bioremediation. Adsorption processes involving the use of activated carbon, zeolites, or other adsorbent materials can efficiently remove organic contaminants from water or air by binding them to the surface of the adsorbents. Colorimetric and fluorometric techniques offer rapid and sensitive detection of organic contaminants, enabling quick and accurate monitoring and analysis. Bioremediation, on the other hand, utilizes microorganisms or their enzymes to degrade organic contaminants into harmless by-products. This natural and sustainable approach can be applied to soil, water, or air environments, providing an eco-friendly solution for organic contaminant management.

By combining these methods, it is possible to develop comprehensive strategies for the effective removal, detection, and degradation of organic contaminants. These approaches offer the potential for efficient and environmentally friendly solutions in managing organic contaminants in various settings, including industrial sites, wastewater treatment plants, and contaminated soils.

Continued research and development efforts are needed to optimize these techniques, improve their efficiency, and expand their applicability to a wide range of organic contaminants. Additionally, interdisciplinary collaborations among researchers, regulators, and industries are crucial to advance the field and ensure the implementation of effective organic contaminant management strategies. Overall, through the use of adsorption, colorimetric and fluorometric techniques, and bioremediation, we can make significant progress in the management of organic contaminants, safeguarding the environment and human health from their harmful effects.

3 Future Directions in Contaminant Management and Conclusion

In the future, managing inorganic and organic contaminants will require a comprehensive and integrated approach to effectively address the challenges. Advancements in treatment technologies will play a crucial role in removing and remediating

contaminants. This will involve exploring innovative filtration systems, nanotechnology-based solutions, and advanced oxidation processes that can efficiently target specific contaminants and improve treatment efficiency.

Sustainability will be a key consideration in contaminant management, integrating principles of green chemistry and engineering. This means minimizing energy consumption, reducing waste generation, and considering the long-term environmental impacts of remediation strategies. By adopting sustainable approaches, we can achieve effective and environmentally friendly solutions. Enhancing risk assessment and management strategies is another important aspect of future directions in contaminant management. Conducting comprehensive risk assessments will help us understand the potential adverse effects of contaminants on human health and the environment. Based on these assessments, appropriate risk management strategies can be developed, including source control, containment measures, and monitoring techniques, to mitigate and minimize exposure to contaminants. The management of emerging contaminants presents a significant challenge. It is crucial to identify and understand the occurrence, fate, and potential risks associated with emerging contaminants such as pharmaceuticals, personal care products, microplastics, and pollutants from industrial and agricultural activities. Developing suitable treatment methods to address these emerging contaminants is essential for safeguarding the environment and human health. Collaboration and data sharing among researchers, regulatory agencies, industries, and communities are fundamental for effective contaminant management. Sharing data, research findings, and best practices can accelerate progress in developing innovative solutions and implementing effective management strategies. This collaborative approach ensures a comprehensive and holistic response to contaminant management challenges. Promoting public awareness and education is vital in empowering individuals to understand the impacts of inorganic and organic contaminants. By increasing public awareness about the sources, risks, and potential mitigation measures, individuals can make informed decisions and actively participate in efforts to reduce contaminant exposure. Education programs should target the general public and professionals in relevant fields. Furthermore, the development and implementation of robust policies and regulations are critical for effective contaminant management. Governments and regulatory bodies need to establish stringent standards for contaminant limits, promote sustainable practices, and provide a framework for monitoring and enforcement. Clear guidelines and regulations ensure that contaminant management practices are carried out responsibly and transparently.

In conclusion, future directions in inorganic and organic contaminant management involve embracing advanced treatment technologies, adopting sustainable approaches, enhancing risk assessment and management strategies, addressing emerging contaminants, fostering collaboration and data sharing, promoting public awareness and education, and implementing robust policies and regulations. By pursuing these directions, we can effectively protect human health and the environment from the harmful effects of contaminants.

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Conventional Wastewater Treatment Methods for the Removal of EPs



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Abstract Pharmaceuticals, personal care and beauty products, pesticides, nanoparticles and nanomaterials, surface-active agents, industrial substances and additives, and pathogens are the prominent classes of emerging pollutants (EPs). One of the current major growing environmental problems is the noticeable amount of these EPs that are present in domestic, municipal, and industrial wastewaters treated by conventional wastewater treatment methods. They are released continuously into the environment due to increasing demand for chemical-based products. However, a majority of the EPs are not controlled or monitored by national or international legislation. Even worse, they can cause direct or indirect harm to human beings and the surrounding ecosystem even at low concentrations. This chapter reviews the concept and applications of conventional wastewater treatment methods to remove EPs in order to understand their limitations. A particular focus is given to filtration, sedimentation, coagulation/flocculation, and activated sludge. Although these conventional methods are intended for removing particles in suspension and colloidal form, organic substances in dissolved state, essential nutrients, and pathogens from wastewater, EPs eventually could also be removed depending on their persistence, physical and chemical properties, treatment methods used, and operational and environmental conditions involved. The most significant groups of EPs that could potentially be removed by the conventional methods are also described. Since these conventional methods cannot guarantee the complete removal of various EPs, it is necessary to study suitable long-term and effective alternatives in the treatment technologies.

Keywords Emerging pollutants · Wastewater treatment · Filtration · Sedimentation · Coagulation · Activated sludge

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1 Introduction

Emerging pollutants (EPs) refer to a wide range of chemicals that are not traditionally regulated but have been found to have harmful effects on human beings and the surrounding ecosystem (Haddaoui and Mateo-Sagasta 2021; Arman et al. 2021). EPs, such as pharmaceuticals and personal care products (PPCPs) and endocrine-disrupting chemicals (EDCs), are increasingly being identified in wastewater and pose a possible risk to both human health and the natural surroundings. Conventional wastewater treatment methods can be employed to remove these pollutants from wastewater. The methods include the following (Ranjit et al. 2021; Phoon et al. 2020):

1. **Physical treatment methods**—include processes like sedimentation, filtration, and flotation, which remove pollutants physically.
2. **Chemical treatment methods**—encompass the utilization of chemicals such as coagulants and flocculants to treat wastewater. The chemicals neutralize the charges of particles, leading to their aggregation and the formation of larger particles that can be readily eliminated.
3. **Biological treatment methods**—entail harnessing the capabilities of microorganisms to break down the pollutants in wastewater. The widely employed approach is activated sludge, wherein microorganisms are used to degrade organic matter in the wastewater.

This chapter reviews the concept and applications of filtration, sedimentation, coagulation/flocculation, and activated sludge to remove EPs in order to understand their limitations. Additionally, the effectiveness of these conventional wastewater treatment methods in removing EPs from wastewater will be further discussed based on the EPs' persistence, physical and chemical properties, treatment methods used, and the operational and environmental conditions involved.

2 Conventional Wastewater Treatment Methods in Removing EPs

2.1 Filtration

Filtration is a physical treatment method that removes pollutants from wastewater by passing the water through a filter medium. Sand, gravel, and activated carbon are just a few materials that may be used as filters. To maximize the elimination of pollutants from wastewater, filtration is often employed alongside complementary treatment methods like coagulation and flocculation (Cescon and Jiang 2020). Adsorption, absorption, precipitation, and straining are the primary methods by which filtering will eliminate EPs from wastewater (Brandt et al. 2017). Straining is when pollutants are physically filtered out through a sieve-like material, such as sand or gravel.

Adsorption is when pollutants bind to the surface of a filter material, typically activated carbon, through physical and chemical means. Absorption occurs when pollutants are taken in by the filter material through its porous structure. Precipitation involves transforming pollutants into a solid state through a chemical reaction and trapping them in the filter material. The choice of mechanism(s) used depends on the filtration method and properties of the pollutants.

Sand filtration, gravel filtration, and activated carbon filtration are all typical filtering processes. Each approach has strengths and weaknesses, and their ability in eliminating pollutants varies depending on the size, concentration, and chemical characteristics of the pollutants (Huguenin and Colt 2002). Sand filtration is a popular method for eliminating contaminants from wastewater that includes passing wastewater through a bed of sand. This process is effective in removing suspended solids such as bacteria and particles, as well as certain dissolved pollutants like pharmaceuticals. Sand filtration used for water treatment can be separated into two categories: slow sand filtration (SSF) and rapid sand filtration (RSF) based on their filtration speed. RSF is utilized as a last step of purification in the water treatment process, unlike SSF. There is a scarcity of research on the application of SSF for the removal of EPs. However, in recent years, biosand filtration (BSF), a type of SSF, has become popular and been utilized for household water purification. These forms of sand filtration have proven to be effective in eliminating suspended particles, harmful microorganisms, and various types of organic contaminants including newly emerging ones (Li et al. 2022).

A study by Pompei et al. (2017) found that BSF was effective in removing diclofenac, naproxen, ibuprofen, and methylparaben from six selected PPCPs. BSF performance used in households was not affected by 2 µg/L of PPCPs in the water. The removal of total coliforms and *E. coli* remained constant, but there was an observable change in the number of bacterial species present between contamination and non-contamination periods. The filter's biomass increased as more filtrations took place. The results suggest that certain bacterial species within the filter are influenced by PPCPs, but *Bacillus anthracis* and *Exiguobacterium* sp. displayed resistance to the effects of PPCPs. D'Alessio et al. (2015) evaluated the performance of two BSF units in removing six pharmaceutically active compounds (PhACs). The study revealed that carbamazepine, gemfibrozil, and phenazone had limited removal rates (less than 10%), while caffeine was completely eliminated. Partial removal (11–92%) of 17-β estradiol [E2] and estrone [E1] was observed in the two BSF units. The presence of certain PhACs, specifically estrogens and caffeine, at a concentration of 50 µg/L in the influent water was found to impact the effectiveness of the *schmutzdecke* in removing total coliforms and *E. coli*.

In 2013, an experiment has been conducted to evaluate the effectiveness of BSF in removing three EDCs: E1, [E3], and [EE2]. The BSF showed minimal removal of the EDCs, with less than 15% removal for all three compounds. However, adding household bleach to the BSF effluent was found to improve the removal of EDCs. When the concentration of bleach was greater than 5 mg/L, the elimination efficiency was greater than 98%. At lower concentrations, removal was between 50 and 70% (Kennedy et al. 2013). Nakada et al. (2007) evaluated the performance of a

combined treatment system consisting of sand filtration and ozonation for the elimination of PhACs from wastewater. The study found that removing PhACs through sand filtration alone was not very effective, likely because the compounds had low hydrophobic properties. However, when ozonation was combined with sand filtration and activated sludge treatment, a high level of removal (over 80%) was observed for all target compounds, including two phenolic antiseptics, five acidic analgesics or anti-inflammatories, two amide pharmaceuticals, seven antibiotics, three phenolic EDCs, and three natural estrogens except for carbamazepine and diethyltoluamide (Nakada et al. 2007).

Gravel filtration operates in a similar manner to sand filtration by passing wastewater through a bed of gravel. It is effective in filtering out bigger pollutants like bacteria and particles from wastewater, but it might not perform as well as sand filtration in eliminating smaller pollutants like specific pharmaceuticals (Hatt et al. 2007). The scarcity of studies on using gravel filtration for removing emerging pollutants is due to factors such as limitations of gravel filtration (lower surface area and inefficient of removing soluble or small size particle), cost and complexity, and lack of knowledge. Thus, it is often combined with other treatment methods to achieve comprehensive and effective treatment of wastewater. Ataguba and Brink (2021) examined the effectiveness of a combined filtration system, comprising rice husk (RH), granular activated carbon (GAC), and gravel (GR) in removing cadmium, copper, lead, and iron from stormwater runoff originating from automobile workshops in Nigeria. Over a 9-week period, stormwater samples were collected from five locations and subjected to filtration using three different combinations of filters: GAC-RH, GR-GAC, and RH-only. The average combined removal of all the metals was 61% for GAC-RH, 52% for GR-GAC, and 46% for RH-only. The findings indicated that further filtration would be necessary to meet the discharge standards set by local and international regulations and future research is recommended to optimize the filtered materials for improved metal removal efficiency.

In the meantime, a pilot-scale hybrid natural wastewater treatment (NWT) system was set up in Nigde stream, to control nitrogen pollution that contaminates Akkaya lake. The system consisted of multiple stages including filtration with gravel, a sedimentation pond, a constructed wetland with a free water surface and no gravel filtration, and a constructed wetland with a gravel filtration-overland flow. The performance of the system was monitored for a year and the results showed that the average removal efficiencies of ammonium and total nitrogen were 75% and 85%, respectively. However, the removal efficiency was impacted by factors such as the cold season and higher hydraulic loading rates. The inclusion of vegetation and filter media was observed to enhance the efficiency of pollutant removal. Tunçsiper (2020) concluded that the implementation of a sequence of NWT systems within streams can effectively mitigate nitrogen pollution.

Activated carbon filtration (ACF) includes passing wastewater through a filter comprised of activated carbon, a porous substance with high surface area. This approach is effective in removing a wide range of dissolved pollutants from wastewater, such as some PPCPs and hormones (Hartmann et al. 2014). The effectiveness

of this method can be impacted by variables such as the type of activated carbon utilized, pollutant content, and the operating parameters including pH and flow rate of the effluent. Similar to sand and gravel filtration, ACF is commonly integrated with additional techniques for the elimination of EPs from wastewater to enhance the treatment efficiency. Pulido-Reyes et al. (2022) assessed the efficacy of a sequential treatment process involving three filtration stages: RSF, ACF, and SSF—for the removal of nanoplastics. The study found that the removal efficiencies exceeded 3-log units predicted. The authors concluded that this study can be applied to estimate the effectiveness of removing nanoplastics in conventional drinking water treatment plants with similar water treatment chains.

Negrete Velasco et al. (2022) conducted a study to investigate the presence of microplastics and synthetic fibers in a conventional plant for treating drinking water in Geneva, Switzerland. The study also examined the impact of coagulation on the removal efficiency of these contaminants through sand and activated carbon filtration. Results showed that the average removal efficiency of microplastics and synthetic fibers was 89% and 81% respectively in the absence of coagulant, but increased to 97% and 96% respectively with coagulation treatment. The chemical composition of these contaminants was found to be more heterogeneous in raw water compared to after undergoing sand and activated carbon filtration.

Scheurer et al. (2012) investigated the environmental behavior of metformin, an antidiabetic medication, and its degradation by-product guanlyurea, which are frequently released into rivers in high concentrations because of inadequate breakdown in wastewater treatment facilities. The effectiveness of different treatment methods applied in water treatment plants was investigated in the study, revealing that flocculation and activated carbon filtration demonstrated limited efficiency, while ozonation and chlorination partially transformed the compounds into unknown substances. The study concluded that biological degradation is likely responsible for the elimination of metformin and guanlyurea, indicating that if surface water is utilized without an underground passage, only minimal traces of these compounds would be present in the finished drinking water.

Filtration may be a useful technique for removing EPs from wastewater when they are suspended or have a large particle size. However, it has certain limitations and drawbacks. Filtration may not be selective for certain EPs, leading to the removal of unintended pollutants along with the target pollutant. This can cause the buildup of impurities in the filter, reducing its efficacy. Sand, gravel, and activated carbon are examples of filtering materials with limited adsorption capabilities. Once the filter reaches its adsorption capacity, it loses its ability to effectively remove contaminants from wastewater, and the filtering materials may need to be replaced frequently, incurring cost and time-consuming efforts (Chi et al. 2013).

Additionally, filtration materials can become clogged over time, reducing their effectiveness in removing pollutants. This is known as fouling, and it can result in reduced flow rates and increased pressure drop across the filter. Depending on the type of filtration material and the contaminants present in the wastewater, the filtration material may need to be regenerated or replaced regularly to maintain its effectiveness. This can be difficult and expensive, especially for filters that use

expensive materials such as activated carbon. Besides, filtration may not be compatible with other treatments that are commonly used in wastewater treatment plants, such as coagulation/flocculation and activated sludge. This can result in decreased performance and increased costs for the overall treatment process. These limitations and challenges associated with filtration for the removal of EPs from wastewater have highlighted the importance of selecting appropriate filtration materials and using filtration in combination with other treatment technologies to achieve the desired level of pollutant removal (Koul et al. 2022).

To summarize, the effectiveness of removing pollutants from wastewater by filtration depends on the size, concentration, and chemical composition of the pollutants. Different filtering methods have their own distinct benefits and drawbacks, and choosing the right method to eliminate EPs requires careful consideration of the individual contaminants and operating parameters involved.

2.2 Sedimentation

One of the most conventional wastewater treatments is the sedimentation process where a physical process is used to remove suspended solids and particulate matter from the wastewater using gravity (O'Melia 1998) and is classified as primary treatment in wastewater treatment as can be seen in Fig. 1. The sedimentation process involves allowing the wastewater to settle in a tank or basin. The heavier solids and particulate matter settle at the bottom of the tank, forming a sediment layer, while the clear wastewater is removed from the top of the tank (Grzegorzec et al. 2023). The sediment layer is then removed and disposed of appropriately; if not, it will affect the environment (Ravindiran et al. 2021). The suspended particles in water depend on several factors such as composition, charge, shape, particle size, and density. By applying the physical forces, it will lead to suspension of the smaller particles in water and the surface charge present on the particles plays the main role.

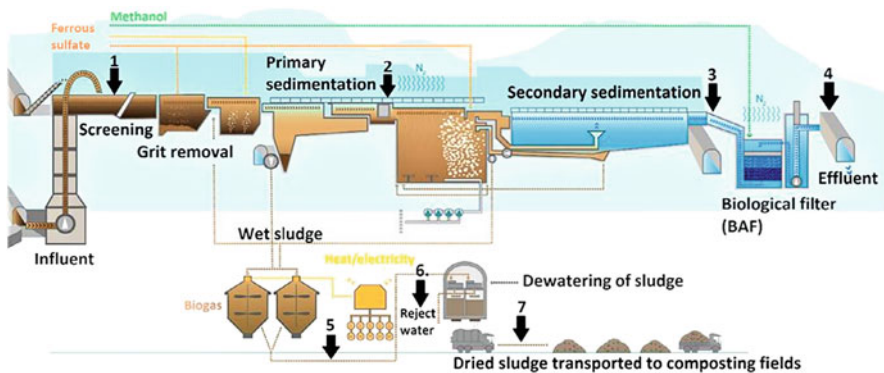


Fig. 1 Sedimentation process in primary wastewater treatment (Ou and Zeng 2018)

Fig. 2 Type of sedimentation tanks



Since most solids suspended in water have negative charge, it will repel each other rather than clumping together and settled out of the water.

Based on Fig. 2, circular and rectangular tank designs are the common designs for sedimentation tank. The rectangular tank is structured to have an inlet for effluent at one end and an outlet pipe for liquid that has undergone sedimentation at the opposite end. Its mechanism depends on the gradual passage of large solid particles through the tank, causing them to settle. By the time the liquid reaches the outlet pipe, the larger particles have settled at the tank's bottom. Conversely, circular tanks are designed with an inlet pipe positioned near the tank's bottom, close to a sludge removal pipe. The pipes for extracting cleaner liquids are situated near the tank's surface.

Sedimentation is an affordable and straightforward pre-treatment technique that utilizes gravity to diminish the presence of solid particles and certain microorganisms in water before employing additional purification methods. It not only enhances the visual appearance of the water but also enhances its appeal to consumers. As water is stored for a longer duration, suspended solids and harmful pathogens gradually settle at the container's bottom. The addition of chemical or natural coagulants can expedite the sedimentation process (Jiang 2015). When sedimentation is implemented following coagulation, its primary objective is typically to minimize the amount of suspended solids, thus optimizing the efficiency of subsequent filtration processes. Coagulation, especially when employing polyelectrolytes, can effectively eliminate protozoa, bacteria, and viruses. In water, certain bacteria and viruses can attach themselves to the suspended particles that contribute to turbidity. Consequently, reducing turbidity levels through coagulation can enhance the microbiological quality of water. Furthermore, coagulation proves to be effective in removing contaminants such as lead and barium.

Other than that, this process makes the subsequent water treatment process easier by requiring only fewer chemicals. It is also a passive treatment process that requires minimal energy input, which can make it an attractive option for wastewater

treatment plants that are looking to reduce their energy consumption. Once the sedimentation process is complete, the wastewater is decanted and sent to the secondary treatment process. The primary treatment process typically removes between 30 and 40% of the pollutants from the wastewater, which significantly reduces the load on downstream treatment processes. There are several factors that affect the efficiency and performance of the process such as flow velocity, temperature, suspension density, or the character of separated particles (Czernek et al. 2021).

Studies have been conducted to evaluate the effectiveness of sedimentation process for removing emerging pollutants from the wastewater. Conventional treatment technologies such as activated sludge, coagulation, sedimentation, and flocculation could not thoroughly remove emerging pollutants such as pharmaceuticals, personal care products, pesticides, pathogens, and others. The effectiveness of the sedimentation process in removing emerging pollutants depends on several factors, including the size and nature of the emerging pollutants, the pH of the wastewater, and the presence of other contaminants in the wastewater (Ahmed et al. 2021). In addition, the sedimentation process is less effective in removing certain emerging pollutants, such as endocrine disruptors, which are not easily removed by traditional wastewater treatment processes (Zamri et al. 2021). Studies reported that only less than 28% removal efficiency of diclofenac and E3 by using this method due to its properties which include high hydrophilicity and high solubility (Behera et al. 2011; Ugochukwu 2019). Also, it is similar to PPCPs which are mostly in hydrophilic in nature and less efficient to be removed by the sedimentation process in WWTPs (Kumar et al. 2023).

Other than less effective in removing emerging pollutants and dissolved chemicals, this process has some other disadvantages such as the usage of coagulant to speed up the sedimentation process. Without using coagulants, a long sedimentation time is needed and there are few drawbacks of coagulants, which are expensive to buy, may be toxic, are not available in a usable form, and need to be prepared. In fact, the effectiveness of coagulants varies from one to another and specific coagulants need to be selected to ensure the effectiveness of the process (Crini and Lichtfouse 2019). In addition, high investment cost for this process can also be the downside of this method since the sedimentation tanks often need reconstruction and expansion (Kowalski 2004).

Despite these limitations, the sedimentation process remains an important component of many wastewater treatment systems. It is often used in combination with other treatment methods, such as biological processes and chemical precipitation in order to achieve the desired level of pollutant removal. Additionally, advancements in sedimentation technology, such as the use of enhanced sedimentation processes and the optimization of tank design, have led to improved sedimentation efficiency and greater pollutant removal.

It is also worth noting that sedimentation alone may not be sufficient for removing emerging pollutants, as these compounds may remain in the dissolved form in the wastewater and not settle out during the sedimentation process. In these cases, several modifications can be made to the process such as increasing the detention

time or adding coagulants or flocculants to the wastewater. In addition, newer technologies such as membrane filtration can be used in conjunction with sedimentation to remove even more emerging pollutants from the wastewater (Dharupaneedi et al. 2019). This method offers high removal capability, low energy requirement, ease of scaling up, and rapid kinetics (Dewi et al. 2021).

One area of research is the development of enhanced sedimentation processes, such as upflow sedimentation and inclined plate sedimentation (Salah Al-Kizwini 2015). These processes use modified tank designs and flow patterns to improve sedimentation efficiency and reduce the time required for settling. Studies have shown that these enhanced processes can improve the removal of suspended solids and certain pollutants, such as heavy metals and some organic compounds, compared to traditional sedimentation processes (Saleh et al. 2022). Several studies have been conducted on the development of enhanced sedimentation process to increase the efficiency of the process. Chemically assisted primary sedimentation (CAPS) or chemically enhanced primary treatment (CEPT) was introduced previously to increase the coagulation, flocculation, and sedimentation of raw wastewater. It proved that the removal efficiency of total suspended solid (TSS) and organic material is higher as compared to simple primary sedimentation (De Feo et al. 2008).

2.3 Coagulation/Flocculation

Coagulation involves the destabilization of colloids by neutralizing the repulsive forces that keep them apart. Chemical coagulants, which are normally positively charged and will balance the negative charge of the colloids, are added to achieve this. As a result of the collision, bigger particles known as flocs are created, which are easier to settle out. Rapid mixing is necessary to distribute the coagulant throughout the entire liquid during coagulant addition. Primary coagulants and coagulant aids are the two different categories of coagulant compounds. The common coagulant used is hydrolyzing metal salts (ferric sulfate, ferric chloride, and aluminum sulfate (alum)), pre-hydrolyzed metal salts (poly aluminum chloride, poly aluminum hydroxy chloride, and poly ferric chloride), and cationic polymers (poly quaternary ammonium chloride-epichlorohydrin-dimethylamine) (Siti Nor et al. 2019).

Alum is effective in attracting inorganic suspended solids. It is widely used in industrial treatment plants (Fig. 3). The optimum pH to be maintained if alum to be used is between 5.5 and 7.5, whereas for ferric chloride and ferric sulfate, the optimum pH range required is between 5.5 and 8.5. For poly aluminum chloride, the working pH range is even wider compared to alum (Abujazar et al. 2022).

Coagulant aids are commonly organic and inorganic materials that increase the density and toughness of the flocs to avoid de-agglomeration during mixing and fast settling. Coagulant aids are commonly expensive, and there are a variety of coagulant aids such as bentonite, calcium carbonate, sodium silicate, aluminum chloride,

Fig. 3 Molecular structure of aluminum sulfate as a coagulant

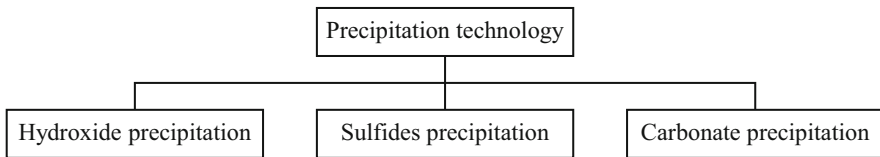
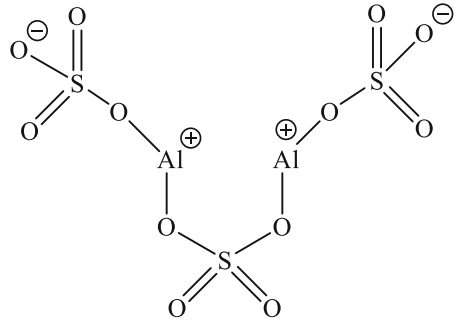


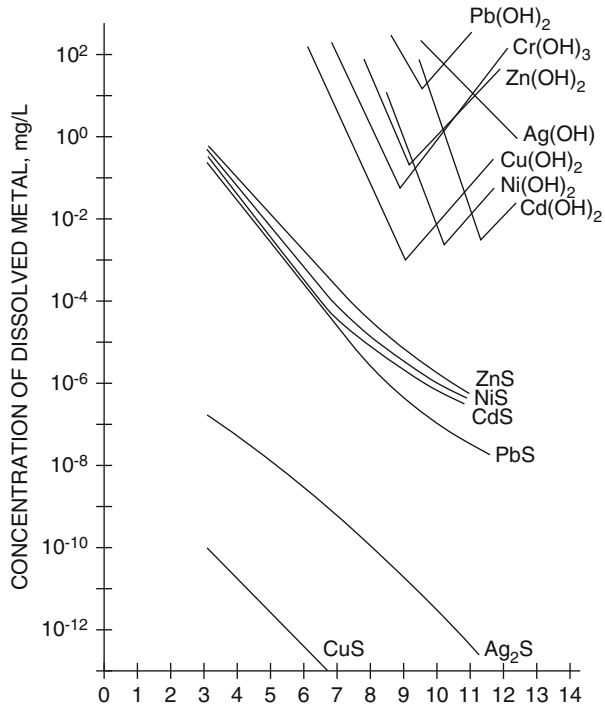
Fig. 4 Coagulant and flocculant applied precipitation technology. Variation of precipitation technology

chitosan, starch, sodium alginate, cationic polymer, anionic polymer, and non-ionic polymer (Aboulhassan et al. 2006).

Flocculation is a process that involves the addition of polymers, which are organic molecules with a high molecular weight, to the coagulated effluent to encourage the aggregation of the suspended solids into particles big enough to settle by generating bridges between the flocs, resulting in less gelatinous sludge and making it easier to dewater (Shamsudin Abd. Latif 2012). Flocculation is also commonly best described as the agglomeration process of particles. To allow for interaction between the small flocs and to agglomerate them into larger particles, it must be introduced while being mixed slowly and gently (Dayarathne et al. 2021). Some common flocculants are sodium silicate, bentonite, metallic hydroxides, starch derivatives, polysaccharides, chitosan, polyacrylamide, anionic polymer, and cationic polymer. The common flocculant used in industries is polyacrylamide.

In the industrial effluent application, the coagulants and flocculants that have been addressed are able to remove the large particles until the settling process becomes sludge. The common process to remove contaminants is by controlling the pH solution. Most of the coagulants and flocculants applied precipitation technology (Fig. 4). Precipitation technology was implemented by controlling the pH and solubility of contaminants including metals and non-metals. There are three types of precipitation technology such as hydroxide precipitation, sulfides precipitation, and carbonate precipitation. Hydroxide precipitation involves the reaction between metals and hydroxide ions to form a hydroxide precipitate. This hydroxide precipitate was then changed to become sediment and tended to agglomerate and wait for the settling process. A sulfide precipitate was formed by the reaction between metals and sodium sulfide to form metal sulfide which now becomes a

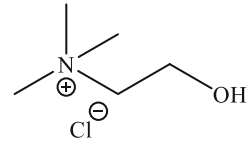
Fig. 5 Solubility of metal hydroxides and sulfides as a function of pH (x-axis).
Source: EPA 625/8-8-003



solid phase. This solid precipitate then becomes sediment and tends to agglomerate and wait for the settling process (Altaş and Büyükgüngör 2008). Carbonate precipitation involves the formation of carbonate precipitate from the reaction between calcium hydroxide, which is used as a precipitating agent with the metals. pH plays an important role in ensuring the contaminant, especially inorganic elements (heavy metals), can change from an aqueous phase to a solid phase based on the metal’s solubility in water. There are two factors that may also affect the coagulation and flocculation processes which are alkalinity and temperature. Alkalinity totally depends on the basic properties of the coagulant and flocculant. The formation of complexes at basic pH might increase the potential of the metals to be removed from the water to become sediment. In the metal’s removal, the common complexes formed such as hydroxide precipitation are well established and an inexpensive technology. However, there are certain metals that require additional steps such as arsenic ions, chromium ions, and selenium ions which require redox reaction prior to sludge formation. Hydroxide precipitation generates large quantities of sludge that are difficult to dewater. In addition, very little precipitation occurs at pH lower than 6.

Alternative technology instead of hydroxide precipitation is sulfide precipitation. The advantage of sulfide precipitation is the concentration required to form is less than hydroxide precipitation (Fig. 5). In Fig. 5, the concentration of metal sulfides formed was lower than that of metal hydroxide which might contribute to the trace

Fig. 6 Molecular structure of choline chloride



amount of the sulfide salts formed being easily removed compared to metal hydroxide salts. Both hydroxide precipitation and sulfide precipitation were commonly conducted under alkaline conditions between pH 7 and 9. If the sulfide precipitation technology is used, the evolution of H_2S gas can be formed if the alkaline environment is not being controlled wisely. In addition, soluble sulfide may generate odor which may cause irritation to the eyes and respiratory problems. By using sulfide precipitation technology, sulfide sludges are easier to dewater compared to hydroxide precipitation technology.

Other than hydroxide precipitation and sulfides precipitation, carbonate precipitation technology is specifically for insoluble carbonates such as lead, manganese, cadmium, and nickel. However, this type of technology is not commonly used in Malaysia.

Future Market Insights claims that throughout the evaluation period of 2022 until 2032, the demand for inorganic coagulants and flocculants will grow rapidly. There are many improved coagulants that have been reported. For instance, the Gas Processing Centre at Qatar University has created a brand-new, environmentally friendly technique for purifying wastewater. They investigated various green materials for the treatment of wastewater contaminated by colloidal suspension with very small suspended particles. Natural deep eutectic solvents (nades) have been used to develop a brand-new coagulant for colloidal suspension based on choline chloride (Fig. 6) (Al-Risheq et al. 2021). The study team created, characterized, tested, and successfully demonstrated the effectiveness of nades based on choline chloride as coagulants.

Another kind of coagulant is produced by converting crab shells into chitosan, a biopolymer generated from by-products of the seafood industry. A liquid that can be used to clean wastewater and stormwater is created from chitosan (Nouj et al. 2021). Chitosan's positive charge bonds to contaminants' positive charges, coagulating them so that they can be removed with ease by a tiny filtration system. Recently, the research on the improvement of the properties of coagulant is drastically increased and it will contribute to the vast impact in sustaining the good quality of water being discharged from the water treatment plant. Other than that, alum nanoparticles have also been synthesized and show better performance to remove Congo Red dye (Garvasis et al. 2020). In addition, the alum nanoparticles were synthesized using leaf extract of *Hemigraphis colorata*, and recently, the alum itself has been tested not only with metals but also organic contaminants.

2.4 Activated Sludge

The activated sludge process (ASP) is widely employed in wastewater treatment plants (WWTPs). This method is used to decrease nutrients such as nitrogen (N), carbon (C), phosphate (P), and organics from industrial and municipal wastewater in aerobic conditions (Shukla and Ahammad 2022). The ASP is a biological wastewater treatment used for treating domestic wastewater that involves a flocculent culture of microorganisms (bacteria, protozoa, and fungi) developed in aeration tanks under controlled conditions (Sharma et al. 2021). It is based on the ability of microorganisms to consume and break down organic pollutants in wastewater. However, the ASP shows limited potential for denitrification, which causes the concentrations of nitrate and phosphate to increase in wastewater that can cause eutrophication in recipient water bodies (Preisner et al. 2021). Even so, the ASP has been successfully applied to treat different types of wastewater. More than 90% of industrial and municipal wastewater WWTPs are used with this treatment.

The process involves several steps, namely, pretreatment, aeration, mixing, settling, recirculation (returned sludge), and disinfection (Fig. 7). Before treating it in the ASP, the wastewater must be pretreated to remove large solids, such as branches, leaves, and other debris that may block the system. After that, the wastewater in the aeration tank is mixed with microorganisms culture. To ensure sufficient oxygen for the microorganisms to consume and break down the wastewater’s organic matter, air is pumped into the tank to create an aerobic environment. The air pumps tend to plug at low return flow rates. The concentration of dissolved oxygen (DO) and biomass is needed to be kept at a certain level to achieve a desirable reduction of COD and BOD. The wastewater and microorganisms are mixed continuously to ensure that the microorganisms have sufficient organic matter in the wastewater. After the aeration process, the mixed liquor can settle in a clarifier

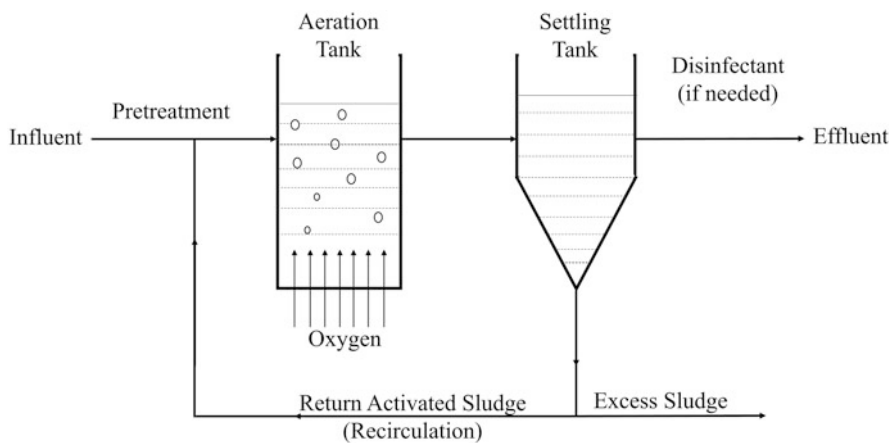


Fig. 7 The principle of the activated sludge (adapted from Fraçz 2016)

tank. After the ASP, chlorination can be done to remove any remaining pathogens in the treated wastewater.

The treated wastewater is discarded from the upper part and the activated sludge settled at the bottom of the tank. Some settled sludge is used to feed the incoming wastewater with microorganisms in the aeration tank, and some sludge is discharged into the concentration tank. The sludge is called excess sludge, which also receives the sludge from the primary tank (Huang et al. 2022). The sludge is treated with thickening and dewatering processes followed by sludge disposals, such as composting and incineration. The excess sludge contains a high concentration of organic matter (60–90%), carbon (50–55%), N (10–15%), P (6–10%), and microbial flocs (Tyagi and Lo 2013).

The efficiency of the ASP depends on different parameters such as chemical oxygen demand (COD), oxygen, biological oxygen demand (BOD), hydraulic retention time, and temperature (Tran et al. 2018). Other than that, the sludge in the ASP can be reused many times, reducing the time required for sludge preparation. Since the ASP is designed to produce high-quality effluent, the nutrient, turbidity, COD, and BOD are expected to be reduced.

There are a few drawbacks of the ASP. Firstly, sludge disposal in low carbon emission (Huang et al. 2022) and sludge bulking (Sam et al. 2022) are the major problems in the ASP. Sludge disposal may affect the environment due to harmful components such as organic compounds, pathogenic organisms, heavy metals, and high phosphorus and nitrogen concentrations (Feng et al. 2015). In the meantime, excessive growth of filamentous fungi and bacteria, the deficiency of nutrients, and the fluctuation of some physicochemical parameters can cause sludge bulking (Lou and Zhao 2012). This affects the treated water quality in the effluent and the efficiency of wastewater treatment. Also, the ASP tends to have a lower sludge retention time, meaning bigger reactor tanks are needed to treat larger effluent volumes, indirectly requiring a bigger land area. The ASP also consumes a large amount of energy, especially for wastewater pumping (12%) and aeration system (60%) (Silva and Rosa 2022). Hence, the cost of energy can be done by using energy-efficient pumps, aeration systems, motors, and blowers. The ASP can also be modified to solve specific conditions by the mixing and flow patterns in the aeration tank and how the microorganisms are mixed with the wastewater influent. Some examples of the modified ASP are conventional modification, contact stabilization plants, tapered aeration, complete mix plants, extended aeration, pure oxygen systems, and step aeration plants.

The WWTPs were originally designed to remove suspended solids, trace elements, and pathogenic microorganisms, and therefore, the WWTPs are reported to be inefficient in removing EPs from wastewater. Therefore, EPs such as personal care products (PCPs), pharmaceutical compounds, endocrine-disrupting compounds (EDCs), pesticides, and plasticizers may be discharged to the environment unchanged or partially removed in low concentrations, ranging from ng/L to mg/L. Due to the low concentration, these compounds can resist degradation and difficult to be removed using conventional wastewater treatment methods.

Personal care products (PCPs) are a class of EPs contaminants, including cosmetic and personal hygiene products such as fragrances, UV filters, deodorants, antimicrobials, and surfactants (Zicarelli et al. 2022). The traces of PCPs have been detected in the environment since 50 years ago (Veach et al. 2012).

Most past research reported that the ASP could potentially remove PCPs. Ahmed et al. (2017) reviewed that the ASP has shown better removal percentage (up to 90%) of the PCPs. Lishman et al. (2006) also observed a similar trend in which triclosan reduced up to 94% in the ASP. The ASP is also able to enhance removal efficiency. This has been proved by Duis et al. (2022), who investigated the removal rates for two sunscreens (octocrylene and butyl-methoxydibenzoylmethane), where both of the sunscreens were removed by the ASP, probably by absorption, up to 80%. Without the ASP, the sunscreens were removed poorly (37%) (Li et al. 2007).

The degradation of PCPs in the ASP may be attributed to different mechanisms such as volatilization, adsorption, and biodegradation. Volatilization occurs at the same time as aeration. Concurrently, the adsorption is affected by physicochemical characteristics such as the compound's properties, temperature, oxygen level, pH, nutrients, and the microbial community. Previous research showed many types of PCPs can be removed, approximately 78–90%, even though maybe some PCPs, such as celestolide and cashmeran, were only degraded up to 60% due to sorption and biodegradation (Buttiglieri and Knepper 2008; Garcia-Rodríguez et al. 2014). Salgado et al. (2012) also observed that some PCPs (galaxolide, tonalide, cashmeran, celestolide, and traseolide) showed higher levels of removal by adsorption (more than 70%) compared to biodegradation. Wang et al. (2023) reported that the removal of triclocarban (TCC) could reach 78–92% in the ASP as a result of the adsorption of extracellular polymeric substances (EPS). The suspended cultures produce EPS at the outer shell of activated sludge. EPS can provide many adsorption sites due to the hydrophobic groups from polysaccharides, proteins, and lysis products (Ma et al. 2021). Besides that, biodegradation also plays a part in PCPs elimination in the ASP which can be enhanced by bioaugmentation (Zhou et al. 2014).

Other than PCPs, pharmaceutical compounds are the typical EPs in the environment. Pharmaceutical compounds such as antibiotics, anti-inflammatories, analgesics, antidiabetics, antidepressants, antihypertensive, blood lipid regulators, β -blockers, and synthetic and natural hormones are able to treat and prevent disease for animals and humans (Ternes et al. 2004). If released into the environment with high mobility, these compounds can persist for a long time. These contaminants can interact with living systems due to their properties and the most prevalent detected compounds (Ulucan-Altuntas et al. 2023).

Previous review papers discussed the removal of different pharmaceutical compounds. Chen et al. (2021) addressed different factors that affect antibiotic removal in the ASP, such as the removal mechanisms, factors, and kinetics, covering different classes of antibiotics (sulfonamides, β -lactam, macrolide, tetracycline, fluoroquinolone, and dihydrofolate reductase inhibitor). Uluseker et al. (2021) reviewed the removal efficiencies of antibiotic resistance in different wastewater treatment technologies. Results showed variations among other methods, but

combining the ASP with advanced tertiary treatment methods like oxidation, ozonation, and ultraviolet will remove more antibiotic resistance than the ASP alone. This is in line with Shukla and Ahammad (2023). They compared the ASP, modified trickling filter, and two tertiary systems (UV and ozonation) in removing pharmaceutical compounds, antibiotic-resistant bacteria (ARB), and antibiotic resistance genes (ARGs). They observed that the ASP showed the poorest treatment compared to other treatments. They also found that ARB, ARGs, and their relative abundance increased in the sludge produced from the ASP.

Different studies reported that the ASP has various impacts on other pharmaceutical compounds based on different physicochemical properties, biodegradability, and concentration in the wastewater. Some compounds were persistent and resistant to being degraded, and some were partially or entirely removed from the wastewater. Ahmed et al. (2017) reviewed that the removal rate for beta-blockers (metoprolol, atenolol) was poor due to the adsorption onto the activated sludge. Joss et al. (2006) studied the ASP and showed that 17 out of 35 compounds were removed less than 50%, and a study by Aboudalle et al. (2021) also concluded that the ASP could only mineralize metronidazole up to 58%. However, in another research, Krah et al. (2016) reported seven types of pharmaceutical compounds (acyclovir, acetaminophen, atenolol, acetyl-SMX, acesulfame, benzophenone-4, and bezafibrate) can be 100% removed by the ASP at 12 h of hydraulic retention time. Kanafin et al. (2021) also observed a 100% degradation of ibuprofen and caffeine but only recorded about 27% degradation of metronidazole after the ASP. ARGs were also proven to be removed after the ASP (Sharma et al. 2016).

Although studies have shown that the ASP managed to reduce the pharmaceutical compounds from the wastewater, there have also been reports that the ASP amplifies the concentration of pharmaceutical compounds. For example, Cheng et al. (2021) found that the ARG concentration increased 30% after the ASP. This may be due to the high bacterial population and nutrients the activated sludge provides, making it suitable for horizontal gene transfer and enhancing the proliferation. The existing ARGs may be released from the activated sludge and cause an increase after the ASP. Calero-Cáceres et al. (2014) also indicated that the bacteria change in population from the water to the solid phase may cause higher ARGs found in the activated sludge.

Endocrine-disrupting compounds (EDCs) are also one of EPs types and can be easily found in many everyday products. EDCs can affect the function of the endocrine system of animals and humans due to their hormone-like behaviors at low concentrations (Gao et al. 2020). EDCs can be found in many different environments, such as water (wastewater, surface water, groundwater), soil, and air. Some examples of the EDCs include dioxin and dioxin-like compounds, organotin compounds, polychlorinated biphenyls, plasticizers such as bisphenol A (BPA), and estrogens (estrone (E1), estradiol (17 β -estradiol or E2), 17 α -ethinylestradiol (EE2), estriol (E3)), and phenolic xenoestrogens (4-nonyl phenols (4-NP)) (Werkneh et al. 2022).

Previously analyzed papers reviewed the different perspectives on removing EDC from the ASP. Azizi et al. (2022) comprehensively reviewed the removal

methods and various suitable technologies, such as physical, biological, chemical, and electrochemical processes. They summarized that the efficiency of the EDC removal was highly related to the characteristics of the EDCs. Werkneh et al. (2022) also reviewed the treatment technologies and different existing and emerging treatments and summarized that the integrated system showed better removal efficiency of EDCs compared to only using a single treatment technique. Ahmed et al. (2017) also concluded that EDCs were well removed by the ASP compared to the existing biological processes such as biological activated carbon, constructed wetlands, and microalgae.

Some researchers reported that the ASP efficiently removes a wide range of EDCs (50–100%) through the elimination mechanism involving biodegradation and sludge sorption (Ahmed et al. 2017) and nitrifying capacity in the ASP (Dytczak et al. 2008). Some studies showed that the ASP could not remove EDCs (2 hydroxy estrone, androstenedione, androsterone, alpha hydroxyl estrone, BPA, E1, EE2, E3, coumestrol, progesterone, testosterone, and octylphenol) entirely due to the microorganisms' ability to easily degrade these compounds (Semblante et al. 2015; Ahmed et al. 2017). Meanwhile, Dias et al. (2021) observed that the ASP could only work with additional treatment where the ASP showed a 50% removal of E2 and EE2 by adding the activated carbon from the regular wastewater treatment process. On the other hand, Baronti et al. (2000) stated that E1, E2, EE2, and E3 were removed up to 85% using the ASP in six WWTPs, while Esperanza et al. (2004) reported that approximately 60–90% of E1 and EE2 have been removed by the ASP via adsorption and biodegradation. Johnson and Sumpter (2002) also found that the ASP can consistently remove more than 85% of E2, EE2, and E3.

Pesticides are also one of the EPs commonly spotted in the environment. Pesticides produced naturally or chemically control various pests in fields such as agriculture and aquaculture (Pathak et al. 2022). There are different types of pesticides, such as herbicides, fungicides, insecticides, nematicides, and rodenticides. Certain pesticides like aldrin, heptachlor, dichlorodiphenyltrichloroethane (DDT), chlordane, hexachlorobenzene, dieldrin, and endrin can have harmful impacts on the environment as well as human health. Pesticides became an important tool to protect plants and enhance crop yield in agriculture. Therefore, pest management is required to control pests and increase crop production. Many pesticides are stable and remain in the environment for a long time. Thus, pesticides can contaminate areas far from their point source.

The ASP potentially removes different pesticides with different removal efficiency. For example, Nakada et al. (2006) reported that the ASP was unable to remove diethyltoluamide (DEET) efficiently. This is the same with Ahmed et al. (2017), who reviewed that different herbicides (atrazine, diuron, and triclosan) were poorly removed during the ASP. However, Morasch et al. (2010) observed that the ASP showed different pesticide removal rates. Some pesticides (chloridazon, irgarol, and tebufenozide) showed high removal efficiency. However, certain pesticides (atrazine, mecoprop, and propiconazole) showed little or were not removed at all. The removal rate of different pesticides by the ASP is between 60 and 80%. For example, DEET was removed approximately 60% (Ulucan-Altuntas et al. 2023),

76% removal of methiocarb (insecticide) (Gusmaroli et al. 2020), and 80% removal of fluoxil (herbicide) (Carboneras et al. 2018). In the meantime, Tazdaït et al. (2018) studied that different concentrations of glyphosate (herbicide) may affect the removal rate and microorganisms' growth. The herbicide was removed at a low concentration (up to 1 g/L), but the microorganism's growth was affected at higher concentrations (up to 5 g/L).

Even though the ASP can potentially remove the pesticides from the wastewater, the ASP alone is still insufficient in completely removing the EPs. Saleh et al. (2020) reviewed the potential removal of pesticides from water from different approaches, such as physical, chemical, physical, and biological treatments. Even though single treatments showed the potential to remove the pesticides, combining collective techniques is the most efficient method to remove pesticides from water. Ulucan-Altuntas et al. (2023) observed that different pesticides, such as methiocarb and buprofezin, were found in the effluent, proving that the pesticides cannot be efficiently removed. Therefore, additional treatment is still needed to completely remove pesticides from the wastewater.

While the ASP has shown promise in removing EPs from wastewater, its effectiveness has limitations. Firstly, EPs were typically detected in the wastewater at low concentrations (less than one microgram per liter) (Rogowska et al. 2020). These low concentrations can make it difficult for microorganisms in the activated sludge to effectively degrade the compounds, as they may not be present in high enough concentrations to support microbial growth. Certain EPs also have very low solubility, hydrophobic, or complex structures, making them resistant to being degraded by microorganisms in the ASP (Letsoalo et al. 2023). Some compounds may even require specialized metabolic pathways or enzymes to degrade EPs, which may not be present in the microbial population in the activated sludge.

Most EPs in wastewater are removed through biodegradation by the microorganisms in the activated sludge (Liu et al. 2009), while other processes, such as primary setting, aerating volatilization, and chemical precipitation, may be negligible. Some EPs, such as stimulant drugs and some metabolites, may have better sorption properties on the suspended solids (Ahmed et al. 2017). Some pharmaceuticals can undergo chemical transformations during the ASP, which leads to the formation of new compounds that may be more resistant to being removed from the wastewater. The EPs can compete with the presence of organic matter in the ASP for the attention of microorganisms in the activated sludge. The microorganisms may consume other organic matter over the EPs that can lead to lower removal efficiencies for EPs. Lastly, the operating condition of the ASP may also affect the removal percentage of EPs in the activated sludge (Chen et al. 2021). The removal efficiency can vary depending on the specific pharmaceutical and the operating conditions of the WWTPs.

Overall, the removal trend for EPs by the ASP can be arranged as follows: surfactants, EDCs, PCPs, pesticides, pharmaceuticals, and beta-blockers (Ahmed et al. 2017). The potential long-term effects of the EPs in the environments, especially in water, are still uncertain and can be severe without notice, as most EPs do not have standard regulations. Organizations such as the World Health

Organization, North American Environmental Protection Agency, and European Union are setting up frameworks to improve and protect wastewater quality. Therefore, more research and further investigations are needed to support this effort and to study the effect and removal technologies to reduce the dissemination of EPs into the environment.

3 Conclusion

The limitations of conventional wastewater treatment methods in removing EPs include a lack of specificity and incomplete removal. Conventional treatments do not specifically target EPs and remove a broad range of substances, both harmful and benign. Despite the best treatment methods, complete removal of EPs from wastewater can still be difficult to achieve. Some EPs are highly soluble and can easily pass through treatment processes, while others are resistant to conventional treatments and persist in the environment after treatment. Advanced treatment methods, such as advanced oxidation processes, can be costly to be implemented and maintained. There are also challenges in implementing new treatment methods for EPs as there is a limited understanding of their properties and behavior and many EPs are not yet regulated. In conclusion, conventional wastewater treatment methods have limitations in removing EPs, and continuous research and development is needed to find more effective methods for treating these pollutants.

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Biotechnology-Based Strategies for Removal of Emerging Contaminants



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Abstract Emerging contaminants refer to materials that are not commonly found in the natural environment. There is a major danger posed to both human health and the ecosystem as a result of the presence of these toxins in water sources. Conventional methods of treating wastewater are often unsuccessful when it comes to eliminating new pollutants. These contaminants include medications, personal care items, insecticides, and substances that affect the body's endocrine system. In recent years, biotechnology-based solutions have emerged as potential ways to handle the removal of these new contaminants. Contaminants are constantly being created and released into the environment. The most recent developments in biotechnology-based solutions that have been developed for the purpose of particularly removing newly discovered toxins from water sources are the primary topic of this study. Bioremediation, a process that utilizes microorganisms to degrade and remove contaminants, has shown great potential in treating emerging contaminants. Microorganisms such as bacteria, fungi, and algae have been employed to break down these contaminants into non-toxic by-products through various mechanisms, including biodegradation, bio-adsorption, and bioaccumulation. Furthermore, the application of advanced biotechnological tools, such as genetic engineering and nanotechnology, has enhanced the efficiency of removal strategies. Genetic engineering allows the modification of microorganisms to improve their degradation capabilities, while nanotechnology enables the development of nanomaterials with high adsorption capacities for targeted contaminant removal. Other biotechnology-based techniques, like enzymatic degradation, phytoremediation, and bio-electrochemical systems, have shown promising results in the removal of new pollutants in addition to bioremediation. In general, the use of biotechnology-based techniques provides a solution that is both sustainable and effective for the elimination of newly discovered toxins in water sources. However, further study is required to optimize these tactics, determine the impacts they will have over the long term,

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and create means of implementation that are both cost-effective and efficient in order to ensure their practical deployment on a broader scale.

Keywords Emerging contaminants · Bioremediation · Microorganisms · Phytoremediation

1 Introduction

In recent years, there has been a growing level of worry among both government agencies and environmentalists over the possible danger that emerging contaminants (ECs) pose to human health as well as the environment (Yadav et al. 2021). The identification of three primary sources of environmental contaminants (ECs) has been documented in the literature. These sources include (1) items that are used on a regular basis by people; (2) hormones or medications that are delivered to animals; and (3) pesticides or nanomaterials that are applied to plants in order to promote nutrient absorption (Ismail and Mokhtar 2020). Contaminants of emerging concern, also known as emerging pollutants, micropollutants, or trace organic compounds (TrOCs), are a class of pollutants that originate from various natural and anthropogenic sources, and have a significant impact on water quality (Mahmood et al. 2022) (Fig. 1). The term “emerging” is applied not on the basis of novelty but rather in response to an increased level of concern (Cozzens et al. 2010). Typically, the presence of these pollutants is observed in minute quantities, spanning from nanogram per liter (ng/L) to micrograms per liter ($\mu\text{g/L}$) within the atmospheric milieu. Emerging contaminants (ECs) are defined by the United States Environmental Protection Agency (USEPA) as “new chemical compounds with the potential to elicit deleterious consequences for human health and the environment” (Khan et al. 2022). The treatment and recycling of wastewater to meet acceptable standards are imperative in order to satisfy water requirements.

Emerging contaminants are introduced to the environment through diverse means. As an illustration, the everyday consumer goods generated by human activity are introduced into the wastewater stream, subsequently undergoing treatment in a conventional wastewater treatment plant lacking any mechanism for eliminating emerging contaminants (ECs) (Sai Preethi et al. 2022). Wastewater that has undergone treatment and wastewater sludge that retain traces of emerging contaminants (ECs) are anticipated to be reintroduced into aquatic environments and utilized as soil fertilizers, respectively. The deposition of electro-conductive substances (ECs) in livestock manure and the direct introduction of ECs from plants into soil are two distinct pathways for the presence of ECs in agricultural environments (Modin et al. 2016). Subsequently, these substances may be carried away by rainwater and ultimately end up in nearby water sources.

The consumption of potable water, specifically, has been observed to increase annually owing to factors such as population expansion, urbanization, industrialization, and modifications in agricultural and land utilization practices (Boretti and Rosa 2019). The accessibility of freshwater is a pressing issue that affects a

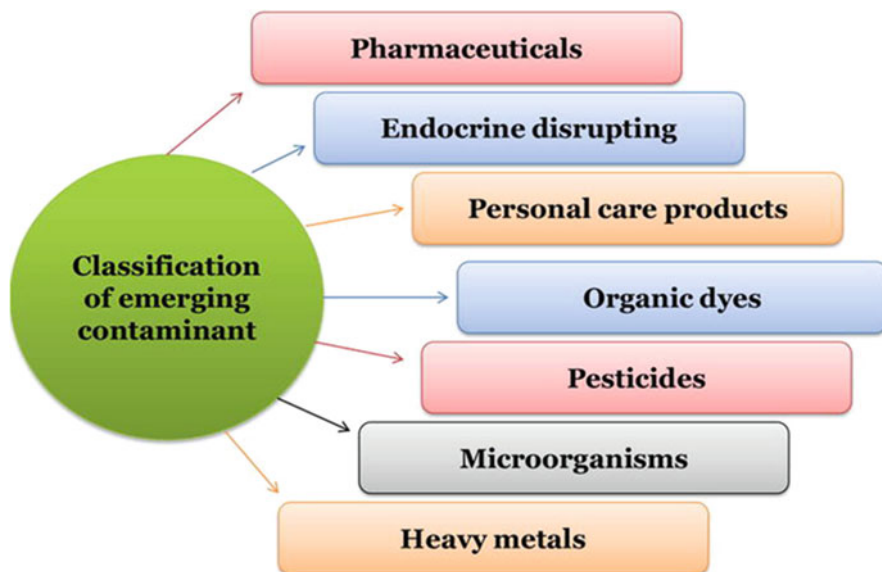


Fig. 1 Classification of emerging contaminant (Saddique et al. 2023)

significant portion of the global population. Sustainable water and wastewater management have been acknowledged by governments and organizations worldwide as essential constituents of operational communities (Dickin et al. 2020). Nevertheless, it has been observed that various categories of emerging contaminants (ECs) have been found in water sources with low EC clearance rates (Varsha et al. 2022). Moreover, a significant challenge in assessing the impact of emerging contaminants (ECs) in aquatic ecosystems is the limited availability of data pertaining to their prevalence, risk evaluation, and eco-toxicological effects (Parida et al. 2021). The rationale for this phenomenon can be attributed, in part, to the constraints of analytical techniques employed for the quantification of ECs at low concentrations, which typically range from parts per billion to parts per trillion. Additionally, the diverse chemical properties of ECs and the intricacy of matrices contribute to this challenge (Huang et al. 2018).

In order to eliminate or treat emerging contaminants (ECs) in water and wastewater, several different techniques have been developed and evaluated in this chapter. These methods were developed to improve established analytical routines. Adsorption, membrane technology, biological therapy, and an accelerated oxidation process are all considered as potential treatment alternatives in this study (Ahmed et al. 2022). It is imperative to consider such information for the purpose of enhancing existing methodologies or devising novel, sophisticated approaches.

2 Harmful Effects of ECs

As per the US Geological Survey, ECs are substances that are either synthetic or naturally occurring and are not typically monitored in the environment (Kumar et al. 2022). These substances are known to cause adverse effects on both ecological and human health. In scientific research, the term “ECs” generally refers to three types of targets, namely (1) newly discovered compounds and molecules, (2) pre-existing contaminants that have not yet been fully studied for their environmental implications or have recently gained attention, and (3) novel information pertaining to the environmental risks posed by legacy contaminants that challenges existing understanding (Abdulrazaq et al. 2020).

Many common household goods, including medications for humans and animals, personal care items, surfactants and their derivatives, plasticizers, and industrial additives, include ECs (Ahammad et al. 2022). These compounds are regularly released into the ecosystem and have a tendency to accrue over an extended period. Despite the significant advantages and convenience that they offer, the increasing utilization of technology poses potential risks and challenges for human beings (Bilal et al. 2021). Electronic cigarettes, often known as ECs, have been linked to a number of significant negative consequences on human health, including the potential to cause cancer, difficulties in reproduction, and endocrine-disrupting side effects (Rasheed et al. 2019). In the 1990s, academic research was begun to investigate the hormonal disturbance of fish that were found in surface waters. Sewage water was the primary source of hormones in surface water; however, they were not effectively eliminated by the treatment procedures (Phillips et al. 2009).

In addition to the potential impacts on human health, the introduction of various substances into the environment is an inevitable consequence of their widespread use in sectors such as healthcare, industry, transportation, and agriculture (Manisalidis et al. 2020). Insufficient elimination of these substances in sewage effluent through wastewater treatment plants is the primary pathway by which emerging contaminants are discharged into environmental water bodies (Ouda et al. 2021). The concentrations of emerging contaminants in surface water can vary widely, ranging from extremely low levels to significantly high concentrations (Morin-Crini et al. 2022). In some cases, even trace amounts of these substances can have ecological consequences that are often underestimated. Furthermore, certain organic compounds have demonstrated persistent properties once released into aquatic environments (Atanasov et al. 2021). Despite the lack of comprehensive risk assessment and inclusion in policy and monitoring programs, it should be noted that the absence of a universally accepted regulatory framework does not imply the absence of potential hazards associated with these substances (Aven 2016).

Numerous endocrine-disrupting chemicals (EDCs), such as ECs, have been identified in the scientific literature. Endocrine-disrupting chemicals (EDCs) possess the capability to impede animal reproduction and development, even when exposed to low levels. This may be accomplished by imitating naturally occurring hormones,

which then attach to a receptor and prevent the endogenous hormone from doing its job. Alternatively, this can be accomplished by disrupting the normal hormonal function (Ghosh et al. 2022). The World Health Organization (WHO) has identified a class of chemicals known as endocrine-disrupting chemicals (EDCs) that can have negative effects on human health, including changes in reproductive function, breast cancer risk, growth patterns, neurodevelopment delays in children, and immune system function (Jatoi et al. 2023). Endocrine-disrupting chemicals (EDCs) encompass both endogenous hormones and exogenous compounds, including synthetic hormones, pharmaceuticals, personal care products (PPCPs), pesticides, plasticizers, nanoparticles, and other industrial and commercial substances that exhibit hormonal activity (Yilmaz et al. 2020).

Wastewater streams predominantly derived from human urine often include detectable levels of the estrogens, estrone, estradiol, and estriol. Estrogens are excreted from the human body endogenously, without the administration of exogenous hormonal medications (Ruggiero and Likis 2002). It is hypothesized that a diverse array of concentrations of natural hormones are present in household wastewater, which is subsequently transported to the wastewater treatment plant via the sewer system. As a result, downstream aquatic species are likely to exhibit increased levels of estrogenic compounds. The exposure of fish to certain dosages of these compounds can result in the manifestation of feminization (Almazrouei et al. 2023).

Prescription pharmaceuticals, over-the-counter medicines, and veterinary medicines make up the bulk of the pharmaceutically active substances that make up domestically generated EDCs. Additionally, antimicrobial disinfectants fall within the umbrella of personal care products (Saha et al. 2022). The potential health hazards posed by these pollutants are a legitimate cause for apprehension in safeguarding a robust aquatic ecosystem and in the realm of water recycling (Manisalidis et al. 2020). Despite the typically low levels of pharmaceuticals found in aquatic environments, their high stability results in significant biological activity. As a result, even trace concentrations of these compounds may have potential impacts on aquatic wildlife (Biswas et al. 2021). Bisphenol-A (BPA) is a prevalent endocrine-disrupting chemical (EDC) that is ubiquitous in households. The aforementioned compound serves as a monomeric building block in the synthesis of polycarbonate and epoxy resins, which find application in distinct categories of polymeric materials (Fenichel et al. 2013). Research has established a correlation between BPA exposure during fetal development and the manifestation of heart disease, infertility, and behavioral and developmental issues in children (Rasdi et al. 2020).

Furthermore, pesticides are a classification of chemical compounds that possess the capacity to elicit a wide range of detrimental and noxious impacts on the natural world, notwithstanding their beneficial characteristics. Environmental pollutants are found in both groundwater and surface water due to their widespread historical or modern-day use (Kalyabina et al. 2021). The current research endeavors to examine the existence in 58 samples of both surface and groundwater for a total of 150 pesticides and their associated metabolites. Based on the findings, it was determined that 17 out of 27 metabolites that were ranked highly can be classified as emerging

metabolites (Reemtsma et al. 2013). As per the findings of the study, it was deduced that metabolites exhibit a higher occurrence rate in groundwater as compared to their corresponding parent compounds (Zind et al. 2021). Beef cattle are given synthetic steroid hormones to speed up their development, and these hormones also have pesticide and herbicide applications (Tudi et al. 2021). Research has demonstrated that significant quantities of bioactive steroids are present in the soil and runoff of expansive feedlots, potentially exerting an impact on the surrounding environment and wildlife in proximity to these bovine feeding facilities (Costa et al. 2022). Therefore, it is crucial to eliminate these trace contaminants from infiltrating water resources, despite due to the lack of attention (Anand et al. 2020).

Another study investigated the impact of phosphoric acid treatment on the adsorption efficacy of rice straw adsorbent, revealing a notable improvement in the sorption of pesticides (Anand et al. 2020). Based on the findings, the authors posited that of the five non-traditional adsorbents employed, the rice straw adsorbent exhibits considerable promise for pesticide manufacturing waste treatment (Qasem et al. 2021). An investigation was carried out to assess the efficacy of rice husk as an adsorbent in wastewater treatment that gets rid of metals. The findings suggested that the inexpensive adsorbent demonstrated notable efficacy in the concurrent removal of Fe, Pb, and Ni, across a concentration spectrum spanning from 20 to 60 mg/L (Swamalakshmi et al. 2018). The objective of the research conducted by the author was to evaluate the effects of different quantities of adsorbent depending on the elimination of certain metals. The results showed that increasing the amount of adsorbent utilized increased the amount of heavy metals removed (Qiu et al. 2021). The study found that heavy metals were adsorbed at a maximum rate of 76–96% under ambient temperature conditions, with an optimal contact duration of 2 h and a pH range of 6.0–7.0 (Liang et al. 2020). Tetracycline, a frequently employed drug in personal care and veterinary practices, is among the analytes that can be eliminated through the utilization of rice husk adsorbent (Daghrir and Drogui 2013). Additionally, a research investigation was carried out to modify rice husk with methanol to augment its adsorption capability towards tetracycline, while concurrently reducing the organic compound content that is intrinsic to the rice husk (Zein et al. 2020). The research conducted a comparative analysis between modified and untreated rice husk adsorbents, indicating a significant enhancement of around 45.6% in adsorption capability over a duration of 12 h and a reduction of 17.2% in equilibrium time (Kayal et al. 2010). According to the report, the increase in tetracycline adsorption can be mainly attributed to the modification of O-containing groups on the adsorbent (Kim et al. 2022).

The term “coconut coir dust” pertains to the by-product that is left over subsequent to the removal of fiber from the coconut husk. The aforementioned residual material constitutes roughly 70% of the mass of the coconut shell (Abad et al. 2005). The research was carried out with the aim of employing acid-activated coconut husk as an adsorbent to remove rhodamine-B (Rh-B) dye (Bello et al. 2019). Researchers looked at how starting concentration, contact duration, and solution temperatures all had a role (Ye et al. 2016). Langmuir, Freundlich, Dubinin-Radushkevich, and Temkin isotherm models were used to perform fitting methods on the adsorption

data and assess the results. The best-fitting isotherm model was the Langmuir isotherm, from which we determined a maximum adsorption capacity of 1666.67 mg/g (Saruchi and Kumar 2019).

3 Detection Methods of Emerging Contaminants

According to prior research, the discharge of newly identified chemical or microbial pollutants into the surroundings may have been transpiring for an extended period, albeit undetected until the advent of novel detection techniques (Miethke et al. 2021). Various techniques such as chromatography, spectroscopy, and metal analysis can be employed for the detection of ECs.

3.1 *Chromatographic Techniques*

Chromatographic techniques are widely employed in analytical chemistry for the purpose of identifying and detecting diverse compounds present in a range of sample types (Kanaujiya et al. 2019). Gas chromatography (GC) is a prevalent analytical methodology utilized for the detection and measurement of nonpolar, thermally stable, and volatile environmental contaminants (ECs). These contaminants may include flame retardants, filters, and specific pesticides. On the other hand, the utilization of liquid chromatography is implemented for the purpose of analyzing ECs that are nonvolatile, polar, and thermos-labile (Annamalai et al. 2022).

High-performance liquid chromatography (HPLC), or liquid chromatography (LC), is an analytical method used to analyze a high number of ECs in various substances and is often associated with gold. These ECs tend to be rather polar and inert. In a number of situations, ultra-high-performance liquid chromatography (UHPLC) has been used instead of standard HPLC. This is because UHPLC techniques allow for smaller particle size, resulting in higher resolution and shorter analytical times (Paliya et al. 2022). Particle sizes of 1.7 μm or smaller are often used in reversed-phase mode with C18 stationary phases for doing ultra-high-performance liquid chromatography (UHPLC) (Perez de Souza et al. 2021). Organic solvents like methanol or acetonitrile, which may also be acidified with formic acid or acetic acid, and acidified water with low concentrations of formic or acetic acid are often employed as mobile phases in the reversed-phase separation of ECs. Acidifying acetonitrile with formic or acetic acid makes it useful as an organic solvent (Kotnala et al. 2022).

3.2 Spectroscopic Methods and Metal Analysis

Heavy metal ions are one of the environmental contaminants (ECs) of concern. These ions are being gradually introduced into the ecosystem from a variety of sources. Scientists utilize inductively coupled plasma mass spectrometry (ICP-MS) to detect dangerous heavy metal pollution and nanoparticles in a broad range of sample types (Briffa et al. 2020). The long-term and irreversible impact of trace metals on environmental pollution is a matter of concern, as even low concentrations of these metals can have toxic effects. An invaluable tool for multi-element analysis, ICP-MS is widely acknowledged as a very sensitive approach for the measurement of trace metals in a wide range of elemental samples (Wilschefski and Baxter 2019). The aforementioned approach exhibits several benefits, particularly its potential for achieving high precision, its cost-effectiveness, and its capacity for conducting concurrent analysis of multiple elements and isotopes present in the periodic table. This type of analysis can be completed within a brief timeframe (Balaram et al. 2022).

3.3 Polymerase Chain Reaction

Analytical techniques in biotechnology play a crucial role in the process of bioremediation. Bioremediation involves the use of microorganisms to degrade or transform toxic pollutants into less harmful or non-toxic substances. Over time, biotechnology has developed various analytical techniques to monitor and enhance bioremediation processes. One such technique is the polymerase chain reaction (PCR).

PCR is a technology that amplifies specific DNA sequences and is utilized to differentiate between different microbial populations, assess microbial diversity, and identify biomarkers associated with bioremediation processes. This technique has been instrumental in quantifying microbial populations, including bacteria, archaea, and fungi, which are essential for effective bioremediation. PCR has also been employed to monitor the biodegradation of hydrocarbons such as polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons, enabling researchers to track the progress of remediation efforts (Bisht et al. 2015).

3.4 Biomonitoring

Biotechnology has developed various analytical techniques that enable the identification and quantification of harmful chemicals within living organisms. Biomonitoring is a process that utilizes analytical biotechnology techniques to assess and mitigate contaminants (Garg et al. 2022). In biomonitoring, biological indicators

are examined to identify changes in environmental quality resulting from pollution. One such technique is the enzyme-linked immunosorbent assay (ELISA).

ELISA is a powerful technique employed to identify and measure specific molecules in biological samples, including proteins and hormones. It has proven instrumental in the measurement and detection of pollutants such as polychlorinated biphenyls (PCBs), pesticides, and heavy metals (Zajicek et al. 2000). Additionally, ELISA has been utilized to identify biomarkers indicative of exposure to various toxins, providing crucial insights into the extent of environmental contamination. By employing ELISA and other biotechnology techniques, biomonitoring contributes to our understanding of the impact of contaminants and aids in developing strategies for their mitigation.

4 Removal or Treatment Method of Emerging Contaminants

Activated sludge and other traditional approaches of treating wastewater are designed to remove pathogens, sediments, and organic loadings from the water. The partial removal of emerging contaminants (ECs) can be achieved through various treatment processes in a wastewater treatment facility (Dubey et al. 2023). However, complete removal of ECs remains a challenging task due to their diverse nature, low concentration levels, and distinctive properties, as evidenced by previous studies. The detection of elevated levels of trace emerging contaminants (ECs) in water and wastewater streams has generated heightened scholarly attention worldwide regarding the exploration of strategies for the elimination or remediation of these micropollutants (Rout et al. 2021). This takes place due to the negative effect that EDCs have on the endocrine system. This issue has been extensively studied and has gained significant attention from the academic community (Kahn et al. 2020).

Remediation alternatives for eliminating or treating emerging contaminants (ECs) from water sources or wastewater include adsorption technology, membrane technology, biological treatment, and advanced oxidation method (Liang et al. 2014). The elimination and management of emerging contaminants (ECs) and their derivatives in aqueous solutions pose formidable challenges owing to their intricate nature in water matrices. Hence, it is imperative to consider the information pertaining to the aforementioned treatment modalities to enhance the existing techniques and devise novel, sophisticated approaches (Rodriguez-Narvaez et al. 2017).

4.1 Adsorption Technology

The term “adsorption” refers to the process by which chemicals are moved from one phase to another, specifically, from a liquid to a solid surface, or from a gas to a

liquid. Through the use of intermolecular interactions, adsorbents serve the objective of removing certain pollutants (adsorbate) from wastewater. This is accomplished by adsorbing the pollutants. Physisorption and chemisorption are two unique types of interaction that may be seen occurring between the solid surface and the adsorbates (Alaqarbeh 2021). The phenomenon commonly referred to as “physisorption” pertains to the interaction between molecules that is primarily governed by weak intermolecular forces, such as van der Waals forces. It is imperative to bear in mind that the outcomes of this particular procedure may be subject to modification or adjustment. Moreover, the phenomenon transpires at a temperature that is either below or in close proximity to the critical temperature of the adsorbate employed (Das et al. 2019). Physisorption involves the development of physical bonds between the adsorbates and the solid surface, while chemisorption involves the production of chemical bonds. In contrast, the adsorption process takes place solely as a monolayer, and the adsorbates exhibit a high degree of resistance to removal due to the strong interaction forces at play. The occurrence of both processes can be simultaneous or alternate, contingent upon the prevailing circumstances (Iqbal et al. 2022). In order to conduct research on the adsorption method, it is imperative to take into account various factors that can impact the adsorption process. The process of adsorption is influenced by a variety of factors, including (1) the surface area, (2) the initial concentration and characteristics of the adsorbate, (3) the pH of the solution, (4) the temperature, (5) the presence of interfering substances, and (6) the characteristics and quantity of the adsorbent. The surface area of the adsorbent is one of the most important aspects of the adsorption process.

The process of adsorption is deemed to be a straightforward and efficient technique; however, it necessitates substantial operational expenses linked to the production of marketable adsorbents such as activated carbons, minerals, and natural clay (Maryjoseph and Ketheesan 2020). Several scholars have endeavored to develop substitute adsorbents using agricultural and industrial by-products as a means of mitigating the expenses and ecological impacts associated with commercial adsorbents. This chapter highlights the utilization of non-traditional adsorbents, specifically agricultural residues, in lieu of conventional commercial adsorbents. Agricultural waste products have the potential to include a wide variety of useful components, including hemicellulose, starch, lipids, proteins, water, lignin, hydrocarbons, and simple sugars (Bhatnagar and Sillanpää 2010). Numerous prior research endeavors have demonstrated that agricultural substances comprising cellulose exhibit a notable propensity for sorbing diverse types of contaminants. It is possible to increase the potential of using them as adsorbents by modifying them chemically using a variety of agents, such as those that boost their chelating functional groups. This will allow the potential of employing them to increase. The processes of complexation, ion exchange, and hydrogen bonding are some of the most prevalent types of adsorption, and each of these three processes has been proposed by a broad variety of academic sources (Karić et al. 2022). Recent research has focused its attention on a broad variety of agricultural solid wastes, such as rice husk and straw, coconut husk and coir dust, wood sawdust and chips, fruit peels and stones, and many more. The primary objective of this study is to determine how

effective and cost-effective certain materials may be in the process of cleaning up water sources. In addition to rice husk, straw, and coconut husk, other possible components include coir dust, wood sawdust, wood chips, and fruit pulp (Goodman 2020).

A study was conducted to assess the efficacy of rice husk as an adsorbent for eliminating heavy metals from wastewater. According to the findings of the study, the inexpensive adsorbent was able to effectively remove Fe, Pb, and Ni concurrently across a concentration range of 20–60 mg/L. This phenomenon was observed irrespective of the initial solution's concentration. The objective of the study conducted by the author was to assess the impact of different concentrations of a particular kind of adsorbent on the removal of a variety of heavy metals (Uddin 2017). According to the results, there was a significant positive link between the amount of adsorbent that was used and the proportion of heavy metals that were removed. The study found that heavy metals were adsorbed to a maximum extent of 76–96% under ambient temperature conditions, with the optimal duration of contact being 2 h and a pH range of 6.0–7.0. Tetracycline, a frequently employed personal care and veterinary drug, is effectively eliminated by the rice husk adsorbent, as reported in the literature (Chakraborty et al. 2020). In the research, a comparison was made between modified rice husk adsorbents and untreated rice husk adsorbents. The results indicated a significant improvement in adsorption capacity of approximately 45.6% after 12 h and 17.2% in equilibrium time. According to their report, the modification of the adsorbent resulted in an increase in tetracycline adsorption primarily due to alterations in the O-containing groups. It was noticed that the changes had an impact on the π - π electron-donor-acceptor interactions that take place between the adsorbent and the tetracycline (You et al. 2021).

Research was conducted on the efficacy of wood chips and wood sawdust as economical adsorbents for the elimination of phenol and metals from aqueous solutions, respectively. The results of these studies indicate the potential of these materials for such applications. Previous research involved the alteration of wood chips through a process of blending with inorganic constituents, followed by pyrolysis and treatment with hydrochloric acid (Danish and Ahmad 2018). Compounds with names like ZnCW-1.0, ZnCW-1.5, FeZnCW-1.0, and FeZnCW-1.5 were produced when the ratio of inorganic to organic ingredients was either 1.0 or 1.5, respectively. When heated to a temperature of 25 °C, the maximum phenol adsorption capacities of ZnCW-1.0, ZnCW-1.5, and FeZnCW-1.0 activated carbons were measured to be 434.2, 667.9, 256.5, and 233.5 mg/g, respectively. According to the results, ZnCW-1.0 and ZnCW-1.5 did an excellent job of decontaminating simulated effluents that were contaminated with phenolic chemicals in an environment that was difficult to work in. Combining phenolic compounds allowed for the production of these by-products (Thue et al. 2016). The second study, on the other hand, evaluated the feasibility of using first-row transition metals (Co, Ni, Cu, and Zn) in the manufacture of activated carbons produced from wood biomass by utilizing microwave-assisted irradiation. In this study, the researchers found that the use of these metals was successful. During the impregnation procedure, the data demonstrated that the metals were successfully associated with the surface functional

Table 1 Agricultural by-products that may be used as adsorbents for the detoxification of different ECs (Liu et al. 2022)

Agricultural by-product	Emerging contaminant	Detoxification mechanism
Rice husk	Heavy metals	Adsorption and ion exchange
Coconut shell	Pharmaceuticals	Adsorption and surface complexation
Corn cob	Pesticides	Adsorption and physical entrapment
Sugarcane bagasse	Endocrine-disrupting compounds	Adsorption and chemical interactions
Olive pomace	Microplastics	Adsorption and physical entrapment
Coffee grounds	Personal care products	Adsorption and electrostatic interactions
Orange peel	Organic dyes	Adsorption and surface interactions
Grape pomace	Phenolic compounds	Adsorption and molecular interactions
Almond shell	Volatile organic compounds	Adsorption and pore-filling mechanisms
Wheat straw	Antibiotics	Adsorption and chemical interactions

groups of the wood biomass through ion exchange and surface complexation interaction. The samples that were generated with zinc chloride had the greatest sorption capacities compared to the other adsorbates that were tested. After that, samples were made by using copper chloride, cobalt chloride, and nickel chloride (Coultas et al. 2021).

Activated carbons obtained from peach stones were used as the adsorbent in order to remove caffeine, diclofenac, and carbamazepine from an aqueous solution. It has been shown that carbamazepine has a higher adsorption capacity, up to 335 mg/g, than both caffeine and diclofenac together (Torrellas et al. 2015). Improved adsorbents had greater carbamazepine adsorption capacity because they had hydrophobic qualities and water solubility features. The oxidation of activated carbon had a substantial impact on fixed-bed adsorption because it increased the hydrophilic character of the material, lowered the adsorption capacity, and altered both the breakthrough periods and the adsorption capacity values. The removal of methylene blue dye as well as platinum metal was achieved with the use of the same adsorbent (Tee et al. 2022).

An adsorption-based approach would surely be a feasible option for the treatment of wastewater that includes contaminants if it were both cost-effective and easily accessible. Adsorbents may be found in plenty. Because the effective removal of different contaminants is dependent on the features of both the adsorbent and the adsorbate, it is necessary to pick an appropriate adsorbent with great care in order to achieve the desired results. A number of environmental conditions and variables, such as the initial concentrations of the adsorbate and the adsorbent, the particle size of the adsorbent, the temperature, the pH, the selectivity, the ionic strength, the contact duration, and the rate of rotation, all play a role in determining the extent to which the adsorption process is effective (Sanganyado and Kajau 2022). Table 1

provides a comprehensive analysis of the many agricultural wastes that have the potential to be used as adsorbents when it comes to the remediation of a diverse assortment of emerging contaminants (ECs). Many ECs may be eliminated by processing this garbage.

4.2 *Membrane Technology*

The utilization of membrane technology presents a promising avenue for the effective elimination of micropollutants from water sources. The aforementioned method employs a number of other non-biological processes in addition to biological ones, such as reverse osmosis, ultrafiltration, and nanofiltration (Othman et al. 2021). A membrane bioreactor (MBR) is a device that combines the principles of membrane filtration (often microfiltration (MF) or ultrafiltration (UF) systems) with those of biological reactors for suspended growth. Membrane bioreactors (MBRs) are rapidly becoming the method of choice for creating reasonably clean water from wastewater by integrating membrane filtration with biological activities (Pervez et al. 2020).

High pressures across membranes are used in non-biological procedures including reverse osmosis (RO), nanofiltration (NF), microfiltration (MF), and ultrafiltration (UF) to remove impurities from water. The aforementioned technologies represent the prevailing membrane-based methods employed for the purpose of water purification (Zhang et al. 2022). The membranes undergo continuous upgrades or modifications to enhance their performance and utilization. As a result, membrane-based filtration techniques are well suited for the elimination of turbidity and microbiological impurities. Nevertheless, the full-scale utilization of this technology is still restricted by high operational expenses. Membranes are susceptible to fouling issues, which may lead to unforeseen interruptions in the processing of aqueous pollutants (Díez and Rosal 2020).

In a membrane treatment system operating at the pilot size, a comparative study of the efficacy of the removal of 27 different PPCPs was carried out. The effectiveness of MBR systems was measured against that of integrated membrane systems (MBR/RO or MBR/NF) for the purpose of this research. The use of integrated membrane systems has the ability to bring about the attainment of removal rates that are greater than 95% for the overwhelming majority of the compounds, as shown by the findings (Lin et al. 2022). After further research, it was shown that the MBR-RO system had greater results by removing 20 substances to levels that were undetectable, in contrast to the MBR/NF system, which eliminated just 13 compounds. According to the findings of a research project, using concentration polarization and surfactant-enhanced surface polymerization allowed RO membrane elements to demonstrate greater rejection of various pharmaceutically active chemicals (PhACs) and EDCs (Aziz and Kasongo 2021). After performing tests using RO membranes that had been changed by grafting poly (glycidyl methacrylate), the researchers compared the findings of those experiments to brackish water RO membranes that are currently available for purchase on the market. This was

done in order to determine whether or not the modified membranes performed better than the standard membranes. According to one of the results, the modified membrane has shown better rejection rates that were on a par with those of the membrane that is already on the market. It is important to note, however, that none of the membranes demonstrated a total rejection of the chemicals that were evaluated (Yamamoto 2022).

4.3 *Biological Treatment*

Biological therapy, especially the secondary treatment stage, is the primary strategy for removing ECs, and several studies have shown the efficacy of biodegradation and adsorption in this regard. This was shown when the ECs were removed from the equation. The activated sludge process (ASP) and the trickling filter (TF) are the two kinds of biological treatment procedures that are used the most often. The participation of aerobic bacteria and other microorganisms, which help in the oxidation or absorption of organic molecules into cellular structures, is one of the distinguishing properties of this process (Ahmed et al. 2021). The presence of an adequate oxygen supply is a prerequisite for the bacterial treatment process. The TF system is characterized by a stationary surface that harbors a significant concentration of microorganisms, whereas the ASP system is distinguished by the coalescence of a substantial population of microorganisms with wastewater. Concentrated microbial biomass is often separated from the aqueous phase by a subsequent sedimentation stage after the TF or ASP procedure (Skouteris et al. 2020).

The treatment of wastewater in both industrial and residential settings is one of the uses of ASP which is now among the most common and widely used applications of this technology. Both the continual cycling of biomass into the aeration tank and the input of air into the reactor are components of the activated sludge system. Activated sludge is used to treat wastewater (Jafarinejad 2017). An activated sludge system comprises of three primary components: (1) a reactor, which employs aerators to maintain the suspension of microorganisms throughout the treatment process; (2) a separator system, which enables solids to settle out in a sedimentation tank; and (3) a recycling system, which transports settled solids back to the reactor. There is a specific role for each of these major factors in the healing process (Sathe et al. 2022).

The utilization of ASP is associated with various advantages and disadvantages, contingent upon its specific type. Certain types of ASP offer advantages such as diminished levels of ammonia, minimal spatial requirements, and absence of malodorous emissions. Aeration tanks necessitate a substantial amount of energy to function, and the modifications in effluent characteristics are highly inflexible. An earlier study found that ASP might be affected by factors such as oxygen concentration, temperature, treated wastewater characteristics, foam-producing detergents, and return rate (Skouteris et al. 2020). The efficacy of ASP in eliminating steroid estrogens in WWTPs was superior (achieving up to 100% removal) in comparison to

that of the trickling filter (which achieved up to 75% removal). In this investigation, the results suggest that the oxidation ditch approach outperformed the A/O and A2/O procedures by a little margin when it came to getting rid of tyrosine-like molecules and tryptophan-like fluorescent chemicals, respectively (Deb and Nag 2022). The advanced oxidation method is a technique that is used in a variety of sectors for the deterioration of organic molecules. Its creation dates back to the 1970s. It is possible to effectively break down endocrine-disrupting chemicals (also known as EDCs) by employing a range of advanced oxidation methods, such as ozone, O_3/H_2O_2 , H_2O_2/UV , Fenton, ultrasonic, photocatalytic, and electrochemical oxidation. These are just a few examples. Other advanced oxidation techniques include electrochemical oxidation and photocatalytic oxidation (Chang et al. 2018).

5 Biotechnological Methods for Removal of Emerging Contaminants

Biotechnological technologies have emerged as potentially useful alternatives for the removal of newly discovered pollutants from a variety of environmental matrices, giving solutions that are both sustainable and effective (Ezeonu et al. 2012). These methods leverage the power of biological systems, such as microorganisms, enzymes, plants, and bio-electrochemical systems, to degrade, transform, or immobilize contaminants, mitigating their potential adverse effects (Hao et al. 2020). Following are some key biotechnological methods employed for the removal of emerging contaminants:

5.1 Biodegradation

Microorganisms, including bacteria, fungi, and algae, are capable of degrading a wide range of emerging contaminants through enzymatic activities (Bala et al. 2022). Biodegradation processes can break down complex organic compounds into simpler and less toxic forms, reducing their environmental persistence (Bala et al. 2022). Genetic engineering techniques have been employed to enhance the capacity of microorganisms to degrade specific pollutants selectively (Rafeeq et al. 2023).

Various types of microorganisms play a critical role in pollution remediation. For example, fungi and bacteria are essential in soil bioremediation, which involves the breakdown of organic substances like hydrocarbons, insecticides, and heavy metals (Deshmukh et al. 2016). Microorganisms employ six primary mechanisms—namely, aerobic biodegradation, anaerobic biodegradation, co-metabolism, biotransformation, and biodegradation of hazardous chemicals—to degrade these compounds (Seo et al. 2009). The specific mechanism(s) employed depend on the type

and concentration of contaminants present in the soil, with these processes operating in different soil environments. Adding organic amendments such as compost, humic substances, and manure to the soil enhances microbial biomass and accelerates the biodegradation of organic pollutants (Barthod et al. 2018). Emerging contaminants (ECs) are mostly eliminated by the processes of biodegradation and adsorption that take place during biological therapy, also known as secondary treatment. This has been confirmed by a large number of studies (Sutherland and Ralph 2019). Microorganisms, including bacteria, fungi, and algae, utilize enzymatic processes to break down a wide range of emerging pollutants. Complex organic compounds can be transformed into smaller, less harmful forms through biodegradation, reducing their environmental persistence.

5.1.1 Oxygen-Dependent Microbial Degradation

In the presence of oxygen, microorganisms engage in a process called aerobic biodegradation, utilizing oxygen as the primary electron acceptor to break down organic pollutants. Bacteria involved in this process utilize organic compounds as an energy source, resulting in the production of carbon dioxide and water as by-products (Bala et al. 2022). Due to its rapid pollutant degradation rate and low generation of hazardous by-products, aerobic microbial degradation is extensively employed in soil bioremediation.

5.1.2 Oxygen-Deprived Microbial Degradation

In oxygen-depleted environments, bacteria employ alternative electron acceptors such as nitrate, sulfate, and carbon dioxide to carry out anaerobic biodegradation. Depending on the specific electron acceptor present, organic pollutants undergo transformation into methane, carbon dioxide, and other chemical compounds in anaerobic settings (Gupta et al. 2017).

The breakdown of mono- and polycyclic aromatic hydrocarbons in anaerobic settings has been the subject of a significant amount of study, which has been carried out with the use of microcosms and enrichment cultures under a variety of redox circumstances. The transformation of aromatic hydrocarbons like BTEX, phenols, naphthalene, and phenanthrene often begins with one of these four processes. According to Funk et al. (2015), one of the mechanisms includes the addition of fumarate, which is then catalyzed by the activity of benzyl succinate synthase. According to Chakraborty et al. (2005), fumarate may be directly added to toluene and ethylbenzene, while benzene and naphthalene must first be methylated by a methyl transferase. Toluene and ethylbenzene can undergo fumarate addition directly. However, Musat et al. (2009) found that a marine sulfate-reducing enrichment culture that was grown on naphthalene required adaptation in order to utilize 2-methylnaphthalene. This culture also lacked the expression of a 2-methylnaphthalene-activating enzyme prior to the adaptation process, which suggests that

methylation is not the activation mechanism for naphthalene in this culture. The process of carboxylation, which is catalyzed by a carboxylase, is yet another mechanism (Erb 2011). According to Payer et al.'s (2019) research, this carboxylation has been shown happening directly with benzene, naphthalene, and phenanthrene. According to Ghattas et al. (2017), there have been instances in which a dehydrogenase has been shown to hydroxylate benzene or naphthalene before the carboxylation step takes place. However, Meckenstock et al. (2000) discovered that a sulfate-reducing enrichment culture that was generated from an aquifer was unable to use naphthol. Because of this discovery, they were able to rule out hydroxylation as the activation mechanism in this culture. In addition, a number of studies argue that benzene is hydroxylated abiotically to produce phenol. This suggests that the direct carboxylation of the benzene ring to produce benzoate may be the more feasible activation option under methanogenic circumstances that include the reduction of sulfate and iron (Laczi et al. 2020).

5.1.3 Co-metabolism

Co-metabolism is a microbiological process where bacteria modify a substance that is not their primary metabolic by-product but rather a secondary compound. An example of co-metabolism is the breakdown of polychlorinated biphenyls (PCBs) by bacteria that utilize biphenyl as their primary carbon and energy source (Sharma et al. 2018). Enzymes produced by these bacteria during the process facilitate the cleavage of PCB bonds, leading to the formation of less harmful byproducts.

5.2 Biotransformation

During biotransformation, pollutants undergo conversion into intermediate compounds that can be easily metabolized by other environmental species. For instance, bacteria can transform polycyclic aromatic hydrocarbons (PAHs) into intermediates that can be further broken down by fungi in the soil environment (Wang et al. 2018). *Cycloclasticus* sp. strain P1, obtained from the depths of the ocean floor, is a bacterium capable of breaking down naphthalene, phenanthrene, pyrene, and other aromatic hydrocarbons (Wang et al. 2018). In this study, the complete genome of *Cycloclasticus* sp. was examined, revealing the presence of six ring-hydroxylating dioxygenases (RHDs).

5.3 Biofilms

According to Obotey Ezugbe and Rathilal's research from 2020, membrane technology, which includes both biological (membrane bioreactors) and non-biological

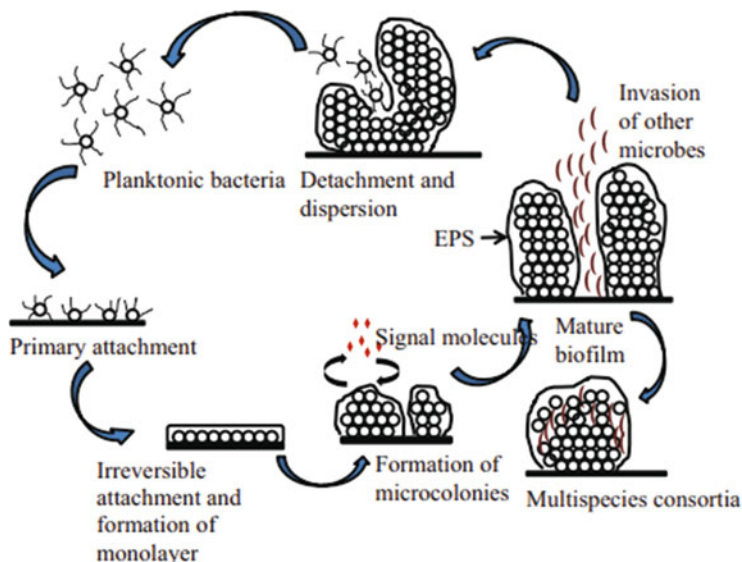


Fig. 2 Formation of microbial biofilm

processes (reverse osmosis, ultrafiltration, and nanofiltration), has the potential to remove micropollutants from water in an efficient manner. Membrane bioreactors, often known as MBRs, are hybrid devices that combine membrane-based filtering procedures, such as microfiltration or ultrafiltration, with biological reactors that support suspended growth. MBRs have gained prominence as one of the most effective and widely used ways for obtaining purified water from wastewater. Non-biological processes, such as reverse osmosis (RO), nanofiltration (NF), microfiltration (MF), or ultrafiltration (UF), utilize high pressure to filter contaminants from water. These membrane technologies are commonly employed for water purification (Cevallos-Mendoza et al. 2022). However, operational costs and fouling issues remain challenges to their widespread implementation. Fouling problems can lead to unexpected interruptions in the treatment of aqueous contaminants.

Biofilm systems represent an advanced technique used in biofiltration for wastewater treatment (Pachaiappan et al. 2022). In this system, suspended growth reactors incorporate solid media that serve as surfaces for biofilms to develop. The enhanced microbial concentration resulting from the solid media facilitates pollutant degradation. Additionally, the biofilm system encompasses other processes such as biomineralization, biodegradation, bioaccumulation, and sorption. The microbes within the biofilm not only break down various contaminants but also degrade trapped pathogens in the wastewater (Pachaiappan et al. 2022). Following biofiltration, the treated water can be used for recreational purposes. Microbial biofilm technology forms the basis of this water treatment method (Fig. 2).

5.4 *Bio-adsorption*

Biological materials, such as activated carbon, bacterial biomass, and algae, possess high adsorption capacities for various emerging contaminants (Almeida-Naranjo et al. 2023). These materials can sequester contaminants onto their surfaces through physical and chemical interactions, effectively removing them from the environment. Surface modifications and functionalization can improve their adsorption properties and selectivity.

5.5 *Enzymatic Degradation*

Enzymes derived from microorganisms or plants can be used to catalyze the breakdown of emerging contaminants (Sondhi 2019). Enzymatic degradation offers high specificity and efficiency in the transformation of target compounds. Immobilization techniques can enhance enzyme stability and reusability, enabling their practical application in treatment processes (Sondhi et al. 2018).

5.6 *Phytoremediation*

Certain plant species have the ability to accumulate and metabolize emerging contaminants. Phytoremediation utilizes plants' natural mechanisms to uptake, transform, and store contaminants in their tissues. Plants can be cultivated in constructed wetlands or hydroponic systems to remediate contaminated water sources, providing an aesthetically pleasing and eco-friendly approach.

In nature, plants can both accumulate and exclude heavy metals. They can biodegrade or transform heavy metals into inert forms within their tissues while also preventing the metals from being stored within their tissues (Jonnalagadda and Nenzou 1997). The absorption of heavy metals involves an intriguing role played by the ion uptake system through proton pumps (ATPases). Phytoremediation employs three main procedures: phytovolatilization, phyto-stabilization, and phytoextraction (Table 2) (Gupta et al. 2018). These methods harness plants' natural mechanisms to uptake, transform, and store contaminants in their tissues. Constructed wetlands or hydroponic systems can be used to cultivate plants for phytoremediation of contaminated water sources, providing an aesthetically pleasing and environmentally friendly approach. However, while phytoremediation technologies offer cost-effective, visually appealing, and environmentally benign ways to contain heavy metals, the process itself is time-consuming and influenced by various environmental and external factors (Ghosh and Singh 2005).

Table 2 Processes for bioremediation of xenobiotics and heavy metals

S. no.	Mechanism	Process	Pollutants	Plants	References
1	Phyto-volatilization	The root system is responsible for the process of absorbing contaminants from the soil, which are then converted into a volatile form and discharged into the atmosphere when the transformation has taken place	Hg	<i>Chara canescens</i> (musk grass) and <i>Arabidopsis thaliana</i>	Ghosh and Singh (2005)
2	Phytoextraction	The translocation of pollutants from the soil to the plants occurs as the roots absorb and accumulate them, acting as hyperaccumulators. Once the pollutants have reached their saturation limit, the plants are cut and disposed of	Pb, As	<i>Glycine max L. Pteris vittata</i>	Aransiola et al. (2013)
3	Phytodegradation/ phyto-transformation	After plants have taken in pollutants from the soil, those pollutants are degraded and mineralized as a by-product of the metabolic activities of those plants	Total petroleum carbon (TPH)	<i>Scirpus grossus</i>	Al-Baldawi et al. (2015)
4	Phyto-stimulation/ rhizodegradation	Contaminants are degraded through microbial activity, utilizing the process of phytoremediation, which enables the degradation of various types of xenobiotics	Biodiesel, phenanthrene, and pyrene	<i>Pisum sativum, Kandelia candel</i>	Zhang et al. (2011)
5	Phyto-stabilization	The process involves the sequestration of pollutants in the soil through absorption and precipitation, effectively immobilizing them	As	<i>Panicum sativum</i>	Jonnalagadda and Nenzou (1997)
6	Rhizoremediation	Plant roots and the bacteria in the soil form a mutually beneficial partnership in the rhizosphere during the process of rhizoremediation. Through root exudates, plants are able to provide essential nutrients to bacteria in this interaction. In exchange, the plants get protection against diseases and support in the process of nitrogen fixation	Cr, lindane, PHCs	<i>Helianthus annuus, Withania somnifera, Lolium perenne</i>	Gupta et al. (2018)

5.7 Bio-electrochemical Systems

These systems integrate microbial metabolism with electrochemical processes for contaminant removal. Microorganisms act as catalysts in the bio-electrochemical reactions, facilitating the degradation or transformation of emerging contaminants (Rafieenia et al. 2022). Bio-electrochemical systems, such as microbial fuel cells and microbial electrolysis cells, offer the advantages of energy generation and simultaneous pollutant removal.

5.8 Nanocellulose

Nanotechnological methods involving cellulose nanoparticles have been developed for the detection of hazardous substances in the environment, as illustrated in Fig. 3. Biodegradable NC exhibits diverse forms, including templates, solid fibers, membranes, films, and three-dimensional networks such as aerogels or sponges, which possess a large surface area with low density and heat transport (Ahankari et al. 2021). These cellulose nanoparticles derived from various sources like sludge, biowaste, plants, and bacteria can be effectively employed for pollution remediation, targeting the bioremediation of organic pollutants, heavy metals, and various chemical dyes in the environment.

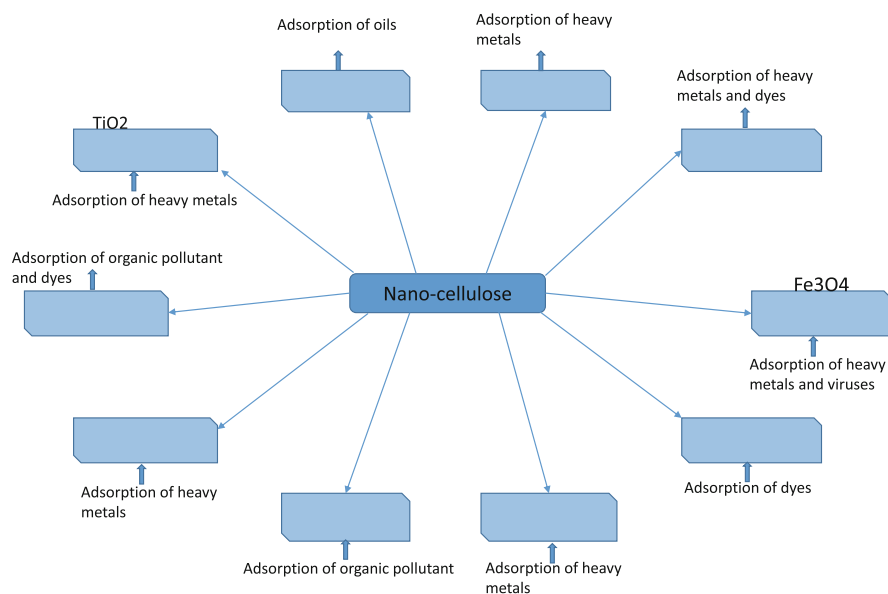


Fig. 3 Nanocellulose-based bio-adsorption for remediation of emerging contaminants

Biotechnological methods for the removal of emerging contaminants hold immense potential for sustainable and effective remediation strategies. However, challenges such as optimization of process conditions, scalability, cost-effectiveness, and long-term effects on ecosystems need to be addressed for their widespread implementation. Further research, technological advancements, and interdisciplinary collaborations are essential to harness the full potential of biotechnology in tackling emerging contaminant issues and ensuring the protection of human health and the environment.

6 Conclusion

Emerging contaminants refer to synthetic toxic compounds that are released into wastewater. This chapter encompasses an analysis of the origins of emerging contaminants, their potential adverse effects on living organisms, and the methods employed for their remediation. ECs are primarily derived from pharmaceuticals, personal care products, and fertilizers. Even at low concentrations, the presence of these substances can have deleterious effects on both human health and marine organisms. Conventional methods of wastewater treatment are incapable of effectively eliminating them. The discourse has encompassed a range of treatment methodologies, including membrane technology, coagulation-flocculation, solvent extraction, adsorption, advanced oxidation processes, and nanotechnology. These methodologies possess both benefits and constraints. Hybrid systems have been determined to be more efficacious in the elimination of EC than singular techniques. Nevertheless, they are confronted with challenges pertaining to temporal, energetic, and financial resources. Nanotechnology presents a promising approach to surmounting these limitations. Therefore, it is imperative to conduct extensive research on wastewater treatment technologies that are both technically and economically viable in order to achieve thorough and effective elimination of emerging contaminants (ECs) from polluted water.

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Microbial Electro-deionisation Technologies for Emerging Pollutants



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Abstract Environmental pollution has developed into a global issue during the past few decades. Rampant human activity combined with industrial effluents has led to the rise of various inorganic and organic pollutants in the environment which is of deep concern. These problems require newer and more efficient cost-effective strategies in order to get rid of these emerging pollutants. In this regard, bio-electrochemical systems (BESs) have been instrumental in reducing the levels of emerging organic and inorganic pollutants and furthermore converting them into value-added products. They can be utilised for simultaneous electricity generation and wastewater treatment. Microbial electro-deionisation cells (MECs), a subgroup of BESs, have been used for the removal of emerging pollutants as well as the production of value-added products. The practicality of the system is still a thing of research, and it has various issues with scale-up. Nevertheless, MECs promise to become a sustainable and cost-effective method for the removal of pollutants. The book chapter attempts to throw some light on the various aspects of MECs with regard to sustainable wastewater treatment and value-added product generation. The technology concept, working principles and setups, membranes, and microorganisms involved have been discussed in this chapter. Furthermore, the challenges and future perspectives of the technology have been discussed in detail. The aim of this book chapter is to familiarise the researchers with the recent advances in technology with regard to MECs.

Keywords Bio-electrochemical systems · Pollutants · Wastewater · Electro-deionisation · Sustainable

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1 Introduction

As a consequence of rapid industrialisation and anthropogenic activities across the globe, the problem of water pollution has grown significantly (Gao and Wu 2018; Boretti 2019; Alkhadra et al. 2022). Water pollution refers to the contamination of water bodies such as rivers, lakes, oceans, and groundwater. It occurs when harmful substances, including chemical, biological, and physical agents, are introduced into water sources, making them unfit for human use or damaging the environment (Waheed et al. 2021). Water pollution has numerous negative impacts on human health, aquatic life, and the environment. Exposure to contaminated water can cause illnesses such as diarrhoea, cholera, typhoid fever, and skin infections. Polluted water can also negatively affect aquatic ecosystems, leading to a decline in the populations of aquatic life, the loss of biodiversity, and the degradation of habitats (Mishra et al. 2021). Additionally, water pollution can lead to the depletion of valuable resources such as freshwater, which can worsen drought conditions. These problems lead to limited access to safe drinking water (Darre and Toor 2018). Sources of water pollution can be natural or anthropogenic. Natural sources include sedimentation, erosion, and volcanic eruptions, while anthropogenic sources include industrial discharges, agricultural runoff, sewage treatment plants, and storm water runoff from urban areas. Pollutants can come in many forms, including chemicals from pesticides and fertilisers, heavy metals from industrial waste, and bacteria and viruses from untreated sewage (Shindhal et al. 2021). To address water pollution, a range of management strategies can be employed, including regulations and policies to limit pollution discharge, wastewater treatment plants, and the use of best management practices in agricultural and industrial practices. Individuals can also take steps to reduce their impact on water quality by properly disposing of hazardous materials, conserving water, and reducing their use of single-use plastics (Azimi et al. 2017).

Water can have various types of pollutants such as organic pollutants, inorganic pollutants, biological pollutants, nutritional compounds, and sediments. Organic pollutants mainly consist of chemicals that contain carbon and other elements such as sulphur, nitrogen, and chlorine as seen in pesticides, petroleum products, and other industrial solvents (Morin-Crini et al. 2022). When it comes to inorganic pollutants it is mostly toxic metals such as lead, mercury, arsenic, and cadmium which are harmful to live organisms (Azimi et al. 2017). Microbial contamination is the main cause of biological water pollution and is caused mainly due to organisms such as bacteria, viruses, and parasites. Nutritional compounds are essential for growing plants and animals but in excess can cause environmental problems such as eutrophication and algal blooms (Riza et al. 2023). The various sources of water pollution are elucidated in Table 1.

The polluted water that has been generated from various sources as mentioned above is not suitable for human use and hence is termed wastewater. As global temperatures are rising and groundwater reserves are depleting at a rapid scale and water scarcity is becoming a pressing issue in many parts of the world, there is an

Table 1 Different sources of water pollution

Type of pollutant	Cause	Effect	Source
Sediments	Erosion of soil	Decreased water quality	Natural
Algal blooms	Excessive growth of algae	Decreased oxygen levels	
Organic matter	Dead and decaying plant and animal bodies in the water	Reduced oxygen levels and growth of harmful bacteria	
Excess nutrients	Animal waste	Increased nitrogen and phosphorous levels	
Pesticides and fertilisers	Agricultural runoff	Toxicity in water bodies	Anthropogenic
Heavy metals, organic compounds, and radioactive elements	Industrial effluents	Chemical toxicity in water bodies	
Sewage waste	Untreated sewage and wastewater from households and industries	Contain harmful bacteria and viruses that cause diseases	
Petroleum products	Oil spills and chemical effluents from petroleum industries	Harmful to aquatic habitats, long-term persistence	
Plastic waste	Plastic waste disposal in water bodies	Ingestion of microplastics by aquatic life, microplastics entering the food chain	

immediate need for the treatment of wastewater so that the wastewater can be reused (Alkhadra et al. 2022). The conventional methods of wastewater treatment include primary, secondary, and tertiary treatment methods. This method involves a pipeline in which the large objects are removed first and the organic matter is broken down with the help of bacteria. The final step involves the filtration and disinfection of water (Rathi et al. 2022). The conventional methods of treating wastewater are time- and resource-consuming and are not stringent with respect to the removal of pollutants. Therefore, the focus has been shifted towards advanced technologies that are more stringent and cost-effective. Research is being done on developing novel strategies for wastewater treatment in order to make it more sustainable and economically feasible (Mistry et al. 2023).

Microbial electro-deionisation (MEDI) is a novel wastewater treatment technology that combines microbial electrochemistry and electrochemical deionisation. This technology is a type of microbial electrochemical cell also known as MEC for short. At the core of the MEDI system is a specialised MEC, which generates electricity while removing the pollutants from the wastewater (Mirza et al. 2022). An MEC is a modified microbial fuel cell. Microbial fuel cells are bio-electrochemical systems that may produce electricity with the assistance of bacteria. MFCs have an anode and a cathode, just like any other electrochemical cell (Varanasi et al. 2015).

The circuit is created by the movement of electrons from the anode to the cathode by means of which power is produced. The substrate, which is found in the anodic chamber, is used by the microorganisms to grow and provide the electrode with electrons. The only difference between a typical MFC and MEC is that the MEC requires an additional power supply of about 0.2–0.8 V to transfer the electrons from the anode to the cathode as the cathode possesses a higher potential than the anode (Pant et al. 2012).

2 Principle of MEC

2.1 Design and Operation

A microbial fuel cell is composed of various parts which include an anode and a cathode chamber. These two chambers are separated by a selectively permeable membrane which helps in the facilitation of cations or a cation-exchange membrane. An external wire connects the chambers which helps in the flow of electrons and completes the circuit, thereby generating electricity. During operation, anaerobic or aerobic conditions can be maintained in the anode or cathode (Mirza et al. 2022). The source of electrons in the MFCs is in the form of a microorganism which acts as an electron donor, thereby facilitating the oxidation of the substrate. These microorganisms generally tend to be exoelectrogenic in nature. In the case of MECs, they can be operated with or without mediators. MECs operated with mediators utilise specific bacteria which can donate electrons. Non-mediated MECs utilise electrogenic bacteria present in an external source such as sludge (Khan et al. 2023). The schematic diagram of an MEC is shown in Fig. 1. In addition to that the MEC consists of a central chamber in between the anode and cathode chambers. This middle compartment is where the treatment of water takes place. This compartment will have two kinds of membranes such as an anion-exchange membrane and a cation-exchange membrane on either side of the central compartment. These membranes are porous and play a vital role in the removal of salts and pollutants.

The working principle of the MEC in treating wastewater is inspired by the design of microbial desalination cells. A schematic of the process is illustrated in Fig. 2. Microbial desalination is another variant of MFC that is used for desalinating salt water to produce pure water. The basic design is the same as that of MFC with anode and cathode chambers with an external wire. There is a desalination chamber in between the anode and cathode chambers. There is an anion-exchange membrane and a cation-exchange membrane on either side of the desalinating chamber. This middle chamber is responsible for the removal of salts from the salt water. The anions that are present in the salt water such as Cl^- migrate into the anode chamber through the anion-exchange membrane (AEM), and the cations such as Na^+ and Ca^{2+} migrate into the cathode chamber through the cation-exchange membrane (Saeed et al. 2015). In the case of MFCs, the external wire attached to the circuit serves as a connection between the anode and cathode where electrodes move from

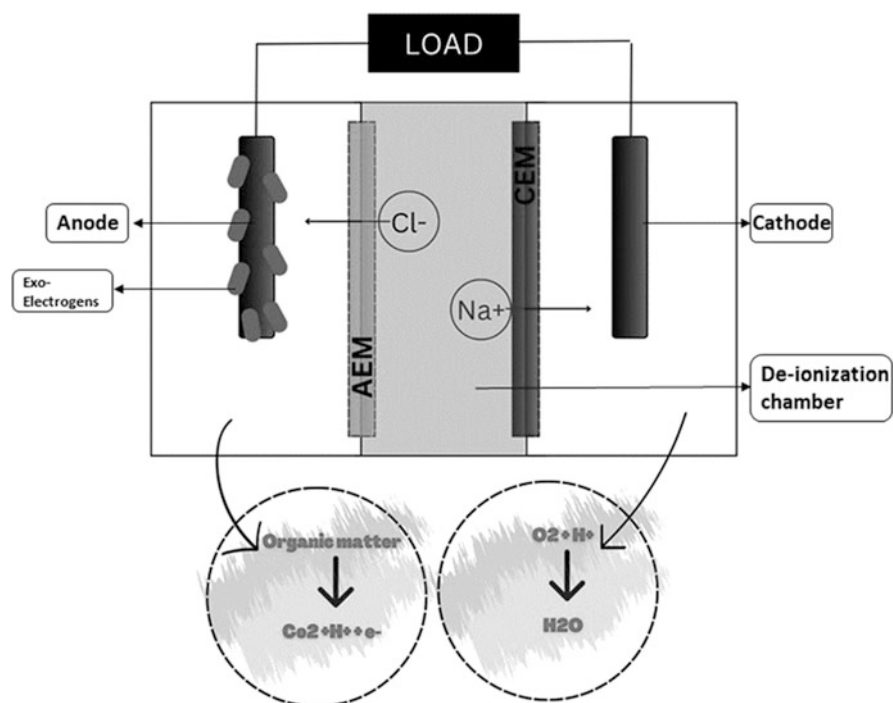
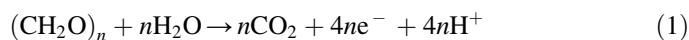


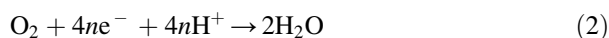
Fig. 1 Design of a microbial electro-deionisation cell

the cathode to the anode. Modern configurations of MFCs utilise air cathodes, i.e. cathodes that are exposed to air (You et al. 2022). A potential difference is generated between the two electrode chambers which finally leads to generation of electricity (Khan et al. 2023). The reactions occurring at the cathode and anode are given by the following equations:

At the anode



At the cathode



Microorganisms (generally bacteria) form a thick coating of biomass on the anode which is called as a biofilm. The biofilm is very important in the context of bio-electrochemical systems. The bacteria utilise organic matter releasing CO_2 and H^+ ions into the anolyte. The potential difference generated in the anolyte results in the migration of anions from the middle chamber towards the anode through the anion-exchange membrane in order to balance the electrostatic difference. The cations migrate towards the cathode through the cation-exchange membrane, thereby

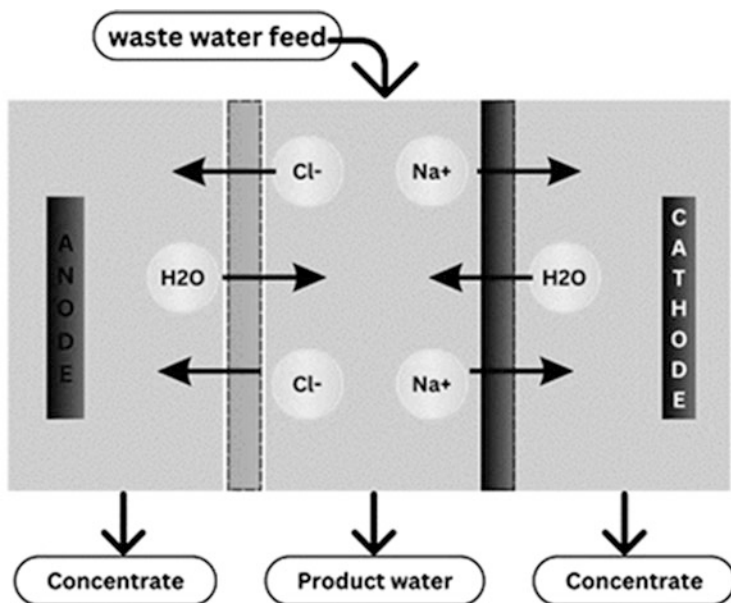


Fig. 2 Working principle of wastewater treatment with MECs

enabling excessive pollutant removal and higher energy generation than required for operation (Nguyen and Babel 2022).

2.2 Membranes Used in BES

Membranes play an important role in the entire design of bio-electrochemical systems. Membranes are mainly used in the two-chambered MFCs. Their function is to physically separate the anode and the cathode compartments in order to prevent direct contact between the two electrodes which would lead to a short circuit. The membrane is also necessary for the selective transport of ions between the compartments. This also prevents the crossover of unwanted substances between the two compartments (Ogungbemi et al. 2019). The regulation of the pH and the redox potential is also maintained by the membranes in the microbial electrochemical systems. The membranes used in BES must satisfy certain criteria such as high ionic conductivity, mechanical stability, low substrate crossover, cost-effective design, and high chemical stability (Dharmalingam et al. 2018). A glimpse of the types of membranes utilised for bio-electrochemical systems is provided in Table 2.

There have been many membranes that were used in BES for different functions. The two most commonly used membrane types are the proton exchange membranes and the anion-exchange membranes. PEM is mainly useful in transporting the protons generated as part of microbial degradation to the cathode. Nafion™ is a

Table 2 Types of membranes used in bio-electrochemical systems

Type of membrane	Function
Anion-exchange membrane	Transport of anions across the membranes and blocking of cations
Cation-exchange membrane	Transport of cations across the membranes and blocking of anions
Proton exchange membrane	Transport of protons to the cathode
Porous membrane	Allows the transfer of ions based on the porosity
Bipolar membrane	Transport H^+ and OH^- simultaneously for balancing the load
Ultrafiltration membrane	Separate pollutants in wastewater based on their molecular weights
Microfiltration membrane	Function as sludge separators for wastewater treatment
Ceramic membranes	Power generation in high-temperature fuel cells

popular membrane used in a variety of BESs for its excellent ionic conductivity. Ion exchange membranes (IEMs) are divided into two groups based on the type of ion conduction occurring in the membrane matrix—cation-exchange membranes and anion-exchange membranes. The cation-exchange membrane has fixed negative charges and allows positive ions to pass through, whereas the anion-exchange membrane has fixed positive charges and allows negative ions to pass through. These IEMs play an important role in pollutant removal using MEC technology.

Apart from these two types of membranes, there are many other types of membranes used in BES for other purposes. These include—porous membranes, bipolar membranes, ultrafiltration membranes, and ceramic membranes. Porous membranes that include glass wool membranes are cheaper in terms of cost when compared to other membranes. Single-chamber MFCs have been reported to use these membranes in the place of expensive PEM to make the design more cost-effective for wastewater treatment and power generation. Ultrafiltration membranes are widely associated with wastewater treatment. They separate particulate contaminants using their different molecular weights. Ultrafiltration membranes are also used to separate fluid between the anode and cathode. Microfiltration membranes are extensively used in wastewater treatment for sludge separation. These membranes are cheaper when compared to classical anion-exchange membranes and are specifically used for wastewater treatment (Dharmalingam et al. 2018).

Studies have been performed in order to estimate the efficiency of anion and cation-exchange membranes for pollutant remediation (by measuring the amount of COD reduced) as well as the energy produced (in the form of coulombic efficiency [CE]). The results elucidated a very slight difference where CEM performed better with 80% COD reduction and 42% CE, whereas the AEM had a 77% COD reduction with 40% CE. Furthermore, a batch process for removal of salts from water estimated a removal of COD with initial salinity of 10 g L^{-1} (Suresh et al. 2021). The removal of total dissolved solids (TDS) was also estimated using both types of membranes (Salman and Ismail 2020). The pH of the system generally varies with changes in salinity (Babanova et al. 2021). The proximity of the membrane with reference to its corresponding electrode is critical for the removal of TDS. It was observed that when the AEM was near the anode and the CEM near the cathode, the

TDS removal was estimated as 50%. Under circumstances where the AEM was in close proximity to the cathode and the CEM near the anode, TDS removal reduced to around 46%, a slight decrease in the process efficiency of the system. However, COD removal remained a constant at 91% for both of the configurations (Davis et al. 2013). In the context of bio-electrochemical systems, in addition to COD removal and lowering of TDS, membranes can be utilised to produce value-added products which are essential for the industry. For instance, with a high flow rate and membrane gaps of 1 mm, formic acid (CH_2O_2) can be produced as a by-product of the process (Lu et al. 2017).

Advances in nanotechnology have provided tools for generation of modified membranes with enhanced capacities. Incorporation of silver nanoparticles into carbon nanotube membranes can help improve the quality of the process by preventing microbial passage through the membrane, thereby preventing membrane fouling (Ma and Hou 2019). Modified membranes can also enhance the performance of the process. Studies on sulfonation of CEM have shown to enhance the process efficiency (Ihsanullah et al. 2015; Ghasemi et al. 2016).

Various challenges exist for continuous use and recycling of the membranes. The major problems associated with membranes are membrane fouling with undesired microorganisms which decrease the overall process efficiency. The biofilms formed present a great variety of genetic variation which could interfere with the regular functioning of the system. In addition to exoelectrogenic bacteria, the biofilm can be contaminated with sulphur reducing bacteria. *Pseudomonas* and *Desulfovibrio* can generate H_2S in the system, thereby degrading the membrane. Along with this problem, very specific types of membranes are utilised for reduction of MDC in the treatment and reduction of salinity which poses a specific challenge to the process. In order to provide an efficient solution to the process effectivity, these factors have to be taken into consideration (Bakonyi et al. 2018).

3 Microbial Communities in MEC

One of the major aspects of the MEC is the usage of microbes in operation. Unlike a normal electrochemical cell, the electrons that are required for the generation of electricity are provided by the microorganisms in any of the microbial electrochemical systems (Singh et al. 2022). The same is the case with MEC. The microbes present in an anodic chamber provide the electrons that are transferred to the anode. From the anode, the electrons are carried by a wire to the cathode forming a circuit through which electricity is generated (Logan et al. 2019). The microbes present in the anodic chamber do this by a unique mechanism known as extracellular electron transfer (EET) and the bacteria that are capable of doing this are termed under the category known as exoelectrogens or electroactive bacteria. Normally electron transport is a universal process seen in prokaryotes and eukaryotes where the electrons that have been generated by the oxidation of substrates are transferred to the electron acceptors present in the cell through a series of steps. This process is

involved in the generation of energy in the form of ATP. The steps between the release of electrons from the donor and the transfer of those electrons to the acceptor involve a series of redox reactions mediated by various molecules. These molecules act as electron carriers. Oxygen acts as the electron acceptor in the majority of organisms (Logan 2009; Slate et al. 2019).

In the case of electroactivity shown by the exoelectrogens, the bacteria possess an extraordinary ability to transfer the electrons extracellularly to an acceptor that is present outside the cell. In other words, the bacteria release the electrons outside their cell into their vicinity. This transfer of electrons happens in two ways. One is the direct transfer known as direct EET in which there is direct contact between the donor and the acceptor. There are no carrier molecules involved here. Another way by which the transfer happens is the indirect way, where there is no contact between the donor and the acceptor. The electrons that have been released from the bacterial cells are transferred to the acceptor with the help of carrier molecules also known as mediator molecules since they mediate the transfer of electrons between the donor and acceptor (Li et al. 2022).

Direct transfer happens with special appendages present on the surface of the bacterial cell such as electrically conductive pili or nanowires. Pili is made up of the protein pilin and shows conductivity as seen in metals. Bacterial nanowires are specialised structures that are not normally seen in bacteria. Nanowires are the extensions of the outer membrane that attach to the acceptor and transfer the electrons with the help of cytochromes present on the surface of the membrane extensions (Slate et al. 2019)

Experiments have shown that bacteria that belong to several classes are considered exoelectrogens. Theoretically, all the species that belong to the class Proteobacteria are capable of transferring electrons extracellularly. But bacteria belonging to very few genera are known to generate a significant number of electrons that can produce a considerable amount of electricity. Bacteria belonging to the genera *Shewanella* which belongs to gamma proteobacteria and *Geobacter* which belongs to β -proteobacteria have been known to be potent exoelectrogens. These bacteria have been widely used in microbial fuel cells to generate electricity. *Geobacter sulfurreducens* uses electrically conductive pili to transfer electrons. *Shewanella oneidensis* uses bacterial nanowires to transfer electrons (Li et al. 2017).

These bacteria can also exist in consortiums if need be and function accordingly based on the conditions they find themselves in. The major survival strategy of these bacteria is the formation of biofilms. These biofilms provide the bacteria with a suitable environment to survive in harsh environmental conditions. The biofilm is formed on the anode in the anodic chamber as these bacteria are metal reducers. This also helps in the direct electron transfer of the electrons to the electrode as the bacteria are closer to the electrode.

Algae are another domain of organisms used in microbial electrochemical systems. It is known that microalgae act as the biocatalyst for the removal of pollutants such as organic matter, nitrogen, and phosphate from wastewater. The use of algae in MFCs or MECs has certain advantages over conventional MFCs. One of those advantages is the production of oxygen as part of photosynthesis which is useful

as the electron acceptor in cathodic reactions. This algal biomass can be in turn used as the carbon source for the cultivation of algae in the anodic chamber. Another advantage of algae is resource recovery. Algal biomass can be used for the recovery of value-added products such as lipids which can be used for the production of biofuels. In this algae-assisted microbial electrochemical systems can be more energy efficient along with wastewater treatment (Arun et al. 2020).

4 Application of MEC in Abatement of Water Pollution

The wastewater is polluted with many materials that may or may not be of biological origin. The major pollutants that are present in the wastewater are broadly classified into two major categories that are organic substances and inorganic substances. Inorganic substances mostly consist of salts. The primary cause of numerous environmental consequences, such as eutrophication of surface waters, hypoxia, and algal blooms degrading potential drinking water supplies, is the direct disposal of wastewater generated from diverse sources, including home, agricultural, and industrial establishments. Based on the design of the microbial electrochemical systems that have been explained earlier, each component in the design is responsible for the removal of different kinds of pollutants. According to the design, the anodic chamber is where the microbes grow and generate electricity. In order for the microbes to grow in significant numbers, they need a substrate on which they can grow. Here, the wastewater acts as the feed on which the microbes grow (Zhou et al. 2023).

When the wastewater first enters the anodic chamber, it comes directly in contact with the electrode that is the anode. Then the bacteria present in the wastewater adhere to the electrode forming biofilm. The electroactive bacteria then perform electroactivity that has been explained earlier. Here, the anodic chamber is designed to provide a suitable environment for the electrochemical reactions that take place. These microorganisms first oxidise the organic matter present in them, breaking them down into simpler compounds such as carbon dioxide, water, and other organic acids. Due to this oxidation, electrons are released by the bacteria that are transferred to the anode. Protons are also produced during this process. Most of the organic pollutants that can be removed using the MEC technology include nitrobenzene and chlorophenols. This includes the breakdown of chlorinated contaminants. On the other hand, sulphates, perchlorates, and nitrates are the chief inorganic contaminants. Most of the electroactive bacteria are metal reducers (mainly sulphate and iron reducers), and sulphate was reduced to sulphide.

As mentioned in the design and operation earlier, an anode chamber, a cathode chamber, and a middle compartment for wastewater treatment will typically be found in an MEC unit. An anion-exchange membrane (AEM) and a cation-exchange membrane (CEM) will be placed on either side of this central compartment. The cathode chamber completes the electrical circuit and regulates the removal of contaminants. The anode chamber manages the breakdown of organic materials

and power generation. The organic material is broken down by bacteria at the anode producing CO_2 and hydrogen ions (H^+), which are then released into the anolyte. The movement of electrons from the anode to the cathode through an external electric circuit generates an electric current that flows through the cell. The cathode's external electron acceptors, usually O_2 , employ these electrons to undergo reduction and generate H_2O . The anode chamber and the cathode compartments have different potentials as a result. In order to maintain the electrostatic balance, anions from the wastewater in the middle chamber travel over the AEM and into the anode. Cations, on the other hand, migrate through the CEM and into the cathode chamber. This procedure can remove more than 99% of the pollution while generating more electricity than what is required for operation (Zhou et al. 2023).

Metal ions in wastewater require specific treatment techniques since they do not biodegrade into harmless by-products (Chen et al. 2023). Additionally, a few of these heavy metal-containing groups have high redox potentials, making them potential electron acceptors for reduction and precipitation. If implemented, this technique could give MFCs the ability to recover heavy metals in addition to eliminating heavy metal ions from wastewater (Gude 2016).

5 MEC and Resource Recovery

One of the most important aspects of MEC is circular economy. The technology is sustainable and provides a way to circular economy by resource recovery and production of value-added products. Bio-electrochemical systems have applications other than wastewater treatment and energy production. One such application is the recovery of the value-added products from the wastewater while removing the contaminants from it using the microbial deionisation and microbial electrolysis technologies. The same technology produces by-products during the process of electricity generation that are of economic value. These include the production of biohydrogen and methane, recovery of precious metals, and other products such as ethanol and hydrogen peroxide.

The biohydrogen production using MEC depends on the principle of bio-hydrogenesis. Bio-hydrogenesis is the process in which the electrons released by the bacteria are combined with the protons in the cathode to produce hydrogen gas. The production processes of both hydrogen and methane are thermodynamically unfavourable. That is the reason why extra voltage has to be applied to the MEC during the production process. Nevertheless, hydrogen production is preferred over methane production as there is a 15% loss of thermodynamic energy during the methanogenic conversion of hydrogen to methane. Still the production of biohydrogen using MEC is not applicable to large-scale production as the cost for the purification of hydrogen produced in this manner is high which makes the method economically not feasible.

The conversion of acetate that has been produced as part of microbial degradation into ethanol is another way to utilise the wet biomass after the pollutant removal. But

the yield of ethanol is very less due to the irreversible reduction at cathode. A very low concentration of hydrogen peroxide is also produced due to the reduction of oxygen. Hydrogen peroxide is an industrially important chemical with variety of uses.

Other gaseous products can be produced as value-added substances from MECs. One of the examples is methane production. It can be produced in MECs either biologically or electrochemically. Microorganisms can utilise the hydrogen produced in MECs along with CO_2 to produce methane. But this way of methane production is coexisting with hydrogen produced, thereby increasing the process costs and decreasing the process efficiency. Another way by which methane can be produced in MECs is through the electrochemical route. The biological methane production can be combined with electrochemical hydrogen production in MECs to produce biohythane (combined hydrogen and methane) which does not require purification and separation of individual gases. This can be used as an alternate route of biofuel production (Liu et al. 2016).

Studies have reported reduction of volatile fatty acids such as acetate to ethanol in MECs utilising the biological microorganisms present in the cathode. This process was termed as microbial electroreduction (Hamelers et al. 2010). This process requires the presence of electrochemical mediators such as methyl viologen which can facilitate the reduction of acetate to ethanol (Marshall et al. 2012). Recent literature has explored the possibility of utilising mixed consortium through direct use of electrons from the cathode. The study reported very low yields of ethanol along with coproduction of various other chemicals. This reduces the process efficiency and very low yields hamper the scale-up of the process. Moreover, further research is required in order to understand the exact mechanism of the electrochemical reduction of acetate to ethanol. Furthermore, techno-economical and life cycle analysis of the process is to be established in order to determine the efficacy and sustainability as compared to conventional and established fermentative processes (Sharma et al. 2013).

Some studies have also reported hydrogen peroxide (H_2O_2) production using bio-electrochemical systems which is generally produced by the Fenton process of oxidation of wastewater. When the cathodes have a provision for air supply which makes it aerated, H_2O_2 can be produced inside MECs. On the contrary, few reports have been presented where H_2O_2 was being produced in MFCs with lower yields as compared to MECs (Kadier et al. 2016). This could be partially due to the fact that potential difference required to produce H_2O_2 in MECs is much lower as compared to other bio-electrochemical systems. But further research is required in order to understand the mechanism as well as increase the yields of the product.

The wastewater from domestic and industrial sources also has trace amounts of metals in it. Though many of such metals are toxic in nature and are removed in the process, there are a few metals that are useful for other industries. Usually, these metals have redox potentials and function as electron acceptors. Due to the electroactivity of the bacteria, these metals get reduced and accumulate in the cathode. These metals are recovered by applying an external voltage. Till now, metal ions such as Zn, Pb, and Ni present in the wastewater have been reduced using

the MEC technology. Apart from the normally found metals, precious metals such as gold and silver are also found in wastewater that comes from electronic, jewellery, and photography industries. These particles can be toxic towards plants and animals. These metals can be recovered as nanostructures or nanoparticles that can be used in sensors. In most of the cases for recovering metals from the wastewater, a combination of MFC and MEC is used. Together in the MFC–MEC system, voltage generated in the MFC system is used to drive the reactions that happen in MEC.

Various other processes which provide resource recovery from the MECs are integrated processes. MECs can be integrated with anaerobic digestion process which can help eliminate the process bottlenecks associated with methane production. Similarly, it can also be integrated with the dark fermentation process to further utilise the volatile fatty acids present in the spent medium. The spent medium of the dark fermentation process produces volatile fatty acids such as acetate and butyrate which can be utilised by the microbial consortia in MECs to produce a varied spectrum of products. Furthermore, the electrocatalyst in MECs can be combined with photocatalysts, thereby directly harnessing the solar energy for the process. These types of MECs are called as biophotolysis cells (Varanasi et al. 2018).

6 Future Prospects and Challenges in MEC Development

The MEC technology coupled with wastewater treatment deals with two major problems that need our immediate attention. One is the removal of pollutants from wastewater and the other is the generation of bioelectricity. The efficiency in both the cases depends on the design of the cell. The major problem with the present-day bio-electrochemical systems such as MEC and MFC is that they produce very low current densities in terms of voltage. The problem lies in multiple areas of the design such as the type of electrode, the amount of electroactivity performed by exoelectrogens, the rate of transfer of electrons to the electrode, the inefficiency of the electron mediators, low transport across the membranes, the kind of substrate used, and many more.

Another major challenge is in terms of scaling up of the process. Establishing large-scale reactors for wastewater treatment and simultaneous electricity production is not feasible economically, although a potential solution that is being explored these days is the usage of stacked BES units as a stack. Changing of the dual-chambered fuels to single-chambered cells has also been tried to reduce the cost of the design which also reported an increase in power output. Apart from these challenges, there are few other limitations. These include optimising reactor design, creating newer techniques for separating anode from cathode, and maintaining low internal resistance while increasing the levels of electrochemically active biomass (Pant et al. 2012).

It is challenging to compare the many designs, which range from two-chambered to single chamber, mediator or without mediator, and membrane or membrane-less. Aside from the design itself, it is practically impossible to compare the results of the

setups used by researchers around the world due to the variety of electrodes used, including those made of graphite foil, rods, granules and fibre brushes, carbon paper, cloth, felt and foam, activated carbon cloth, reticulated vitreous carbon, electrodes modified with conductive polymers, and metals like aluminium, nickel, or stainless steel. There are several methods that have been described for resolving these issues (Pant et al. 2012).

The process of pollutant removal using BESs is complex with a plethora of organisms performing various functions with varied metabolic activities. Therefore, it is very difficult to provide models which could predict the outcome of the process. Traditional techniques include modifying each factor at a time which proved to be time-consuming and labour-intensive. These problems could be solved by using modern techniques based on machine learning and artificial neural networks (ANN) (Sadeghipour Chahnasir et al. 2018; Sedghi et al. 2018). Various studies have utilised ANN-based approaches in order to predict the outcome of the process in real time (Anita et al. 2014; Karimi et al. 2016; Nilashi et al. 2019; Shariati et al. 2019). These machine learning-based mechanisms can be efficiently utilised to predict the behaviour of the system without knowing much about the operation of the system in particular. Moreover, models such as response surface methodology (RSM) and artificial neural networking–particle swarm optimisation (ANN-PSO) can predict the estimated levels of the factors involved, thereby optimising the process efficiency. Modelling also helps in developing an acute idea about the scale-up of the system and the problems involved in it (Shariati et al. 2019; Trung et al. 2019; Safa et al. 2020; Yazdani et al. 2021).

To sum up the limitations of microbial electro-deionisation cell for treating wastewater, the following aspects such as limited efficiency, energy requirements, contaminant specificity, limited scalability, and cost-effective maintenance can be taken into consideration. To advance this technology, it is necessary to create new plans and strategies along with the regulations in the government policies.

7 Conclusion

Water pollution is a serious environmental problem that endangers the environment, aquatic life, and human health. Water supplies can get polluted from both anthropogenic and natural sources by a variety of pollutants, including nutrients and organic and inorganic materials. However, cutting-edge approaches to wastewater treatment, such the microbial electro-deionisation cell, offer promise in terms of delivering affordable and eco-friendly solutions. The microbial community on the anode surface must be optimised, the right kind of membranes and electrode materials must be chosen, and the characteristics and treatment goals of the wastewater must all be taken into account when designing an effective BES for treating wastewater such as MEC. The promise of lowering total treatment costs while lowering the output of biomass makes electricity recovery from wastewater an appealing option. In terms of the generation of electric current and power, the

investigation of new materials and cell components is becoming increasingly crucial since MECs' wide range of applications will be substantially increased by their competitive pricing and excellent performance.

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Algae-Based Bioremediation of Emerging Pollutants



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Abstract Future global connections between economic development, the rise of living standards, and environmental safeguards have always been an imbalanced triangle, resulting in various emerging organic (mostly from agriculture, industry, and household trash) and inorganic (from anthropogenic activities including manufacturing, handling, storing, and disposing of chemicals) pollutants in aquatic environments. A wide range of immediate and long-term consequences for aquatic biodiversity, human health (e.g., neurological disorders, endocrinal disruption, cancers, and immunotoxicity), and ecosystems, owing to the imprudent discharge of pollutants from documented and undocumented sources both in land and water, provoked severe worries. In recent days, algal remediation has been gaining more attention compared to existing treatment technologies due to its polymorphic bioremediation features (biosorption, bioaccumulation, biouptake, biodegradation, and photodegradation) and co-remediation of numerous standard and emerging pollutants (inorganic and organic) in the environment (air and water). With the advancement of bioremediation of emerging pollutants via algal biotechnology, this green way of detoxifying emerging pollutants prompted further research for a better understanding of the physiology, genetics (adopting genetic engineering strategies to ameliorate tolerance to emerging pollutants and biodegradation potentiality of selected highly productive algae strains), and biochemical properties of algae to optimize the organisms and the environment in which they are grown. Parallel to

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improving treatment techniques, merging effect-based, class-based, and green synthesis-based approaches in the global science-policy interface could protect public and ecosystem health, ensuring minimal to zero emission of emerging pollutants.

Keywords Emerging pollutants · Biosorption · Bioaccumulation · Biodegradation · Microalgae

1 Introduction

The unregulated chemical substances that enter the different compartments of the environment (geo-, bio-, hydro-, and atmosphere) and pose potential health risks to living organisms (human and aquatic biota) and the environment itself are called emerging pollutants (EPs) or pollutants of emerging concern (Bilal et al. 2019; EPA 2008; Escapa et al. 2016; Pereira et al. 2015). While EPs represent the millennium's trilogy concept "One Health," these remain the focus of public interest, research, and policy attention. To date, researchers have classified EPs into different conventional and unconventional groups. Within conventional groups, the pollutants include but are not limited to pharmaceuticals (different drugs and antibiotic/antimicrobial resistance), personal care products, endocrine disruptors, pesticides, heavy metals, chemicals (synthetic organic) from industries, and microplastics. Among diverse compounds of unconventional pollutants, several classes are highlighted: steroids, surfactants, fire retardants (brominated and organophosphate), high-technology rare earth elements, industrial additives (gasoline), hormones, nanomaterials, organometallic compounds, perfluorinated compounds, microbeads, toxins (from algae and cyanobacteria), and by-products of disinfectants (Gwenzi and Chaukura 2018; Gwenzi et al. 2018; Lambert and Wagner 2018; Rogowska et al. 2018; Westerhoff 2009; Ng et al. 2020; Nguyen et al. 2021; Wanda et al. 2017; Sousa et al. 2018; Peña-Guzmán et al. 2019; Pereira et al. 2015). There is no way to take a U-turn from the high burden of EPs in the environment while the diverse use of EPs becomes an integral part of economic advancement and cultural norms of modern lifestyle (Richmond et al. 2017). Moreover, the impact becomes more perilous due to the amassment of EPs in living organisms or their tissues and disseminated through the food web employing bioaccumulation and biomagnification (Zenker et al. 2014).

Researchers documented various origins of EPs, including healthcare facilities, industrial sites, agricultural activities, and households. Direct application or disposal in soils, animal excretion, direct discharge into sewage, and inefficient water treatment in wastewater plants are just a few of the numerous courses that dispatch EPs to the environment from the earlier-mentioned sources (Houtman 2010; Pal et al. 2014). Exposure to these EPs results in environmental degradation and hazardous impact, including genotoxicity, carcinogenicity, endocrine disruption, and immunological toxicity to a wide range of living organisms (from microorganisms to top-level organisms, i.e., humans) (Sairam et al. 2023; Nataraj 2022; Vasilachi et al. 2021). Tropic transfer of EPs through food webs is attributed to different

organ (e.g., respiratory, cardiovascular, reproductive, immune, and nervous systems) dysfunction of humans depending on the level and period of exposure (Kaur and Kaur 2018). Other inhabitant organisms, including aquatic animals (Hasan et al. 2021), algae, and microorganisms, are directly or indirectly impacted by exposure to EPs; however, these consequences have not been entirely intelligible (Gomes et al. 2020).

The poor understanding of the toxicological significance of these EPs to the health of humans and the environment and their incomprehensive toxicity mechanism prevents most countries from developing EPs specific policies and regulations addressing the potential impacts of these concerning pollutants (Gwenzi and Chaukura 2018; Gwenzi 2020, 2021; Petrović et al. 2003). Even researchers and regulatory agencies are facing the challenge of having the ubiquitous presence of EPs with their divergent nature in diverse environments, and this embodies an unsettled inquiry of “What is the best way to prioritize research on emerging contaminants?” Accompanying this uncertainty and while a complete understanding of the consequences of these EPs on human and environmental health is still lacking (Mastropetros et al. 2022a, b; Koutra et al. 2021), researchers step forward to treat EPs with an attempt to develop conventional (physical and chemical) and technologically advanced (biological) methods (Aboagye et al. 2021; Rout et al. 2021; Xu et al. 2021), and confirm as well that these methods are eco-friendly, affordable, and effective. In conventional (chemical) methods, different approaches are amalgamated, such as coagulation/flocculation, chlorination, flotation, chlorination, photocatalysis, ozonation, coagulation, adsorption, filtration, ultraviolet light, and electrocatalysis (Ahmed et al. 2022; Saleh et al. 2022; Shahedi et al. 2020; Vidu et al. 2020; Al-Tohamy et al. 2022; Yusuf et al. 2020). However, the evidence of EPs coexistence (Magana-Arachchi and Wanigatunge 2022) and unverified pollutant characterization methods (Gondi et al. 2022) proved the limitation of these conventional processes. Exorbitant expenses, significant energy demands, limited dewatering capacity, greenhouse gases emission, suboptimal eco-friendliness, and engendering of hazardous by-products responsible for secondary pollution are some other drawbacks of these chemical processes (Al-Tohamy et al. 2022; Daud et al. 2022; Edo et al. 2020; Qu et al. 2019; Wang et al. 2022). In an analogy of these conventional physicochemical methods, biological methods (incorporating bacteria, fungi, and algae; Zhang et al. 2022; Lin et al. 2022) become a chic and famous arena of research because of their ecologically sustainable approach (Kumar and Singh 2017).

To date, many research articles have been reported on removing EPs utilizing bacteria and fungi, with some limited reports prioritizing potential microalgae-based remediation of EPs. In order to comprehend the significant role of microalgae in eliminating emerging pollutants from aquatic environments, a thorough comprehension of the intricate mechanisms underlying the bioremediation process is imperative. To this end, this chapter has comprehensively compiled information from various sources to explore and understand the intricacies of algae to bioremediate EPs, including classification, source and pathways, geo-, bio-, hydro-, and atmospheric impacts, and existing policy for edging EPs. Specifically, this study delves

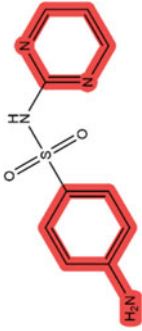
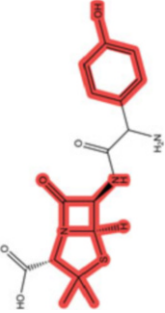
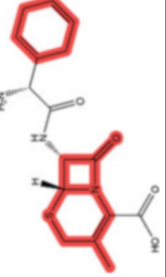
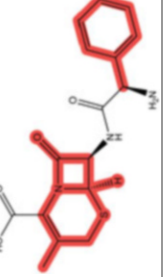
into biosorption, bioaccumulation, and biodegradation processes, which are fundamental to microalgae-based bioremediation.

2 Classification of EPs and Their Physico-toxicological Properties

In the NORMAN network (<http://www.norman-network.net>), EPs have been classified into pharmaceutical pollutants such as personal care products, microplastics, persistent organic pollutants, endocrine disruption chemicals, and artificial sweeteners. Here in this study (review-based), this classification has been adopted and re-classified into heavy metals, pharmaceuticals, pesticides, dyes, and microplastics. Inflation of the global population and economics escalated the consumption of a diverse class of EPs. More than 700 EPs, including their metabolites and converted by-products (belonging to the categories mentioned earlier) individually characterized by the NORMAN network, have been found ubiquitously in all environmental matrices (groundwater; surface water of streams, lakes, estuaries, seawater, and river and influents and effluents of wastewater treatment plant) worldwide. Among these reported EPs, a range of 10 and 50% (based on their LD50 value) is the primary concern of the research community, and based on their incremental impact on human or other animals and environmental health, substances from each category were reviewed in this study regarding their physicochemical and ecotoxicological properties (Table 1). Among different physicochemical properties, we considered EPs' solubility, logP value (partition coefficient), and pKa value (dissociation constants). Solubility provides insights into the fate of EPs in their associated aquatic environment (Lapworth et al. 2012; Pal et al. 2010; Yamamoto et al. 2009); log P value explains the potentiality of EPs owing to bioaccumulation and biomagnification in aquatic organisms (Díaz-Cruz et al. 2003); and pKa value unveiled how this fate of EPs is being influenced by divergent hydrolysis, biodegradation process, sorption, photodegradation, and partition (Pal et al. 2010; Yamamoto et al. 2009).

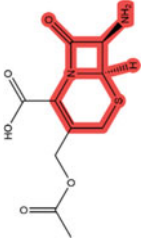
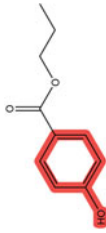
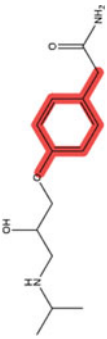
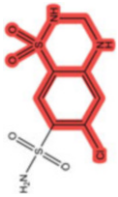
Unlike chemicals, pharmaceuticals, physical, biological, and structural features give birth to the complexity of framing pharmaceuticals within a homogenous classification compared to other EPs (Taylor and Senac 2014). In an analogy of other EPs pharmaceuticals, molecular weight remains within 500 kDa with some exceptional ones (Lipinski et al. 1997), the same for our reviewed pharmaceuticals. The solubility of our selected pharmaceuticals was diverse, with many of them moderately soluble in water, and this water solubility feature was expressed earlier by Lipinski et al. (1997) with some other properties, including lipophilic ones for the pharmaceutical compounds having molecular weight <500 kDa. Based on logP value of progesterone (3.87), propylparaben (3.04), phenanthrene (4.46), gemfibrozil (4.387), and sulfamonomethoxine (3.53) (Table 1), these pharmaceuticals have the high potential of bioaccumulation in living organisms for having their

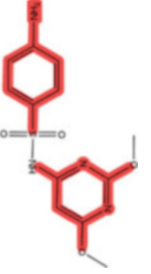
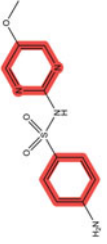


Table 1 Classification and physico-toxicological properties of emerging pollutants

Category	Name	Molecular weight	pKa	Solubility	LogP	Toxicity release compound part	LD50 (mol/kg)	<i>T. pyriformis</i> toxicity value (log ug/L)	Mimow toxicity (log mM)	Toxicity
Pharmaceuticals	Sulfadiazine	250.283	6.36	77 mg/L	-0.09		1.931	0.274	2.394	Hepatotoxicity, micronuclear toxicity, respiratory toxicity, reproductive toxicity, mitochondrial toxicity, nephrotoxicity, fish aquatic toxicity
	Amoxicillin	365.411	2.6	3.43 mg/L	0.87		1.735	0.285	4.969	Carcinogenicity, micronuclear, hepatotoxicity, fish aquatic toxicity, nephrotoxicity, mitochondrial toxicity, reproductive and reproductive toxicity
	Cefradine	349.412	pKa1 = 2.6; pKa2 = 7.3	21,300 mg/L	-1.5		1.541	0.285	3.267	Hepatotoxicity, micronuclear toxicity, respiratory toxicity, reproductive toxicity, mitochondrial toxicity, chondrial toxicity, nephrotoxicity, fish aquatic toxicity
	Cephalexin	347.396	pKa1 = 5.2; pKa2 = 7.3	10 mg/mL	0.65		1.704	0.285	4.24	Hepatotoxicity, micronuclear toxicity, respiratory toxicity, reproductive toxicity, mitochondrial toxicity, chondrial toxicity, nephrotoxicity, fish aquatic toxicity

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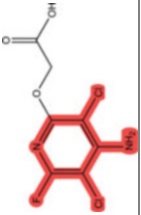
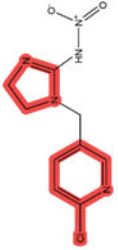


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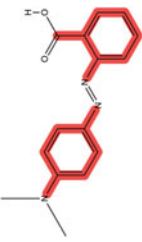
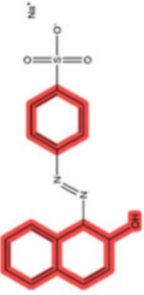
Category	Name	Molecular weight	pKa	Solubility	LogP	Toxicity release compound part	LD50 (mol/kg)	<i>T. pyriformis</i> toxicity value (log ug/L)	Mimow toxicity (log mM)	Toxicity
	7-Aminocephalosporanic acid	272.282	N/A	N/A	N/A		1.631	0.285	3.797	Eye irritation, hepatotoxicity, micronuclear toxicity, respiratory toxicity, reproductive toxicity, mitochondrial toxicity, nephrotoxicity, fish aquatic toxicity, skin sensitization
	Propylparaben	180.203	8.5	5.00×10^{-2} mg/L	3.04		1.816	0.713	1.295	Eye irritation, nephrotoxicity, fish aquatic toxicity
Pharmaceuticals	Atenolol	266.341	9.6	13,300 mg/L	0.16		1.875	0.509	3.238	Hepatotoxicity, micronuclear toxicity, respiratory toxicity, reproductive toxicity, mitochondrial toxicity
	Hydrochlorothiazide	297.745	7.9	722 mg/L	0.07		1.694	0.336	2.385	Hepatotoxicity, micronuclear toxicity, respiratory toxicity, reproductive toxicity, mitochondrial toxicity, nephrotoxicity, crustacea aquatic toxicity, fish aquatic toxicity

Sulfadimethoxine	310.335	N/A	343 mg/L	1.63		1.951	0.282	1.227	Micronuclear toxicity, hepatotoxicity, respiratory toxicity, reproductive toxicity, mitochondrial toxicity, nephrotoxicity, fish aquatic toxicity
Sulfamer	280.309	N/A	0.313 mg/mL	0.53		1.916	0.279	1.505	Micronuclear toxicity, hepatotoxicity, respiratory toxicity, reproductive toxicity, mitochondrial toxicity, fish aquatic toxicity
Tributyltin	290.059	N/A	0.0813 mg/mL	N/A		1.884	2.319	-0.676	Eye corrosion, eye irritation, hepatotoxicity, nephrotoxicity, respiratory toxicity, fish aquatic toxicity
4-Androstene-3,17-dione	286.415	N/A	57.8 mg/L	2.75		1.759	1.049	0.584	Hepatotoxicity, carcinogenicity, skin sensitization, respiratory toxicity, reproductive toxicity, mitochondrial toxicity, crustacea aquatic toxicity, fish aquatic toxicity
Lead	207.2	N/A	Insoluble	N/A	Pb	2.147	-0.491	2.138	Hepatotoxicity, immunotoxicity
Mercury	200.59	N/A	0.28 µmoles/L	N/A	Hg	2.215	-0.53	2.032	Hepatotoxicity, immunotoxicity
Arsenic	74.922	N/A	Insoluble	N/A	As	2.215	-0.666	2.433	Hepatotoxicity, immunotoxicity
Uranium	238.029	N/A	Insoluble	N/A	U	2.19	-0.463	1.923	Hepatotoxicity, immunotoxicity
Barium	137.328	N/A	-	N/A	Ba	1.991	-0.066	1.463	Hepatotoxicity, immunotoxicity

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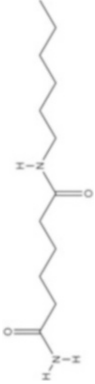
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Category	Name	Molecular weight	pKa	Solubility	LogP	Toxicity release compound part	LD50 (mol/kg)	<i>T. pyriformis</i> toxicity value (log ug/L)	Minnow toxicity (log mM)	Toxicity
Pesticides	Fluroxypyr	255.082	2.94	0.091 g/L	2.2		1.747	0.142	1.667	Micronuclear toxicity, hepatotoxicity, respiratory toxicity, reproductive toxicity, mitochondrial toxicity, nephrotoxicity
	Imidacloprid	255.665	pKa1 = 1.56; pKa2 = 11.12	6.1×10^{-2} mg/L	0.57		2.054	0.352	1.629	Ames mutagenesis, micronuclear toxicity, hepatotoxicity, carcinogenicity, skin sensitization, respiratory toxicity, reproductive toxicity, mitochondrial toxicity, nephrotoxicity
	Naphthalene	128.174	N/A	31 mg/L	3.3		1.942	0.584	0.52	Eye corrosion, eye irritation, hepatotoxicity, carcinogenicity, skin sensitization, nephrotoxicity, crustacea aquatic toxicity, fish aquatic toxicity
	Glyphosate	169.073	0.8	12,000 mg/L	-4		1.981	0.283	3.706	Eye corrosion, eye irritation, micronuclear toxicity, hepatotoxicity, respiratory toxicity, mitochondrial toxicity, nephrotoxicity, crustacea aquatic toxicity


Dye	Pyrene	202.256	N/A	0.135 mg/L	4.88		1.978	-1.382	-1.382	Eye corrosion, eye irritation, hepatotoxicity, carcinogenicity, skin sensitization, respiratory toxicity, nephrotoxicity, crustacea aquatic toxicity, fish aquatic toxicity
	Indigo	262.268	N/A	N/A	N/A		2.035	0.758	0.636	Eye irritation, Ames mutagenesis, micronuclear toxicity, hepatotoxicity, respiratory toxicity, reproductive toxicity, mitochondrial toxicity, nephrotoxicity, fish aquatic toxicity
	Methyl red	269.304	pKa1 2.5; pKa2 9.5; pKb 4.8	Almost insoluble	N/A		1.913	0.303	0.399	Eye irritation, Ames mutagenesis, micronuclear toxicity, hepatotoxicity, carcinogenicity, respiratory toxicity, mitochondrial toxicity, nephrotoxicity, fish aquatic toxicity
	Orange II	350.331	N/A	N/A	N/A		1.9	0.285	-0.459	Eye irritation, micronuclear toxicity, hepatotoxicity, carcinogenicity, skin sensitization, respiratory toxicity, fish aquatic toxicity

(continued)

Table 1 (continued)

Category	Name	Molecular weight	pKa	Solubility	LogP	Toxicity release compound part	LD50 (mol/kg)	<i>T. pyriformis</i> toxicity value (log ug/L)	Minnow toxicity (log mM)	Toxicity
	Acenaphthylene	152.196	N/A	N/A	N/A		2.012	1.283	1.283	Mutagenicity, carcinogenicity, skin sensitization, eye corrosion, eye irritation, nephrotoxicity, fish aquatic toxicity, crustacea aquatic toxicity
Microplastics	Polyethylene terephthalate (PET) [ethylene terephthalate] ^a	228.2	N/A	N/A	N/A	 	1.488	0.275	2.871	Eye irritation, nephrotoxicity
	Polystyrene (PS) [styrene] ^a	104.152	N/A	300 mg/L	2.95		1.83	-0.018	1.136	Eye corrosion, eye irritation, hepatotoxicity, carcinogenicity, skin sensitization, reproductive toxicity, crustacea aquatic toxicity, fish aquatic toxicity
	Nylon-66	224.304	N/A	N/A	N/A		1.979	1.126	1.066	Nephrotoxicity, crustacea aquatic toxicity

N/A, not available

 Toxicity release compound part^a Monomer of plastics

hydrophobic behavior, while Palma et al. (2015) reported this case for pollutants with $\log P > 3$.

Regarding pK_a value, EPs are considered more vital acids with lower pK_a and vice versa for higher pK_a (Ranjan et al. 2022). This dichotomous fact could change the fate and behavior in the following three ways of our studies of pharmaceuticals following the pH of aquatic systems where these substances persist. For example, highly alkaline pharmaceuticals having $pK_a > 9$ (paracetamol, atenolol, formestane, and spiramycin (Table 1)), (1) when pH (surrounding environment) $< pK_a$ (mentioned pharmaceuticals) the water solubility of these compounds will reduce and protonated (ionized) form will bioaccumulate in the fatty tissue of aquatic organisms (Gaohua et al. 2021). Conversely, (2) when pH $> pK_a$ deprotonated (nonionized) form of the substances will augment their water solubility and mobility within the environmental compartment. Even (3) there may arise an equilibrium situation (pH = pK_a) where 50% of the substances will be in their ionized form and the remaining 50% will be in their nonionized form (Hale and Abbey 2017). The first two cases experienced a reverse situation for acidic pharmaceuticals. As a result of the bioaccumulation of these pharmaceuticals and their metabolites, a wide range of toxicity has been reported to target organisms (for details, see Table 1).

Heavy metals, including lead, mercury, arsenic, barium, and uranium are among the most significant emerging pollutants (Boyd 2010). These compounds exhibit exceptional physicochemical properties; their molecular weights remain within 250 kDa. Uranium has the highest molecular weight of 238.029 kDa compared to other mentioned heavy metals (lead (207.2), mercury (200.59), arsenic (74.922), and barium (137.328)). Regarding solubility, all compounds are insoluble in water except for mercury (0.28 $\mu\text{moles/L}$) (Table 1). There is evidence that these compounds entire composition is released and is responsible for toxicity production (Jaishankar et al. 2014). The LD50 value of most compounds is approximately 2.00 mol/kg, with mercury and arsenic having the highest value (2.215) and the lowest barium (1.991 mol/kg). In addition, arsenic has the maximum level of *T. pyriformis* toxicity ($-0.666 \log \mu\text{g/L}$). The other heavy metals are moderately toxic to *T. pyriformis*, but curiously, barium has the lowest level of toxicity ($-0.066 \log \mu\text{g/L}$). As part of Minnow toxicity, most of the compound's toxicological value is $>2.00 \log \text{mM}$, with barium having the smallest quantity (1.46 $\log \text{mM}$). Both hepatotoxicity and immunotoxicity were observed for the tabulated heavy metals (Renu et al. 2021; Koedrith et al. 2013).

Pesticides (fluroxypyr, imidacloprid, naphthalene, and glyphosate which this chapter focuses on) are a specific form of a chemical used to kill various insects, pests, weeds, etc. Currently, they are also considered EPs (summarized in Table 1) (Kaur et al. 2019). The compounds have distinct physicochemical characteristics, and their molecular weight ranges from about 128 to 255 kDa. Regarding the solubility of these pollutants, fluroxypyr (0.091 g/L) and imidacloprid ($6.1 \times 10^{+2} \text{ mg/L}$) exhibited the highest water solubility compared to the remainder of the compounds. The log P value of the compounds is more significant than 0.5, with naphthalene (3.3) having the highest value. For instance in pK_a values, an idiosyncratic pattern was observed for listed heavy metals (fluroxypyr (2.94), imidacloprid ($pK_{a1} = 1.56$

and $pK_{a2} = 11.12$, and glyphosate (0.80)). In contrast, the toxicological profile of these compounds has been determined by evaluating several parameters and the entire compound discharging capacity of some of these components (information extracted from Yadav and Devi 2017; Alengebawy et al. 2021 presented in Table 1). The LD50 for these chemicals is about 1.7–2.0 mol/kg, where imidacloprid (2.054) holds the highest value. From the collected information about the toxicity of *T. pyriformis* of these pesticides, the fluroxypyr value is minimal (0.142 log $\mu\text{g/L}$). *T. pyriformis* was found to be more toxic to the chemicals naphthalene (0.584 log $\mu\text{g/L}$). All compounds' toxicity to minnows is remarkable. Consequently, pesticides have been found to give a wide range of toxicity, including eye irritation, micronuclear toxicity, hepatotoxicity, carcinogenicity, skin sensitization, respiratory toxicity, reproductive toxicity, nephrotoxicity, crustacea aquatic toxicity, Ames mutagenesis for different biological organisms (Wallace and Djordjevic 2020; Mathur et al. 2010; Mostafalou and Abdollahi 2017).

Dye is a prevalent substance that imparts color to various substances, including textiles, paper, leather, and other materials. The maximum number of synthetic dyes that the chemical industry can produce with a specific substance is petrochemicals (Forgacs et al. 2004). Some chemical dyes (pyrene, azo dye, crystal violet, malachite green, Reactive Black 5/Remazol Black B, indigo, methyl red, Orange II, and acenaphthylene) are categorized as EPs for having their essential physiochemical and toxicological functions (Khan et al. 2022).

For listed dyes (Table 1) reviewed in this chapter, the molecular weight remains within a specific range, i.e., <500 kDa. Indigo, Orange II, and acenaphthylene were found to have unknown solubility patterns, whereas the solubility patterns of the remaining compounds are listed as pyrene (0.13 mg/L) and methyl red (almost insoluble). From the reviewed group of dye-based pollutants, the logP and pK_a value was available only for pyrene (4.88) and methyl red ($pK_a 1 = 2.50$; $pK_a 2 = 9.50$; $pK_b = 4.80$). Alternatively, these EPs have a greater level of toxicity and can release either the entire compound or a portion of it (Khan et al. 2022). Most of the compounds' LD50 value was ~ 2.00 mol/kg or greater. *T. pyriformis* toxicity and Minnow toxicity of Pyrene (−1.382) and Acenaphthylene (1.283) were the same, with a slight difference for others (negative value for Orange II). Eye irritation, human ether-a-go-go-related gene inhibition, carcinogenicity, micronuclear toxicity, hepatotoxicity, skin sensitization, respiratory toxicity, mitochondrial toxicity, aquatic fish toxicity, and numerous other forms of toxicity are expressed by these dyes in either biological or aquatic systems (Chung 2016; Affat 2021; Hussain et al. 2022).

The persistence of microplastics has become an enormous threat to ecosystems worldwide compared to other EPs in recent years. Microplastics (MPs) are polymers of giant molecules and composed of numerous (>3) monomers. Earlier inquests by Yalkowsky et al. (2010) showed that microplastics are soluble in water (e.g., styrene has a solubility of 300 mg/L in water at 25 °C) and express some other features, including lipophilicity. The solubility of MPs varies with their polarity, molecular weight, branching, degree of crosslinking, and crystallinity of polymers (Verschoor 2015). Many of our selected microplastics have a highly lipophilic nature and a wide

range of molecular weights (about 104–228 kDa). Based on the log P value of studied microplastics (available in Table 1), this lipophilic polymer of microplastic has high potential to enhance hydrophobic organic contaminations. Apart from this information, various toxicological properties and other parameters of studied microplastics are available in Table 1 that could be translated and placed in logical arguments like other EPs discussed earlier.

3 Source and Pathways of Emerging Pollutants Towards Aquatic Environment

Pharmaceuticals are natural or chemical products mainly used for human health, disease management, and cosmetics preparation (Maletz et al. 2013; Wang and Huang 2019). In addition, huge quantities are also used for disease treatment and health management (Heal et al. 2021), as well as to boost the production of edible animals (Ekpeghere et al. 2017; Bishnoi et al. 2022). Therefore, pharmaceuticals include antibiotics, hormones, veterinary drugs, etc., and about 5000 pharmaceutical commodities are available worldwide for different purposes (Van Doorslaer et al. 2014). After their application and function in humans and animals, these pharmaceuticals find their way into the environment as active compounds or residual substances (Sui et al. 2015). These forms of pharmaceuticals can be found in the wastewater, which might further find ways in the surface waters, including lakes, rivers, seas, oceans, and groundwater, through leaching (Ojemaye and Petrik 2019; Reis-Santos et al. 2018; Fekadu et al. 2019) (illustrated in Fig. 1, this is also the same case for other EPs discussed later). Pharmaceutical industries' discharge is another primary source of pharmaceutical contamination in surface water and groundwater (Phillips et al. 2010; Sim et al. 2011; Cardoso et al. 2014). Antibiotics are the most important pharmaceutical product because of their chemical nature and persistent capability in nature (Mukhtar et al. 2020). Antibiotics were recorded in river waters worldwide (Peng et al. 2011; Bilal et al. 2020) entering from food production systems and augmenting the crisis of antimicrobial resistance (Bell et al. 2023; Thornber et al. 2022). Moreover, antibiotic adsorption depends on the aquatic environment and varies with the soil and other factors, while the adsorption on marine sediment varies with different hydrodynamic conditions (Xu et al. 2023). Apart from these, the use of hormones and endocrine disruptor drugs is increasing owing to industrial growth. This incidence made pharmaceutical compounds (hormone and endocrine disruptors) available in wastewater bodies. It can persist with improper treatment methods, an anticipated source for surface waters (Andrade-Eiroa et al. 2016; Gröger et al. 2020; Li et al. 2020). Apart from antibiotics there are other drugs including anti-inflammatory, antiulcer, antiparasitic and other drugs used for therapy might also pollute surface water (Esplugas et al. 2007).

Heavy metal pollution in aquatic environments is less visible; however, their high concentration harms the aquatic ecosystem. The most common heavy metals that are

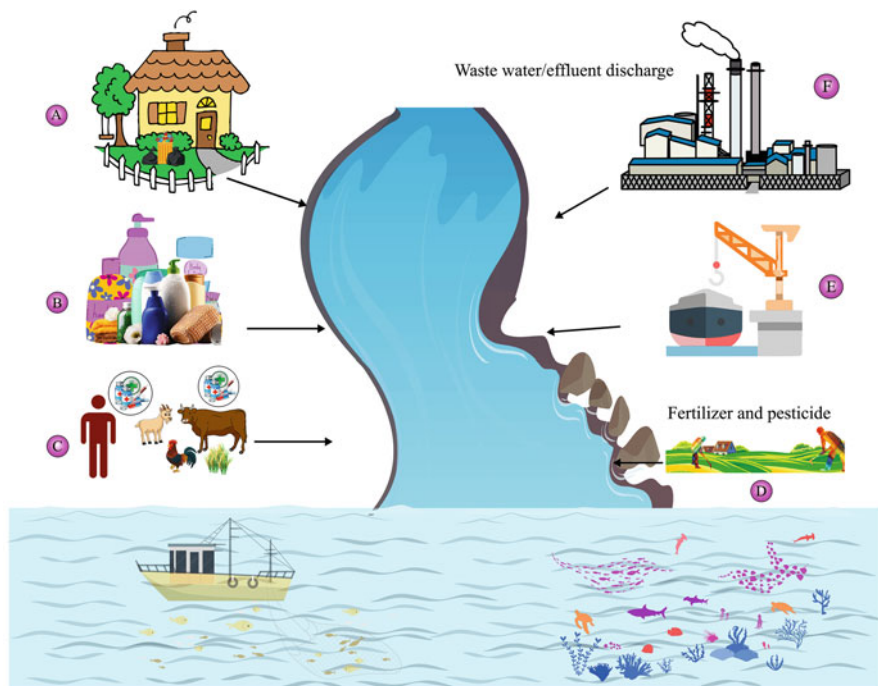


Fig. 1 Potential entry routes of EPs to the environment. Waste from different household activities (A), use of personal care products for improving living standards (B), pharmaceuticals use for health benefit of both humans and livestock animals (C), and fertilizers and pesticides from agricultural activities (D) get discharged into water and are slowly degraded. Moreover, ship building activities (E) and wastewater or untreated effluent discharge from industry (F) are some other sources of environmental EPs

considered contaminants in high quantity are copper, zinc, cobalt, lead, mercury, arsenic, chromium, cadmium, etc. Cadmium is used in the nuclear industry and electroplating, whereas lead is helpful in machine manufacturing and shipbuilding activities. Heavy metals from all these industrial operations find their way into water through waste discharge. The source of other heavy metals, such as arsenic, can be natural volcanic eruptions or anthropogenic sources, and chromium is mainly used in electroplating and dye industries. Naturally, these heavy metals can enter the marine environment differently, including volcanic activity, mining, and polluted rivers. However, several anthropogenic sources, such as industrial and oil pollutants and agricultural fertilizers, are also responsible for this heavy metal pollution. Urban and industrial development are other anthropogenic sources of heavy metals in the environment (Nagajyoti et al. 2010), especially in aquatic waterbodies (Qin and Tao 2022).

Moreover, waste from leather, glass manufacturing, pharmaceutical industries, and domestic activities potentially exaggerates environmental heavy metal pollution (Wuana and Okieimen 2011). The pathways of heavy metals to aquatic water bodies

vary with the source and type. Heavy metals from agricultural fertilizer can contaminate groundwater through leaching and the surface waters through runoff (Dissanayake and Chandrajith 2009). In an aquatic environment, heavy metals are settled in the sediment that makes the sediment heavy metal pool for aquatic waterbodies (Zahra et al. 2014; Fernandes and Nayak 2012), and excessive deposition of heavy metals in sediments can contaminate groundwater (Sanyal et al. 2015).

Pesticides are mainly used to control pests and insects in agriculture and are employed in golf courses, roadside areas, and forest areas (Carvalho 2017). Pesticides can be classified as insecticides, herbicides, and fungicides, based on their usage purpose (De et al. 2014). These pesticides are deliberately used in crop fields and get to different layers of aquatic environments, including surface waters (Abrantes et al. 2006), where they could persist, bioaccumulate, and biomagnify depending on their water solubility and nature. Agricultural lands are considered non-point sources of pesticides in surface and groundwater, and it is more likely that runoff of pesticides occurs immediately after applying it on the soil between 0.25 and 0.85 cm (Aydinalp and Porca 2004). Although surface runoff and leaching are the sources of pesticide contamination in water, the contamination rate depends on the chemical composition and application methods of pesticides and the soil type of the area.

In contrast, pesticides are more easily absorbed in the soil and end up in surface water through soil erosion (National Research Council 1993). In urban areas, pesticides are applied indiscriminately, especially for home gardening, mostly in groundwater or surface water (Zubrod et al. 2019). In Asia, pesticides' contamination in surface waters was observed to occur through runoff and leaching in different countries; in the Tenggi River of Malaysia (Elfikrie et al. 2020), Kurose River of Japan (Derbalah et al. 2003), Huangpu River of China (Xu et al. 2020), and Yamuna River and its canals of India (Kaushik et al. 2008). Some synthetic organic pesticides (e.g., chlorinated hydrocarbons) do not contaminate water though there is evidence of their sustainability in the food chain. Conversely, the quick decomposition behavior of particular pesticides (organophosphorus) allows them to contaminate water occasionally. Pesticides that cannot be absorbed in soil (carbamate) are also available cases of surface water contamination from these substances. Around eight pesticides (AMPA, dieldrin, metolachlor, atrazine, chlorpyrifos, CIAT, desulfinyl fipronil, glyphosate) were identified as having a detection rate of 66–84% from 38 streams of the USA (Bradley et al. 2017), left warning message for a future challenge.

Dyes are another significant source of aquatic pollution from different industries such as textiles, silk factories, printing industries, and so on. Dyes are organic compounds with complex chemical structures and high affinity to water (Mahapatra 2016). Thus, they quickly find their way to aquatic ecosystems and are hard to remove by traditional treatment methods (Hassan and Carr 2018). There are several dyes, including direct, reactive, acid, metal complex, disperse, and coating materials, and all these dyes can create a mixture of dye wastewater (Parthasarathy et al. 2022). Only 1500 types of dye with different chemical compositions have been reported though this number is more than 5000 (Lyubomirs 1987).

In contrast, dyes are categorized depending on their application methods and chemical structure (Marcucci et al. 2001). The quality of wastewater discharged from the dye industries varies and contains dyes, acids, alkalis, and other impurities. The dyes can reach the aquatic environment directly from wastewater discharge from dye industries. Moreover, mixed wastewater effluents from different spinning and knitting plants are also a source of dyes that contaminate water. Mostly, these dyes reach aquatic environments through industrial effluents without any treatment (Bhatia 2017). These dyes are non-biodegradable and persist in the waterbodies once they enter (Orts et al. 2018).

Increased plastic production worldwide and widespread utilization are becoming a significant concern in the present world because of microplastic pollution in every compartment of the environment, especially the aquatic environment. Microplastic is plastic particles having less than 5 mm dimension. About 10–15% of the produced plastic is direct waste annually, which is alarming, and land-based plastics source is the primary source of plastic pollution in aquatic water bodies (Andrady 2011). The presence of microplastic in the marine environment was recorded in the early 1970s (Carpenter and Smith 1972). This scenario is increasing day by day because of several factors. Different ways of microplastic transportation toward the aquatic environment include indiscriminate waste dumping and management, plastic manufacturing industries, sewage management, personal care products, fishing activities, and seashore activities (UNEP 2009). Consequently, microplastics are entering deliberately into the marine environment, and their accumulation and persistence are more alarming (Cole et al. 2011). Moreover, vast quantities of microplastic pollution were recorded in freshwater habitats (Dris et al. 2015; Eerkes-Medrano et al. 2015).

4 Impact of EPs

All groups of EPs are discharged to water resources and the environment via a broad spectrum of sources, including agricultural runoff, aquaculture, animal feeding operations, domestic and industrial wastewater, hospital and industrial waste streams, landfill leachate, final products, chemical and recycling industry, and effluent discharge from wastewater treatment plants (Gwenzi et al. 2022b; Ilyas et al. 2022; Castiglioni and Zuccato 2010). EPs are synthetic persistent organic chemicals and toxic substances, which means they are not easily degraded in the environment and remain for extended periods. In addition, they are not routinely monitored in the environment. Consequently, they can potentially negatively impact the health of humans and the ecosystem (Sairam et al. 2023; Nataraj 2022; Vasilachi et al. 2021).

4.1 Impact on Environment (Geo-, Hydro-, and Atmosphere)

EPs are frequently found in many parts of the environment, particularly water, soil, and air; nevertheless, they are most effective in aquatic environments. The earliest EPs were found to exist in aquatic habitats at the beginning of the 1800s (Nawaz and Ahmad 2022; Vasilachi et al. 2021). Several studies confirmed EPs such as nanomaterials (NMs) and polycyclic aromatic hydrocarbons (PAHs) (Bayabil et al. 2022; Sairam et al. 2023; Yan et al. 2010), pharmaceuticals (Barroso et al. 2019; Mandaric et al. 2016; Nataraj 2022; Kurwadkar et al. 2015), perfluorinated compounds (PFCs) (Mandaric et al. 2016; Wang et al. 2018), microplastics (MPs) (Enyoh et al. 2020; Sairam et al. 2023; Yardy et al. 2022), pesticides (Khan et al. 2023; Sairam et al. 2023; Zhang et al. 2009), and heavy metals (Calvo-Flores et al. 2018; Haroon et al. 2022) in the water, soil, and air environment. However, EPs are considered hazardous when their concentration is between 10 and 100 mg/L, toxic when their concentration is between 1 and 10 mg/L, and extremely toxic when their concentration is less than 1 mg/L to water resources (Khan et al. 2022). Another study by Vasilachi et al. (2021) showed that EPs could be found in water in a wide range of amounts, from ng/L to g/L, and their effects on living things include toxicological effects, disruption of hormones, and both short- and long-term toxicity. Pesticides present in surface water can be transported over significant distances. Pesticides in rivers can be detected over long distances of up to hundreds of kilometers (Zhang et al. 2009). Introducing additives (i.e., plasticizers, heat stabilizers, colorants, foaming agents) from MPs exacerbates water pollution in the environment (Zhao et al. 2022). According to Richardson and Kimura (2020), perfluorooctane sulfonate (PFOS) was identified as the primary chemical compound detected in the river water, with concentrations reaching as high as 3.91 ng/L. The presence of various active pharmaceutical ingredients, including paracetamol, ibuprofen, 2-hydroxy ibuprofen, CBZ-diol, oxazepam, iopromide, and clofibrac acid, has been detected in freshwater lakes (Nataraj 2022). Various caffeine metabolites, including paraxanthine, 3-methylxanthine, 1-methylxanthine, and theophylline, have been found in the groundwater (Calvo-Flores et al. 2018). Pharmaceuticals degraded water quality, perturbed aquatic flora and fauna, and negatively affected organisms. Antibiotics such as norfloxacin, SMX, and erythromycin are the pharmaceuticals with the highest risk to algae, fish, and invertebrates (Zhao et al. 2018). *Toxins* are molecules, peptides, or proteins that can cause disease through direct contact or absorption by body tissues by interacting with enzymes or cellular receptors. Brevetoxins, commonly known as “red tide” toxins, are frequently detected in coastal waters, resulting in water contamination and poisoning (Calvo-Flores et al. 2018). The buildup of EPs within soil has diminished soil productivity, decreased microbial activity, and decreased crop yield (Sairam et al. 2023). For instance, MPs have the potential to cause harm to the structure of the soil, reduce its density, and impede its ability to infiltrate water. In addition, MPs may contribute to decreased dissolved organic phosphorus, nitrogen, and carbon levels in the soil. In the soil environment, MPs accumulate significant amounts of organic matter or

heavy metal pollutants, including but not limited to pesticides and metals like copper. Eventually, these pollutants have the potential to hinder microbial growth (Ding et al. 2022; Guo et al. 2022). NMs are distributed throughout the soil and induce alterations in the aggregation of soil particles, the capacity for suspension, the bioavailability, and the transportation of such particles (Sairam et al. 2023). Once antibiotics are introduced into the soil, they have the potential to alter the composition of the microorganism community. This is because even antibiotics with a wide range of activity can have selective effects on different microorganism groups (Botelho et al. 2015). The degradation of pesticides can interact with the soil, soil microbes, and biochemical processes, ultimately impacting microbial diversity and enzyme activity (Khan et al. 2023). The primary EPs detected in the surrounding atmosphere are predominantly volatile organic compounds, such as benzene, chlorobenzene, 1,2-dichlorobenzene, 1,3-dichlorobenzene, particulate matter, and microorganisms. The inhalation of these pollutants can potentially induce a range of respiratory disorders (Egbuna et al. 2021). Brominated flame retardants (BFRs) have been detected in both indoor and outdoor air samples. Due to their hydrophobic nature, most BFRs exhibit an affinity for particulate matter, specifically dust, in the atmosphere (Yan et al. 2010). There is evidence of the presence of pesticides in the atmosphere across the world, with a diverse range of pesticides being detected in precipitation, such as air, rain, snow, and fog. The phenomenon of gas vapors of pesticides in motion is called vapor drift, which is not perceptible to the naked eye (Zhang et al. 2009). Fine dust particles containing toxic elements, such as heavy metals, have the potential to enter the atmosphere and negatively impact air quality (Calvo-Flores et al. 2018). For reference, the annual emission of chromium (Cr) into the atmosphere amounts to 30,000 metric tons (Haroon et al. 2022). MPs have found fibrous MPs to exist in the atmosphere. For instance, at one urban site and one suburban site in the Paris Megacity, fibrous MPs were detected in the total atmospheric fallout, including dry and wet deposition (Gasperi et al. 2018).

4.2 Impact on Aquatic Organisms

EPs metabolites and environmental transformation products should be routinely monitored (mentioned earlier). EPs' destiny, behavior, and ecotoxicological impacts are unknown in existing procedures and regulatory bodies. Despite the absence of information and monitoring, our study synthesized some harmful effects on aquatic creatures from literature studies. Highly toxic EPs can have a wide variety of impacts on aquatic creatures (see Table 2), including genotoxicity, carcinogenicity in laboratory animals, endocrine disruption, immunological toxicity, and hormonal interference in fish (Vasilachi et al. 2021). Fish and shellfish exhibit elevated levels of toxic elements, including As, Cd, and Hg, making them a significant concern for human consumption. The species of shellfish have been observed to exhibit the highest values for total As, with values reaching up to 50 mg/kg ww. Similarly, the highest values for Cd have been detected in the liver of certain fish and the

Table 2 Emerging pollutants—an inextricable burden for living organisms of aquatic environment

Emerging organic contaminants	Organisms	Exposure route and concentration	Health risks or impacts
<i>Pharmaceuticals and personal care products (PPCPs)</i>			
Diuron (herbicide), triclosan (antimicrobial)	River biofilm communities	—	Biofilm recovery after exposure to short-term pulses of triclosan and diuron
Fluoxetine (antidepressant), citalopram (antidepressant)	Algal and invertebrate benthic communities	Concentrations of fluoxetine of 20 µg/L	Suppression of primary productivity and community respiration on biofilms (algae). Increased stream insect emergence
Oxazepam (antidepressant)	European perch (<i>Perca fluviatilis</i>)	Oxazepam concentrations ranged between 11 and 24 µg/L	Increased feeding rates and locomotor activity (direct); implications for prey populations (indirect)
Triclosan (antimicrobial)	Stream benthic communities	Triclosan (antimicrobial) concentration of 1–10 µg/L	Increase in abundance of triclosan-resistant bacteria and stimulation of periphyton growth
Wastewater treatment plant (WWTP) effluent	Benthic bacterial communities	—	Field experiment changes in bacterial abundance and community composition above and below WWTPs
Organophosphates: Tris (2-butoxyethyl) phosphate (TBOEP), Tris (2-chloroethyl) phosphate (TCEP)	Atlantic salmon (<i>Salmo salar</i>) fish	—	Increased neural- and inter-renal steroid genesis
Oxybenzone	Tadpoles (<i>Bufo arabicus</i>)	—	Malformation, teratogenicity, and neurodegenerative effects
Cimetidine (antihistamine)	Invertebrates (<i>Gammarus fasciatus</i> and <i>Psephenus herricki</i>)	Surface waters (0.07–70.0 µg/L)	Reduced growth and biomass of <i>Gammarus fasciatus</i> , low survivorship of <i>Psephenus herricki</i> when exposed to high concentrations

(continued)

Table 2 (continued)

Emerging organic contaminants	Organisms	Exposure route and concentration	Health risks or impacts
<i>Surfactants</i>			
Anionic surfactant [linear alkyl benzene sulphonate (LAS)]	Fresh and brackish water shrimp (<i>Desmoscaris trispinosa</i> and <i>Palaemonetes africanus</i>)	(31.25, 62.5, 125, 250, and 500 mg/kg) of the chemical (Neatex)	Mean mortality and estimated lethal concentration LL_C values varied with species type, concentration, and exposure duration
Alkyl benzene sulphonate (LAS) homologues (C10 and C13)	Marine microalgae (<i>Nannochloropsis gaditana</i> , <i>Tetraselmis suecica</i> , <i>Rhodomonas salina</i> , and <i>Isochrysis galbana</i>)	–	The inhibitor effect was higher for the C13 LAS homologue than for C11. Among microalgae species, <i>Rhodomonas salina</i> exhibited the highest sensitivity.
Linear alkyl benzene sulphonates (LAS)	Marine benthic organisms, marine mud shrimp (<i>Corophium volutator</i>)	–	Mortality was recorded
<i>Flame retardants</i>			
PBDE congeners	Marine mammal species harbor seal (<i>Phoca vitulina</i>) and harbor porpoise (<i>Phocoena phocoena</i>)	–	The lipid-normalized levels of the six major PBDE congeners in fish were similar to the levels in the invertebrates, but a biomagnification step in concentrations of generally more than an order of magnitude occurred from gadoid fish to marine mammals.
Brominated flame retardants (BFRs)	Four invertebrate species: polar cod (<i>Boreogadus saida</i>), ringed seals (<i>Pusa hispida</i>), and polar bears (<i>Ursus maritimus</i>)	–	A noticeable exception occurred at the highest trophic level, the polar bear, in which only BDE-153 was found to increase from its main prey, the ringed seal, indicating that

(continued)

Table 2 (continued)

Emerging organic contaminants	Organisms	Exposure route and concentration	Health risks or impacts
			polar bears appear to be able to metabolize and biodegrade most BFRs
Brominated and chlorinated flame retardants (hexabromocyclododecane (HBCD) and dechlorane plus (DP))	White croaker (<i>Genyonemus lineatus</i>); shiner surfperch (<i>Cymatogaster aggregata</i>); double-crested cormorant (<i>Phalacrocorax auritus</i>); harbor seal (<i>Phoca vitulina</i>)	PBDEs, HBCD, and DP, respectively, were 4.3, 0.3, and 0.2 ng/g dry weight	Bioaccumulation of flame retardants was recorded in all species
<i>Endocrine-disrupting compounds</i>			
Natural and synthetic steroidal estrogens and chemicals that mimic estrogens	Male roach, <i>Rutilus rutilus</i>	—	Concentrations of the egg-yolk protein vitellogenin are elevated, sex steroid hormone dynamics are altered, and gonad development is disrupted. Individuals produce low-quality sperm
Persistent and nonpersistent pesticide	American alligator (<i>Alligator mississippiensis</i>)	—	Altered plasma hormone concentrations, reproductive tract anatomy, and hepatic functioning, impaired reproductive development, and abnormalities of the reproductive system in alligators
Pharmaceuticals (ibuprofen, fluoxetine, and ciprofloxacin)	Fish	Pharmaceuticals concentrations of 6, 10, and 10 µg/L, respectively [low treatment (LT)]; 60, 100, and 100 µg/L, respectively [medium treatment (MT)]; and 600, 1000, and	Fish mortality occurred in the MT. Phytoplankton increased in abundance and decreased in diversity. Zooplankton also showed increased abundance and

(continued)

Table 2 (continued)

Emerging organic contaminants	Organisms	Exposure route and concentration	Health risks or impacts
		1000 µg/L, respectively [high treatment (HT)]	decreased in diversity in the HT No data reported on the effects of interaction of 3 pharmaceuticals
Caffeine (CF), acetaminophen (AC), and diclofenac (DF)	Algal, cyanobacterial, and bacterial biomass	AC, CF, DF, AC +CF, AC +DF, CF +DF, AC+CF +DF at 5 µg/L	Algal biomass was unaffected by AC or CF in combination with DF but significantly reduced by all other treatments Cyanobacterial biomass was influenced only by the AC + DF application All treatments other than AC resulted in a significant decrease in bacterial biomass Diclofenac or DF + CF and DF + AC resulted in increases in micrometazoan grazing
Anionic [sodium dodecyl sulphate (SDS)], cationic [dodecyl dimethyl benzyl ammonium chloride (1227)], and nonionic [fatty alcohol polyoxyethylene ether (AEO)]	Zebrafish larval (<i>Danio rerio</i>)	AEO at up to 1 µg/mL	EO exposure resulted in smaller head size, smaller eye size, and shorter body length
Carcinogenic polyaromatic hydrocarbons (PAHs), polybrominated diphenyl ethers (PBDEs) and polychlorinated biphenyls (PCBs), and toxic chemicals (PBTs), and emergent contaminants of concern (ECCs)	White sturgeon (<i>Acipenser transmontanus</i>)	—	Organ tissues such as the liver and gonad contained high lipid content

(continued)

Table 2 (continued)

Emerging organic contaminants	Organisms	Exposure route and concentration	Health risks or impacts
<i>Illicit drugs</i>			
Caffeine (stimulant), acetaminophen (pain reliever), diclofenac (anti-inflammatory)	Protozoa, micrometazoa, and algae	—	Increased abundance of organisms and feeding activity (direct), decreased biofilm (algal) biomass (indirect)
Amphetamine (illicit drug)	Stream benthic communities	Amphetamine concentration of (3–630 ng/L) and 1 µg/L	Suppression of gross primary production on autotrophic biofilms, compositional shift of bacterial and biofilm communities, increased dipteran (stream insect) emergence

From Gwenzi, W., Simbanegavi, T. T., Marumure, J., & Zakio Makuvara. 2022. Ecological health risks of emerging organic contaminants. In W. Gwenzi (Ed.), *Emerging Contaminants in the Terrestrial-Aquatic-Atmosphere Continuum: Occurrence, Health Risks, and Mitigation*. 215–242. <https://doi.org/10.1016/B978-0-323-90051-5.00011-0>. Used with permission of Elsevier Limited

hepatopancreas of crustaceans, with values reaching up to 30.0 mg/kg. Furthermore, the methylmercury form of the Hg is highly poisonous to various types of aquatic fauna (Calvo-Flores et al. 2018).

Pesticides encompass a diverse array of chemical compounds that have the potential to leach into waterways, leading to deleterious effects on aquatic organisms, including but not limited to bone degradation in fish (Khan et al. 2023). The effects of EDCs in wastewater on aquatic organisms, including estrogenic and androgenic contaminants, have been found to impact fecundity. Among small fish, 17 β-estradiol has been identified as the most sensitive to these contaminants. Prolonged exposure to parabens, even at low levels, may induce vitellogenin synthesis in fish (Arman et al. 2021; Zhao et al. 2018). Pharmaceuticals and personal care products (PPCPs), such as triclosan and sunscreen compounds, have bioaccumulated in fish. Mottaleb et al. (2015) and Champagne (2009) investigated the drugs in medaka fish (*Oryzias latipes*), cocaine in zebra mussels (Gwenzi et al. 2022b; Sultana et al. 2023), and diclofenac in rainbow trout (*Oncorhynchus mykiss*) (Svanfelt et al. 2010). The ingestion of MPs by fish has been found to result in liver poisoning and inflammation potentially. For instance, in the zebrafish (*Danio rerio*) investigation, 5-µm polystyrene (PS) MPs were distributed throughout the gills, liver, and gut, while 20-µm PS MPs were gathered in the gills and stomach. MPs build up in zebrafish embryos' chorion, yolk sac, endotherm, muscle fibers, eye, and spinal cord (see Fig. 2) (Anwaruzzaman et al. 2022; Zhao et al. 2022). Marine toxins

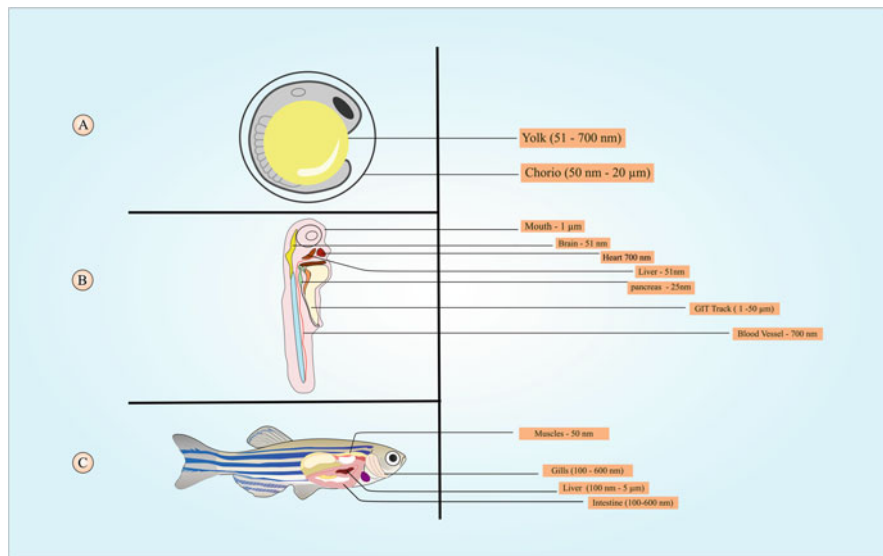


Fig. 2 Accumulation of EPs (micro- and nano plastic) in different organs of *Danio rerio* (A: embryo; B: larvae and C: adult) (adapted from Anwaruzzaman et al. 2022)

such as Spirolides, Gymnodimines, Pinnatoxins, and Pteriatoxins have been identified in shellfish. Tetrodotoxin has been detected in the Tetraodontidae family of puffer fish, while ciguatoxins have been identified in *Seriola* spp. (Calvo-Flores et al. 2018).

In a study, exposure of the green shore crabs (*Carcinus maenas*) to varying concentrations of diclofenac ranged from 10 to 100 ng/L, over a period of 7 days. Also, another study found that exposure to MPs also had a similar effect on the shore crabs (*Carcinus maenas*) (Gwenzi et al. 2022a; Svanfelt et al. 2010). Aquatic species may be exposed to ecological dangers from surfactants. Gwenzi et al. (2022b) examined how *Desmoscaris trispinosa* and *Palaemonetes africanus*, two species of fresh and brackish water shrimp, responded to the anionic surfactant linear alkyl benzene sulphonate. The utilization of diclofenac in veterinary medicine has been found to be the cause of renal failure among avian species specifically vultures, thereby contributing to a significant reduction of over 95% in the vulture population in Pakistan.

According to experts, the loss of vultures is estimated to be around 40 million, regarded as the most severe case of wildlife poisoning to date, surpassing the number of birds impacted by DDT a few decades ago (Richardson and Kimura 2020) and investigated the accumulation of PFOS and its associated adverse effects in two avian species, namely the great tit (*Parus major*) and the blue tit (*Cyanistes caeruleus*).

The measured concentrations of PFOS were 86–2788 and 317–3322 ng/g ww for tremendous and blue tits, respectively. Zhang et al. (2009) found out the presence of

DDT in western gulls (*Larus occidentalis*), Bolong et al. (2009) examined the organochlorine compounds such as PCBs and DDT in Baltic seals, which lead to the syndrome of embryonic abnormalities, and Yan et al. (2010) showed that the PBDEs had been detected in avian species inhabiting the Baltic and North Sea regions. Teratogenic, estrogenic, and other physiological abnormalities may occur in developing mammalian embryos exposed to endocrine disruptors such as phytoestrogens (Arman et al. 2021). The presence of MPs has been found to have adverse impacts on various species, such as water turtles, whales, harbor seals, and polar bears. For example, the prevalence of MPs' ingestion among sea turtles in Brazil totals 60.5% (Anwaruzzaman et al. 2022). Caffeine toxicity has been observed in sea urchins and coral, as documented in Bruton et al. (2010). Calvo-Flores et al. (2018) laid out the detection of carbaryl insecticides in corals. MPs have also been found in sea urchins and corals, as noted by Anwaruzzaman et al. (2022). Furthermore, a study by Egbuna et al. (2021) detailed the occurrence of oxybenzone identified in corals. Arman et al. (2021), Nataraj (2022), and Champagne (2009) reviewed that triclocarban and triclosan are harmful to algae, phytoplankton, and invertebrate. Pereira et al. (2015) indicated surfactants in microorganisms such as *Vibrio fischeri*, *Ceriodaphnia dubia*, *Carassius auratus*, *Artemia salina*, and *Daphnia magna*; Calvo-Flores et al. (2018) found cigarette butts in freshwater microorganisms; Bruton et al. (2010) stated that caffeine disrupts the structure of dictyosomes; Calvo-Flores et al. (2018) showed metalaxyl fungicide is toxic to algae and zooplankton; Zhao et al. (2022) showed that MPs reduced the chlorophyll content of algae; Hyder et al. (2022) and Sultana et al. (2023) indicated that antibiotics such as amoxicillin, benzylpenicillin, and sarafloxacin are toxic to cyanobacteria (blue-green algae); and Richardson and Kimura (2020) studied NMs toxicity in *Daphnia magna* and *Vibrio fischeri*.

4.3 Impact on Biodiversity

'Biodiversity' is an expression for 'biological diversity,' and at first glance, the notion seems straightforward as well: biodiversity is the whole of all biotic variation, from the level of genes to that of ecosystems (Purvis and Hector 2000). The utilization of pesticides could potentially result in adverse effects on the population of earthworms. Carbamate insecticides exhibit high toxicity toward earthworms (Khan et al. 2023). The utilization of insecticides has the potential to cause negative impacts on non-targeted pollinators such as honeybees and *Lepidoptera*, as well as insects like *Ephemeroptera* and *Trichoptera* (Ilyas et al. 2022). Parolini et al. (2022) investigated the accumulation of PFOS in various invertebrates, including earthworms (family Lumbricidae), slugs (order Stylommatophora), millipedes (class Diplopoda), and woodlice (order Isopoda). Parolini et al. (2022) and Pereira et al. (2015) studied that the black-spotted frog (*Rana nigromaculata*) exhibits an accumulation of PFAS in its liver, while TBBPA has teratogenic effects on *Xenopus tropicalis* embryos. Freshwater biodiversity is threatened by harmful algal blooms.

Certain outcomes may lead to the death of fish, either indirectly by decreasing the availability of dissolved oxygen or directly via the production of toxins (Reid et al. 2019). Mueller et al. (2023) indicated EDCs have detrimental effects on the reproductive systems of both vertebrate and invertebrate species. These effects include impaired reproduction, biased sex ratios, decreased fertility, and an increased risk of declining species diversity and populations. Polar bears, snails, and insects are among the species that have been found to be negatively impacted by EDCs. In addition, the impacts on wildlife are related to kidney injury and genotoxicity due to exposure to Cd and Cr bioaccumulates in aquatic and terrestrial habitats. Triclosan and its decomposition products are frequently found to contaminate biodiversity (Rathi et al. 2021). Both DEHP and MEHP have been found to induce toxic effects in the liver, kidneys, and testicles of rats and mice (Pereira et al. 2015). The macroinvertebrate community, comprising numerous species inhabiting various materials dispersed on the riverbed (e.g., bedrock, stones, sediments) along with organic matter like wood, leaves, or aquatic vegetation, is susceptible to the damaging effects of EPs (Mandaric et al. 2016). MPs have negative effects on earthworm survival growth and digestive health after being consumed. Soil microorganisms are another target of MPs' toxic effects. There are a number of microorganisms capable of accelerating polyurethane breakdown, including *Cladosporium cladosporioides*, *Xepiculopsis graminea*, *Penicillium griseofulvum*, and *Leptosphaeria* sp. (Ding et al. 2022; Guo et al. 2022).

4.4 Impact on Human

Bioaccumulation belongs to the buildup of a harmful substance within an organism, while biomagnification deals with the amplification of the concentration of a particular pollutant throughout a given food chain (Ali and Khan 2019; Chacón et al. 2022). It has been discovered that fish-eating birds and marine mammals may contain quantities of persistent organic pollutants (POPs) that are several times higher than those found in the fish on which they feed (Bolong et al. 2009). EPs are transported from non-living surroundings to living organisms, where they accumulate within biota across various trophic levels, ultimately leading to the contamination of food chains or webs. The transfer of EPs through trophic levels in food webs has major implications for human health (see Fig. 3) (Ali and Khan 2019).

For example, pesticides including DDT have the ability to accumulate in the fat cells of both humans and other animal species (Chacón et al. 2022). Briefly, we have listed some adverse human health impacts in various literature studies. Exposure to PAHs is known to result in various health issues such as eye irritation, vomiting, skin disease, diarrhea, nausea, allergy, and confusion. Of the 60 PAHs that were analyzed, benzopyrene was classified as having cancer-causing effects in humans (Bayabil et al. 2022; Sairam et al. 2023). Nawaz and Ahmad (2022), Bolong et al. (2009), Chacón et al. (2022), and Ilyas et al. (2022) have shown that the presence and

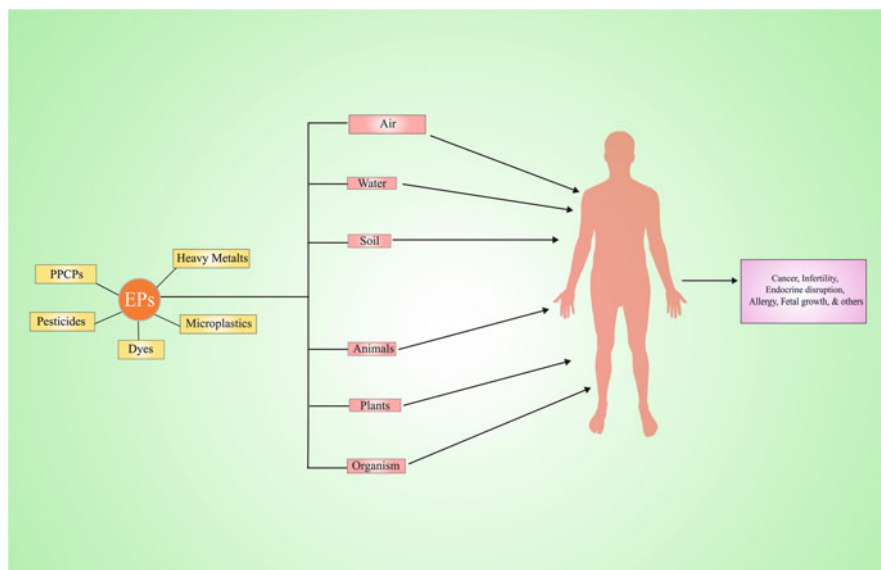


Fig. 3 Impact on human from the exposure of EPs (adapted from Calvo-Flores et al. 2018)

exposure to EDCs may lead to reproductive disorders such as a 50% decrease in sperm count, reduced fertility, breast and cervical cancer in women, prostate cancer in men, premature start of puberty, and genital abnormalities. In addition, PCBs have been linked to adverse effects on cognitive function, including nervous disorders, decreased IQ, and difficulties with thinking and writing skills in human populations. The use of dyes both in terms of color and odor has been linked to various health issues in humans. These include allergic reactions, skin irritations, and dermatitis. For instance, benzidine-derived azo dyes have been found to possess carcinogenic properties in humans, specifically in relation to bladder cancer. Nawaz and Ahmad (2022) have shown toxic effects of heavy metals such as Pb on fertility, hormones, and irregularities in the menstrual cycle. The ingestion of Cd has been found to result in adverse health effects such as vomiting, diarrhea, bone deformation, and liver and kidney damage. Chromium and mercury are known to cause skin allergies, ulceration, nervous toxicity, and immune system disorders.

5 Reducing the Burden of Emerging Pollutants Following Algae-Based Bioremediation

Microalgae play a crucial role in the bioremediation of inorganic, organic, and emerging pollutants. There are various kinds of reaction mechanisms that have been involved during the remediation of toxic pollutants such as biouptake, bioaccumulation, biosorption, biodegradation, and photodegradation.

5.1 Biosorption

The biosorption process involves the binding of pollutant to the surface or intracellular compartments of microalgae. It is the most convenient technique for the removal of heavy metals, pesticide, dye, and pharmaceutical or personal care products from wastewater. Algae is a potential biosorbent due to the existence of proteins, lipids, and polysaccharides on their surface, which provide adsorption sites (El-Naggar et al. 2018). There are two types of biosorption: physisorption and chemisorption. Chemisorption is when molecular bonds are made. Physisorption happens when the molecules of the solute encounter the binding sites on the surface of the sorbent. This approach is beneficial considering that it is not much expensive, it is easy to use, it does not make sludge, and it can clean up big amounts of wastewater with low concentrations of pollutants. Mainly heavy metals are generally facilitating the absorption in cell wall surface through swapping ions by physisorption or chemisorption (Gondi et al. 2022). The composition of the algal cell wall is important for electrostatic attraction and chelation or complexation, which in turn affects the efficiency of algal biosorption. Effective algal bioremediation can be attributed to the presence of functional groups, such as the carboxyl group, on the cell surface of algae (Inyang et al. 2016). Positive EPs react with the negatively charged microalgal cell wall during the biosorption process. The rate of biosorption is affected by several variables, the most prominent of which are dissolved oxygen concentration, starting pH, hydraulic retention time, and emerging pollutant concentration. Because of their higher porosity and surface area, carbon generated from MOFs is under consideration (Hao et al. 2021). Studies have shown that heavy metals including lead, mercury, arsenic, uranium, and barium are efficiently removed about 73–100 % with microalgae such as *Chlorella* sp., *Coelastrum proboscideum*, *Mougeotia genuflexa*, *Ulothrix cylindricum*, and so on. The role of biosorption in the overall elimination depends on intrinsic features of pharmaceutical contaminants and algal species. Studies found that sulfadiazine, cephalixin, 7-aminocephalosporanic acid, propylparaben, and many other pharmaceutical compounds are remediated 44–100% from using diverse group of microalgae species. Atenolol (99%) and propylparaben (80–100%) demonstrated maximum biosorption when induced by *Tetradesmus dimorphus*, *C. vulgaris*, *Phormidium* sp., *Scenedesmus acuminatus*, *Pseudanabaena acicularis*, and *Scenedesmus acutus* (Table 3). In addition, removal approaches through absorption find pesticides, dye, and some microplastics. As a consequence of this, the process of biosorption might not play a significant part in the elimination of emerging contaminants for certain pollutants, whereas other processes might have more significant role.

Table 3 Potential microalgae, their working mechanism, and efficiency to reduce different emerging pollutants

Category	Name	Algae name	Mechanism	Removing efficiency (%)	Reference
Pharmaceuticals	Sulfadiazine	<i>Chlamydomonas</i> sp. <i>Tai-03</i>	Biodegradation, photodegradation, biosorption, and hydrolysis	54.51	Xie et al. (2019)
	Amoxicillin	<i>C. regularis</i>	Biodegradation	88	Zhang et al. (2021)
	Cefradine	<i>C. pyrenoidosa</i>	Biodegradation	90	Guo and Chen (2015)
	Cephalexin	<i>C. regularis</i>	Biosorption, biodegradation	95	Zahra et al. (2023)
	7-Aminocephalosporanic acid	<i>Chlorella pyrenoidosa</i>	Biosorption, bioaccumulation, biodegradation	96.07	
	Propylparaben	<i>C. vulgaris</i>	Photodegradation, biosorption, volatilization	80–100	Vale et al. (2022)
		<i>Phormidium</i> sp.			
		<i>Scenedesmus acuminatus</i>			
		<i>Pseudanabaena acicularis</i>			
		<i>Scenedesmus acutus</i>			
	Atenolol	<i>Navicula</i> sp.	Biodegradation, bioaccumulation, photodegradation	93	Ding et al. (2020)
		<i>Tetradesmus dimorphus</i>		99	Gentili and Fick (2017)
	Hydrochlorothiazide	<i>Mixed microalgae culture</i>	Biodegradation	44–84	Hom-Diaz et al. (2017)
	4-Androstene-3,17-dione	<i>Chlamydomonas reinhardtii</i>	Biodegradation	83	Silva et al. (2019)
		<i>Scenedesmus obliquus</i>			
	<i>Chlorella pyrenoidosa</i>				
	<i>Chlorella vulgaris</i>				
Sulfadimethoxine	<i>C. reinhardtii</i> , <i>S. obliquus</i> , <i>C. pyrenoidosa</i> , <i>C. vulgaris</i>	Biodegradation	56–78	Zhou et al. (2014)	
Sulfamer			81–88		

(continued)

Table 3 (continued)

Category	Name	Algae name	Mechanism	Removing efficiency (%)	Reference
Heavy metals	Tributyltin	<i>Chlorella vulgaris</i>	Biosorption, biodegradation	>90	Luan et al. (2006)
	Lead	<i>Coelastrum proboscideum</i>	Biosorption	100	Molazadeh et al. (2015)
		<i>Chlorella pyrenoidosa</i>		93	
		<i>Aphanothece</i> sp.		80	
	Mercury	<i>Chlorella vulgaris</i>	Biosorption	72.9	Goswami et al. (2022)
		<i>Spirogyra</i> sp.		76	
Arsenic	<i>Mougeotia genuflexa</i>	Biosorption	96–98		
	<i>Ulothrix cylindricum</i>				
Uranium	<i>Nostoc</i> sp.	Biosorption	60	Ismail et al. (2022)	
Barium	<i>Nannochloropsis</i> sp.	Bioaccumulation	88–99	Theegala et al. (2001)	
Pesticides	Fluroxypyr	<i>C. reinhardtii</i>	Bioaccumulation, biodegradation	57	Zhang et al. (2011)
	Imidacloprid	<i>Scenedesmus</i> sp.	Biodegradation	71.24	Goh et al. (2023)
		<i>Chlorella</i> sp.		57–62	
	Naphthalene	<i>Chlamydomonas angulosa</i>	Biodegradation	60–98	Mondal et al. (2019)
Glyphosate	<i>Oscillatoria limnetica</i>	Biodegradation	90–99	Salman and Abdul-Adel (2015)	
Dye	Pyrene	<i>Oscillatoria</i> sp.	Biodegradation	95	Aldaby and Mawad (2019)
	Indigo	<i>Phormidium</i> sp.	Biodegradation	91.2	Dellamatrice et al. (2017)

	Methyl red	<i>Nostoc linckia</i>	Biodegradation	82	El-Sheekh et al. (2009)
Microplastics	Orange II	<i>Lyngbya lagerlerimi</i>	Biosorption, biodegradation	47.06	Sarkar and Dey (2021)
		<i>Stoechospermummarginatum</i>		35.62	
	Acenaphthylene	<i>Nannochloropsis oculata</i>	Bioaccumulation	95	Marques et al. (2021)
	Polyethylene terephthalate (PET)	<i>C. reinhardtii</i>	Biodegradation	35	Kim et al. (2020)
	Polystyrene (PS)	<i>Pseudokirchneriella subcapitata</i>	Biosorption	94.5	Padervand et al. (2020)
	Nylon-66	–	–	–	–

5.2 Bioaccumulation

Bioaccumulation occurs when hazardous pollutants, insecticides, and other chemicals build up in the cell's cytoplasm. Bioaccumulation is energy-intensive, is slower than bioaccumulation and biosorption, has distinct routes of pollutants, and usually occurs simultaneously that makes the quantification difficult. Biosorption is the first stage of bioaccumulation where microalgae accumulate emerging contaminants in three ways: passive diffusion, passive-assisted diffusion, and energy-dependent/active uptake across the cell membrane (Sutherland and Ralph 2019).

Emerging contaminants can travel through the cell membrane from high concentration to low concentration via a process known as passive diffusion. The hydrophobic structure of the cell membrane makes this procedure feasible for non-polar and lipid-soluble molecules. Emerging contaminants with a high molecular weight and polarity are unable to penetrate cells by passive diffusion (Sutherland and Ralph 2019). However, in earlier studies researchers had demonstrated that carbamazepine and phthalate acid esters might enter microalgal cells through a process known as passive diffusion (Huang et al. 2019). With the help of transporter proteins, EPs can move through the cell membrane via a process known as passively assisted diffusion. The third process is called energy-driven active transport, and it is responsible for moving EPs from low concentrations to high concentrations using transporter proteins. Microalgae are responsible for this process, which involves the active transfer of EPs into the cell and the subsequent direct utilization of these EPs as a source of carbon (Tiwari et al. 2017).

Microalgae such as *Chlorella pyrenoidosa*, *Navicula* sp., *T. dimorphus*, *C. reinhardtii*, and *Nannochloropsis oculata* have been found to contribute to the removal of pharmaceuticals, pesticides, and dyes such as 7-aminocephalosporanic acid (96.07%), atenolol (93–99%), fluroxypyr (57%), and acenaphthylene (95%) through bioaccumulation (Table 3).

The accumulation of pollutants in microalgae leads to an increase in intracellular antioxidant responses, such as reactive oxygen species (ROS), superoxide dismutase (SOD), catalase (CAT), peroxidase (POD), glutathione s-transferase (GST), glutathione (GSH), and malondialdehyde (MDA), as well as a decrease in chlorophyll fluorescence index (Fv/Fm) and cellular energy allocation (CEA). ROS are produced via proton transfer of triplet-excited Chl-a, which can cause oxidative damage to organelles and cellular components and even programmed cell death in excess. SOD and CAT are important antioxidant enzymes that neutralize free radicals and prevent their toxic effects. Therefore, it is crucial to study the appropriate concentrations of pollutants to avoid cell death and select suitable microalgal strains (Yu et al. 2022).

5.3 Biodegradation

Biodegradation is one of the most efficient ways to remove contaminants from effluents because it breaks down complicated molecules into simple and harmless

chemical building blocks. Bioaccumulation and biosorption use microorganisms as biological filters to concentrate pollutants and separate them from the water, but bioremediation breaks down target pollutants either by complete mineralization to CO₂ and H₂O or by biotransformation, which uses enzymatic reactions to produce metabolic intermediates (Sutherland and Ralph 2019). The best method for eliminating pollutants has been established to be biodegradation.

Biodegradation is responsible for 81.55% of the elimination of 0.5 mg/L sulfamethoxazole by *C. pyrenoidosa*, while bioaccumulation and biosorption accounted for 2.87% and 6.87%, respectively (Gao et al. 2022). In a similar way, another study found that *Chlorella* sp. UTEX1602 was able to remove 87.3% of 156.8 mg/L of thiamphenicol through biodegradation, 0.5% through bioaccumulation, and 4.2% through biosorption (Song et al. 2020). According to Posadas et al. (2014) the ideal wastewater C:N:P ratio for emerging pollutant biodegradability is 100:18:2. Biodegradation has effective capability to reduce toxicity of emerging pollutants in the algal cell walls compared to bioaccumulation and/or biosorption. The biodegradation that occurs by microalgae can take place extracellularly, intracellularly, or in combination. The biodegradation process begins with the synthesis of extracellular materials, which is then followed by the destruction of intracellular breakdown metabolites (Tiwari et al. 2017). Extracellular polymeric substances secreted by microalgae degrade extracellularly. It stays on the outside of the cell walls, which lets microalgae mineralize toxins while they are still in solution and act as an external digestive system. Also, extracellular polymeric substances work as a lubricant in the form of biosurfactants to make pollutants more bioavailable in the environment, thereby facilitating their future bioaccumulation by microalgae. Intracellular biodegradation of pollutants by microalgae is a highly complex process depending on the enzymes and can be divided into three phases. During the initial phase of the process, cytochrome P450 enzymes oxidized, reduced, and hydrolyzed the pollutants. This process also adds a hydroxyl group to lipophilic molecules, which transforms them into hydrophilic ones. During the second step, electrophilic substances form conjugate bonds with glutathione to shield cells from the effects of oxidative damage. Laccases, decarboxylases, carboxylases, and dehydrogenases are all used during the third step of the process. Following the conclusion of these operations, the intermediate pollutants are then discharged back into the surrounding environment. The degradation of sulfamethoxazole by *Chlorella pyrenoidosa* occurs in two-phase reactions. The phase I reactions involve oxidation and hydroxylation of the amine group with subsequent phase II reactions consisting of formylation and pterin-related conjugation (Xiong et al. 2020).

The biodegradability of compounds is primarily influenced by the complexity of their structure. The complexity of pollutants structure is the main factor of biodegradability. Simple compounds with unsaturated structures and electron-donating groups have more tendency to biodegrade at a faster compared to complex compounds with cyclic structures. For example, microalgae such as *S. obliquus*, *Navicula* sp., and *C. pyrenoidosa* have demonstrated up to 95% biodegradability (Ding et al. 2020). The study conducted with *C. regularis*, *P. kessleri*, *Microcystis aeruginosa*, *C. reinhardtii*, and *Scenedesmus* sp. algal species demonstrated better

removal efficiency against wasted pollutants from pharmaceutical and personal care products (Gayosso-Morales et al. 2023).

Also, some studies are conducted for removal of pesticide and dyes by using the algae-based system and effective results were revealed (95% for glyphosate and about 80–95% for other substances (indigo, methyl red, and pyrene)) (Table 3). Various chemical and enzymatic reactions are involved in the degradation process of microalgae. Therefore, it is necessary to conduct further investigation of the reaction mechanisms using omics technology and bioinformatics. Additionally, the degradation products should be studied in detail using mass spectrometry to gain a better understanding of the process.

5.4 *Biouptake*

Effective capability to enter the algal cell wall has emerging pollutants that interact with intracellular proteins. The different between biouptake and bioaccumulation is that biouptake takes place only in living microalgal cells (Mulla et al. 2019). Microalgae are one of the important parts of the environment that uptake the highest amount of unfavorable emerging pollutants. Microalgae have been shown to be an effective and efficient method for detoxifying pharmaceuticals with a lipophilic molecular structure in bioaccumulation (Gattullo et al. 2012). According to Maes et al. (2014), *Desmodesmus subspicatus* remove approximately 23% of 17 α -ethinylestradiol through biouptake process. Other investigations demonstrated that Pb (II) and Cd (II) are highly uptaken by *C. kessleri*. It was also identified that Pb (II) was notably higher uptaken than Cd (II) (Wilde and Benemann 1993). Several kinds of physicochemical parameters are responsible for the biouptake process irrespective of the mechanism like metabolic inhibitor, unhealthy cell wall, pH, and temperature. Although algae can be used in EPs' elimination, biouptake does not offer a long-term remedy while it facilitates only in the breakdown of EPs into other forms. The technique may become unfeasible if the toxic algal biomass is not used to create biofuels or other value-added bioproducts. As a consequence of this, research must be conducted on environmentally friendly methods of algal bioremediation as well as the process of post-treatment, which must include the reduction of the toxicity of emerging pollutants through the use of algal cells.

5.5 *Hydrolysis and Volatilization*

Hydrolysis is an effective breakdown approach to removal EPs from the environment, especially pharmaceuticals compounds. This process is subjected to influence by some physiochemical properties including temperature, pH, and so on. A handful number of studies found hydrolysis pertinent to the chemical structure and pollutants concentration (Gondi et al. 2022). Ampicillin, cefoxitin, cefradine, and amoxicillin

are highly effective in hydrolysis breakdown process. Also their hydrolysis amount demonstrated more alkaline than acidic or neutral nature (Mitchell et al. 2014). The β -lactam antibiotic breaks down through the ring opening process in hydrolysis (7-ACA); due to β -lactam ring opening, amoxicillin facilitates redox, transamination, and decarboxylation reaction (Guo et al. 2016). An experiment showed that sulfadiazine incorporating *Chlamydomonas* sp. Tai-03 removes the substance 54.51% (Xie et al. 2019). On the other hand, volatilization converts the pollutants' liquid state to atmosphere stage depending on physiochemical properties of the substances (likewise Henry's constant, hydrophobicity) and outer conditions (Tran et al. 2018). *C. vulgaris*, *Phormidium* sp., *Scenedesmus acuminatus*, *Pseudanabaena acicularis*, and *Scenedesmus acutus* are found to be involved in propylparaben elimination approximately 80–100% through volatilization (Vale et al. 2022).

5.6 Photodegradation

The approach of EPs through photodegradation could be both direct and indirect. In direct photodegradation, UV radiation breaks down the bonds, aromatic rings, and functional groups of pollutant molecules where there is no association of microalgae (Gondi et al. 2022). Microalgae mainly get involved in indirect photodegradation following the construction of reactive oxygen species (ROS) that destruct harder pollutants. Indirect photodegradation is essential for the transformation of micropollutants, and chlorophyll and enzymes serve as photosensitizers to encourage the biodegradation of pharma-based pollutants. Indirect photodegradation also plays an important role in the removal of other EPs. In the presence of ultraviolet light, photosensitizers release reactive radicals; the efficiency of indirect photolysis is affected by photosensitizers, as well as pH and temperature. Fe^{3+} has the ability to boost the generation of hydroxyl radicals from carboxylic acids generated by *C. vulgaris*, which in turn speeds up the process of bisphenol A's photodegradation (Bai et al. 2022). An increase in the concentration of Fe^{3+} causes a slow but steady rise in the amount of bisphenol A that is removed (Bai et al. 2022). Microalgae drive photodegradation leading to different effects on various pharmaceutical drugs. According to Tian et al. (2019), extracellular organic matter (EOM) influences the photodegradation efficiency of chlortetracycline, and this varies with the change of microalgae species. *Chlamydomonas* sp. Tai-03, *C. vulgaris*, *Phormidium* sp., *Scenedesmus acuminatus*, *Pseudanabaena acicularis*, *Scenedesmus acutus*, *Navicula* sp., and *T. dimorphus* contribute to remove 54.51%, 80–100%, and 93–99% of sulfadiazine, propylparaben, and atenolol, respectively (Table 3). On the other hand, some studies illustrated that UV radiation is more effective than sunlight (32%), simulated natural light (15%), and fluorescent radiation (14%) for cefradine removal employing *C. reinhardtii* species (Jiang et al. 2019).

6 Current and Future Outlook

While aquatic pollution is an ongoing issue, caused by economic growth, industrialization, and urbanization, algae-mediated bioremediation has gained enormous attention for breakdown, removal, and/or biotransformation of emerging pollutants/nutrients which would otherwise lead to eutrophication, imbalanced ecosystem, and cascading food webs (Goh et al. 2023; Touliabah et al. 2022). Instead of using bacteria and physicochemical treatments, algae-based bioremediation of emerging pollutants, including heavy metals, microplastics, oil spills, inorganic pollutants, organic pesticides, etc., has been well adopted (Goh et al. 2023) due to the fact that the uptake of pollutants by algae does not require any oxygen which is a major limiting factor for the bacterial breakdown process. In addition to the reduction of cost (compared to physical and chemical methods), phyco-remediation co-benefits its ecosystem by accelerating carbon sequestration and reducing biological oxygen demand (Dwivedi 2012). Moreover, the versatility of algae-based remediation satisfies the varying nature and extent of pollutants because of their autotrophic, heterotrophic, and mixotrophic metabolic pathways. As a result, intensified research argued for the use of microalgae to remove or biotransform heavy metals, xenobiotics, and microplastics in a sustainable and more efficient manner (Morais et al. 2022).

Algae-based bioremediation is becoming a promising platform for ensuring hygiene society, improving carbon footprints, and contributing circular bioeconomy with several features which offer increasingly important roles in environmental cleanup efforts. Some of the most significant traits of algae-based bioremediation include (1) algae are relatively easy and inexpensive to grow, making them a cost-effective solution for bioremediation; (2) algae can be grown in a variety of environments, from ponds and lakes to bioreactors, and can be scaled up or down depending on the specific application; (3) algae-based bioremediation does not generate additional waste or pollution and has the potential to be used as a source of renewable energy or other valuable products; and (4) algae have been shown to be effective in removing a wide range of pollutants, including heavy metals, organic compounds, and nutrients.

Researchers are exploring the use of algae for treating wastewater and removing nutrients such as nitrogen and phosphorus (Dubey et al. 2023; Vidyashankar and Ravishankar 2016). Certain microalgae have been found to be capable of treating industrial wastewater with higher organic loads, COD, and temperature due to their environmental ability to survive in extremophile and acidophile conditions. For example, *Galdieria sulphuraria*, which can tolerate temperatures up to 56 °C and thrives in acidic pH, is being effectively used in treating industrial wastewater (Ahmad et al. 2021). Algae also show potential for cleaning up oil spills. Researchers are investigating the use of algae as a natural absorbent material to soak up oil from water (Kuttiyathil et al. 2021). This method could potentially be more environmentally friendly than current cleanup methods, which often involve using chemical dispersants. Furthermore, when algae work in collaboration with

certain bacteria, they can absorb heavy metals such as lead, mercury, and cadmium. These consortia exist as a biofloc and could be used further for aquaculture production. However, challenges still exist in selecting compatible strains along with their extent of cooperation and competitiveness. Researchers are investigating ways to optimize algae growth and absorption of heavy metals, potentially leading to a more effective and cost-efficient remediation method. For instance, the development of transgenic *Dunaliella* through editing the Cu-transporter gene has resulted in increased uptake of Cd (Puente-Sánchez et al. 2018). However, overcrowding of microalgae could result in eutrophication, and their optimum abundance must be maintained through proper laboratory-based investigation. Moreover, to accelerate phyco-remediation, the incorporation of pollutant-degrading bacterial genes into algae could be a novel approach. This could potentially enhance the efficiency and specificity of the remediation process, but further research is needed to investigate the effectiveness and safety of this approach.

Algae-based carbon sequestration is indeed a promising method for mitigating the impact of greenhouse gases on the environment. However, more research is required to optimize the natural carbon-capture ability of algae, as well as to identify and develop strains that are most effective at sequestering carbon. Nanobubbles have been proposed as a potential solution for enhancing carbon sequestration by algae (Patel et al. 2021), but further investigation is needed to understand the trade-offs between carbon sequestration and carbon production by the microbial community that decomposes dead algae. In addition to their potential for bioremediation and carbon sequestration, microalgae also have applications in the production of valuable products such as pigments, lipids, and polysaccharides. However, the accumulation of heavy metals and toxic compounds in algae-based products can raise public health concerns (Xiong et al. 2019), and it is important for researchers to assess the persistence and bioaccumulation of these pollutants in algae-based products intended for human consumption or secondary product development. Furthermore, the identification of specific strains with added benefits depending on the nature of the by-products must be regulated through defined risk assessment tools to ensure safety and acceptability (Patel et al. 2022b). For example, the heavy metal-accumulating *Phormidium* strain can break down heavy metals to a limited extent, but the semi-broken heavy metal ions can be more toxic than their natural forms (Shanab et al. 2012).

A significant limitation in current knowledge is the cost-effective harvesting of algal biomass, which needs to be resolved. While many studies have suggested the configuration of microbial communities as a cheap tool to scale up the harvest, the latest trend focuses on recyclable nanoparticles as a viable solution. For example, the magnetic adsorbent capacity of iron nanoparticles has recently gained tremendous attention as an efficient harvesting tool for algal biomass and breaking down certain heavy metals (Patel et al. 2022a). However, it is imperative to better understand the extent of energy bypass, cost-effectiveness, and the potential nano-toxicity of the final harvest.

7 Policy and Recommendations to Take the Edge off EPs

Many countries and regional organizations have established different policies and regulatory frameworks to assess and maintain the safety of EPs throughout their life cycle (for details, see Table 4). These policies and frameworks are in place to ensure that the potential risks associated with these pollutants are identified and managed appropriately. However, the non-existence of an international enforceable regulatory authority makes loops in policy interventions. For example, despite the USA being a significant producer and exporter of waste producing EPs, they did not endorse any conventions (Stockholm, Minamata, Rotterdam, and Basel) (Puri et al. 2023) to protect human and environment health from anthropogenic release and emissions of EPs. Apart from this, many countries substantiated their willingness to comply with terms of international accords and take necessary actions to achieve the objective of sustainable environment management following the approach of environment-friendly industrialization.

One ideal illustration of this is Zimbabwe—one of the lower middle-income countries (LMICs) imposed obligation to attain certificate and registration for insecticides and any commercial medication from the authority of Tobacco Research Board and the Medicines Control (Kosamu et al. 2020). For prudential management of EPs (particularly pharmaceuticals and pesticides) in South Africa, they depend on monocentric South African Health Products Regulatory Authority. Nevertheless, there is evidence of unintentional release of “ghost” synthetic compounds to aquatic environment from laws regarding manufacturer confidentiality, ineffective regulatory system, and unlawful practice of these synthetic substances (Utembe and Gulumian 2015). Contrarily, existing slow, inefficacious, polycentric, and market-oriented approach makes the situation inimical to attaining sustainable management of ECs in many parts of the world. For example, disparate regulations and directives exist for pesticides (Reg (EC) No 1107/2009), pharmaceuticals (Directive 2001b/82/EC), and industrial chemicals (Reg (EC) No 1907/2006a) in the European Union (van Dijk et al. 2021).

The absence of adequate institutes with sufficient capability and regulatory structure to enforce proper policy negatively impacts response to EPs. Below are some recommendations for prudent management of future EPs:

- In this prospect, a holistic approach like omics technology (e.g., transcriptomics, lipidomics, metabolomics, and proteomics) could be integrated within the safety testing guidelines of the World Health Organization and US Environmental Protection Agency in order to develop a more comprehensive guideline for ecological risk assessment prioritizing freshwater systems’ mixture toxicity.
- Existing Pesticide Properties Database (<http://sitem.herts.ac.uk/aeru/ppdb/en/>) could be more updated including consumption data with an engagement of international science-policy body for harmonizing regional and international chemical registration and allocating a digital interface for geo-science-policy reciprocity.

Table 4 Organizational set-up, policies, legislation, and regulatory framework to manage EPs between developed and developing countries (countries were selected based on GDP and information was extracted from different literature including Puri et al. 2023)

	Country	Period	Organization or policies and regulatory response	Benefaction from organization function or policies and regulatory framework
Developed countries	USA	1906	Food and Drug Administration	During formation of any policy assess the associated hazards of chemicals
		1976	Toxic Substances Control Act (TSCA)	Reporting, record-keeping and testing requirements, and restrictions relating to chemical substances and/or mixtures
		Late 1900s and early 2000s	Undocumented regulatory framework	Grow the focus of government about problems from the presence of EPs
		1996	Unregulated Contaminant Monitoring Program	Listed unregulated pollutants with their health effects, occurrence, and exposure level
			US EPA EC program	Formed chemical pollutant list and their standard screening
		2019	Recycled Water Policy	Hazards of EPs evaluation from recycled water
	Europe	2000	Water Framework	Safe drinking water
		2006	Registration, evaluation, authorization, and restriction of chemicals (REACH)	Restricting and monitoring contaminants use. Established the limits of ECs in surface water and cosmetic products
		2008	Directive (2008)/105/EC	Listed 33 priority substances and their environmental quality at standards for surface water
		2009	European legislation (Regulation no. 1223/2009)	Permissible concentration (maximum) of UV filter in cosmetic products
		2015	Inventory, legislation, governance, and policy	Regulate, monitor, and remediate perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA)

(continued)

Table 4 (continued)

	Country	Period	Organization or policies and regulatory response	Benefaction from organization function or policies and regulatory framework
	Australia	1986	Pollution of Waters by Oil and Noxious Substances Act 1986 (Vic)	Protection of the sea and certain waters from pollution by oil and other noxious substances and to implement the MARPOL Convention
			Water Act 1992 (NT)	Regulating ECs in environment
		2005	Cooperative Research Centre for Contamination Assessment and Remediation of the Environment (CRC CARE)	Forming guidelines regarding pollutants of emerging concern
		2009	Environmental Protection (Water) Policy 2009	Regulating ECs in environment
		2011	Australian Drinking Water Guidelines	Constituted National Water Quality Management Strategy
Developed countries	Canada	1999	Canadian Environmental Protection Act (CEPA)	Prevent pollution (hazardous waste, air pollution, greenhouse gas emissions, ocean disposal) with an assessment of dangers of chemicals, polymers, and living things for protecting environment and public health
		2006	Registration, evaluation, authorization, and restriction of chemicals (REACH)	Reduce the releases of tetrabromobisphenol A from industrial sources implementing risk management measures
	Japan	1993	National environmental policy	53 substances designated as "Monitor Substances"
		2002	Drinking Water Quality Standards (DWQS)	Set standards for chemicals (potentially harmful for human health) and methods of their purification. Developed "Annual Water Quality Examination Plan"
Developing countries	Brazil	2014	SES RS 320/2014 ordinance	Regulate flutriafol and epoxiconazole

(continued)

Table 4 (continued)

	Country	Period	Organization or policies and regulatory response	Benefaction from organization function or policies and regulatory framework
		2017	Ordinance Consolidation (Annex XX)	Regulate 21 pesticide contaminants
		2018	National Water Resources Information System (SNIRH)	Consolidate and provide easy access to information (water quality and emerging pollutants data) on water resources in Brazil
	China	Consultation stage	Hazardous Chemicals Safety Law	
		2021	14th Five-Year Plan	Update management system following the assessment and monitoring of chemicals having environmental impact as well as identify high-risk pollutants
		2022	New Pollutant Control Action Plan	Restriction and bans on manufacturing, processing, application, import or export, as well as reduction of discharging new pollutants
	India	1986	Environment Protection Act (EPA)	Framework for environmental protection and management
		1991	India's drinking water standards (IS 10500)	Regulatory standards for particular pesticides
		2006	National Environment Policy (NEP)	Use of clean technologies and environmentally friendly practices for protecting human health and the environment from hazardous substances and pollutants

- For synthetic compounds that hold analogous chemical structure and physico-chemical attributes (e.g., microplastics, homogenous pesticides (organophosphate)), a class-based approach could be developed. In this class-based approach an enantiomer-specific assessment (Sanganyado et al. 2017) of synthetic substances could be performed to discriminate their ecotoxicological behavior and environmental fate.

- For accomplishing zero or minimal emissions of EPs, green synthesis approach (an environment-friendly production process reported by Zimmerman et al. (2020) could be adopted for designing nontoxic, nonpersistent, and nondepleting chemicals.

While river basins are the end points of EPs, an integrated river basin management approach could be developed bestowing the provided tools (e.g., priority mixtures and priority solution identification, simulation and management of chemicals and associated hazards, effect-based monitoring of EPs) from SOLUTIONS project (for a better understanding, see Brack et al. 2015).

8 Concluding Remarks

Unavoidable emerging pollutants in aquatic environments, which have increased due to global economic and population growth, are recognized as the strongest driving force behind the Anthropocene era. They pose significant risks to public health, environmental health, and animal health. These emerging pollutants encompass a wide range of categories, exhibit diverse modes of action, have various routes and sources of entry, vary in persistence levels, and most importantly, exert profound impacts on ecosystems, animals, and humans. The diversity of these pollutants necessitates pollutant-specific control measures, which can be achieved through chemical treatments, physical measures, or biological means. However, these treatments carry inherent risks, such as the potential for introducing additional pollutants into the environment and the cost-effectiveness of the treatment methods employed. Moreover, some treatments, such as chemical interventions, may lead to ecosystem degradation by depleting oxygen levels or causing other unintended consequences.

In light of these challenges, there has been a recent surge in the adoption of algae-mediated wastewater treatment approaches. Algae-based treatment methods offer several advantages, including enhanced pollutant removal efficiency, promotion of healthier aquatic environments, and the potential for the development of eco-friendly by-products. Algae possess the unique ability to efficiently remove and transform pollutants through processes such as absorption, bioaccumulation, biodegradation, biouptake, hydrolysis and volatilization, and photodegradation. Moreover, they have a high growth rate, can thrive in diverse environmental conditions, and require minimal energy inputs compared to traditional treatment methods. These attributes make algae-based bioremediation an economically viable and environmentally friendly option for wastewater treatment. However, the successful implementation of algae-based bioremediation in real-world applications requires careful consideration of several actions, for example, optimizing carbon capturing capacity of algae, improving, and developing strain with better pollutant-degrading ability. Future research should focus on addressing these challenges and exploring the potential synergies between algae-based bioremediation and other wastewater treatment technologies. Additionally, biomass production from algae that can be further utilized for

bioenergy generation, as animal feed, or as a raw material for various industries to ensure circular economy should be taken into account. In promoting sustainable water management practices, the chapter also suggests a range of policy actions at both national and international levels. These recommendations include incorporating algae-based remediation as green approach in national and international development agenda, developing holistic framework for regular monitoring and surveillance by regulatory bodies to ensure country-specific targets and achievements, and endorsing the technology as mitigation and adaptation technology in international conventions.

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Phytomediated Approach for Management of Emerging Pollutants



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Abstract Any manufactured or naturally occurring chemical or microorganism that is not routinely monitored or regulated in the environment and has the potential to have detrimental impacts on the ecosystem and human health might be considered an emerging pollutant. Chemicals from pharmaceuticals, personal care items, insecticides, commercial and domestic goods, metals, surfactants, industrial additives, and solvents make up the majority of these contaminants. These chemicals are being used in industry, transportation, agriculture, and urbanization at a rapid rate, and as a result, more hazardous waste and non-biodegradable substances are being released into the environment. Due to their negative consequences, it is imperative to learn more about the causes, evolution, and effects of this new generation of pollutants in order to provide cost-effective treatment options and ensure the best possible environmental quality. A low amount of persistent pollutants may be accumulated, immobilized, and transformed through vegetation-based remediation or phytoremediation. Plants serve as filters and digest chemicals produced by nature in natural ecosystems. A developing technique called phytoremediation makes use of plants to purge pollutants from water and soil. There are many plants with the potential to remediate the environment which is cost-effective and safe without residual action.

Keywords Phytoremediation · Phytoaccumulation · Phytotransformation · Emerging Pollutants

1 Introduction

We have been paying attention to the big issues such as heavy metal accumulation and poisoning, nuclear material leakage, climate change, CO₂ emission, fossil fuel, desert encroachment, etc. that we could not notice that our environment is affected

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by pollutants released from our households. We are just becoming aware of the presence and significance of some chemical and/or their metabolites in our environment.

When detected outside of its typical environment or in concentrations above normal, all matter, regardless of its form, has the potential to become a contaminant. Chemical contaminants, however, become pollutants when enough of them accumulate to harm the environment or endanger living things. There are thousands of industrial chemicals available today that can be harmful to both people and the environment (Brusseau et al. 2019).

Some of the chemicals we use on a daily basis, such as prescription and over-the-counter medications, personal hygiene items like soaps and disinfectants, and their chemical additions like preservatives, are prevalent in the environment. Since many of these pollutants are produced industrially yet are released into the environment as a result of residential applications, they are collectively referred to as “contaminants of emerging concern” and reflect a change in conventional thinking (<https://www.epa.gov/wqc>). Some emerging pollutants (EPs), such as natural toxins and by-products of the breakdown of man-made chemicals, can also be created in the natural environment by organisms like animals, plants, and microbes (Boxall 2012).

2 Emerging Pollutants/Contaminants

Pollutants are artificial or naturally occurring chemicals that are not always observed in the environment but have the potential to do so and have been known or suspected to have detrimental effects (<https://toxics.usgs.gov/pubs/FS-027-02/>). There are different definitions of emerging pollutants, but they all have the same target.

According to the British Geological Survey, emerging contaminants are compounds that are not yet regulated but may be harmful to the environment or human health. These include pharmaceuticals, cosmetics, and industrial chemicals like plasticizers (<https://www.bgs.ac.uk>). According to research on their (eco) toxicity, potential health effects, public perception, and monitoring data regarding their occurrence in the various environmental compartments, emerging pollutants—which are currently excluded from routine monitoring programs—might be candidates for regulation in the future (<https://www.norman-network.net/?q=node/19>). An “emerging” contaminant may also be discovered from an unidentified source, a fresh human exposure, or a cutting-edge detection method or technology (Murnyak et al. 2009; Gavrilescu et al. 2015). These chemicals affect the endocrine system and disrupt hormonal functions, affecting the health of both human and animal species even at low concentrations because of their high production, consumption, and ongoing introduction into the environment. They do not need to be persistent to have a significant negative impact (Petrovic et al. 2004). In this chapter, we discuss the natural approach to remediating or managing these pollutants.

3 Nature and Sources of Emerging Pollutants

The term “emerging pollutants” (EPs) refers to a variety of chemicals created by humans that are used on a global scale and are essential to modern society (Thomaidis et al. 2012). These chemicals include insecticides, cosmetics, personal care products, home cleaners, and medications. Hospitals, animal husbandries, home trash, businesses that manufacture medications, and wastewater and sewage treatment facilities are among the most significant producers of EPs (Stefanakis et al. 2016; Pal et al. 2010).

Pharmaceutical excretion, municipal, industrial, and agricultural waste disposal inputs, and unintentional spills have a significant impact (La Farré et al. 2008).

A wide variety of synthetic chemicals that are used globally, such as perfluorinated compounds, water disinfection by-products, gasoline additives, medicines, man-made nanomaterials, and UV filters, which are important for the advancement of contemporary society, are among the emerging pollutants (Gavrilescu et al. 2015; Richardson 2008).

Drugs or their metabolites in the human body or as climate changes might be emerging pollutants. An illustration of the anti-inflammatory medication diclofenac’s photo transformation products, such as 8-chlorocarbazol, 8-hydroxycarbazol, or diphenylamine derivate, which are both more poisonous and more stable than diclofenac themselves (Richardson 2008) (Fig. 1).

Over 50% of the overall chemical production between 2002 and 2011 consisted of environmentally hazardous substances, according to statistics from EUROSTAT published in 2013; chemicals with a considerable environmental impact make up more than 70% of these (<http://epp.eurostat.ec.europa.eu/tgm/table.do?tab=table&init=1&>). The European Commission tasked a team of experts in 2015 with creating a “first list” of new contaminants. The prescription medications diclofenac, 17-beta-estradiol (E2), and 17-alpha-ethinylestradiol (EE2) were the three substances already chosen for the list. The European Commission’s Joint Research Centre (JRC) was charged with suggesting seven more compounds and analytical techniques to monitor them. The risk quotient, knowledge gaps, and “emerging” contaminants were the scientists’ key areas of concern when creating the list. Each drug was chosen after consideration of the exposure, risk, and hazard it posed as well as the dearth of data from EU-wide monitoring programs. The following seven chemicals or sets of

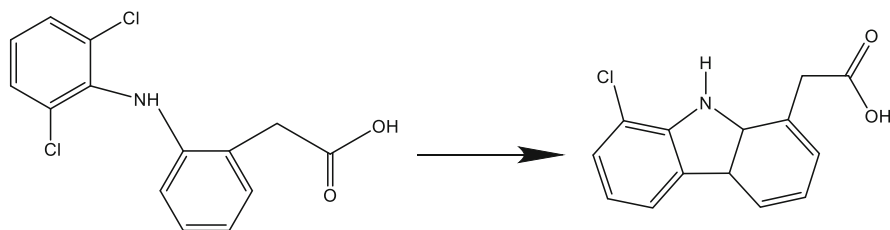


Fig. 1 Photo transformation of diclofenac to chlorocarbazole acetic acid

substances were suggested by the report to complete the initial Watch List: oxadiazon, methiocarb, 2,6-ditert-butyl-4-methylphenol, tri-allate, imidacloprid, thiamethoxam, clothianidin, acetamiprid, erythromycin, clarithromycin, azithromycin, and 2-ethylhexyl-4-methoxycinnamate are some examples of related compounds. The Watch List is a dynamic framework that will be consistently updated to help determine the most effective risk mitigation strategies (<https://ec.europa.eu/jrc/en/news/first-watch-list-emerging-water-pollutants> Downloaded On 19/11/2020). In a different survey, the most frequently found chemicals (found in more than half of the streams) were coprostanol (a fecal steroid), cholesterol (a plant and animal steroid), N-N-diethyltoluamide (an insect repellent), caffeine (a stimulant), tri (2-chloroethyl) phosphate (a fire retardant), and 4-nonylphenol (a nonionic detergent metabolite). The chemical classes that were discovered most commonly were steroids, over-the-counter medications, and insect repellents. In general, the concentrations of detergent metabolites, steroids, and plasticizers were higher (<https://www.epa.gov/ccl-4>).

3.1 Emerging Contaminants in CCL-4

Chemicals that are perfluorinated include PFOA and PFOS, pharmaceutical DBPs (such as nitrosamines and NDMA), items that are a result of pesticide breakdown, algal toxins, perchlorate, nanomaterials, sucralose (Splenda), benzotriazoles, dioxane, and brominated flame retardants (PBDEs), compounds in sunscreen (UV filters), petrol additives, acids naphthenic, pathogens, and hormones.

3.2 Microbial Contaminants

These include *Legionella pneumophila*, *Mycobacterium avium*, *Naegleria fowleri*, *Salmonella enterica*, *Shigella sonnei*, *Escherichia coli* (O157), *Campylobacter jejuni*, *Enterovirus*, *Helicobacter pylori*, and hepatitis A virus.

3.3 Chemical Contaminants

Chemical contaminants include DBPs (5 nitrosamines, formaldehyde, acetaldehyde, benzyl chloride, chlorate, and bromochloromethane), pesticides, and pesticide degradates (such as acetochlor ethanesulfonic acid), chemicals used in industry (such as solvents and other chemicals), chemicals used in consumer products (such as urethane), additives in food (such as butylated hydroxy anisole), explosives like RDX, MTBE as a gasoline additive (e.g., cobalt, molybdenum, tellurium, and

vanadium inorganics), algal toxins, PFOA, and PFOS (including anatoxin-a, cylindrospermopsin, and microcystin-LR) (<https://www.epa.gov/ccl-4>).

3.4 Pharmaceuticals

Acetaminophen, atrazine, benzoylecgonine, bisphenol A, caffeine, carbamazepine, cocaine, diclofenac, estrone, ibuprofen, progesterone, sulfamethoxazole, triclosan, and trimethoprim are the ECs that have been investigated the most in the waterways of the American continent (Vélez et al. 2019).

3.5 Landfills

Landfills are also a source of emerging pollutants. The result of a National Landfill Leachate Study conducted in 2012 is as follows: CECs were detected in all 20 leachate samples, 50% of samples had 17 or more detections, with 89 of 130 CECs (68%) found, and 10% of samples had 59 or more detections (Kolpin et al. 2002).

3.6 Flame Retardants

PBDEs (polybrominated diphenyl ethers) are present in samples from humans. 200,000 tons are generated globally, largely used in the USA and Canada, with harmful developmental effects. It can be found in plastics, textiles, especially in furniture, and consumer electronics. According to EPA Method 527, deca was still manufactured despite octa- and penta- being phased out in 2004 due to their persistence and broad use (www.epa.gov/safewater/lr).

3.7 Sucralose

Sucralose (Splenda) is a popular and stable artificial sweetener that can be used in baking. It is quite persistent in river waters, up to 1 g/L. Samples from the UK, Belgium, the Netherlands, France, Switzerland, Spain, Italy, Norway, and Sweden are where it is most frequently discovered. Marine and coastal waters in the USA have the potential for unknown biological impacts. Wastewater effluents can include up to 118 g/L and up to 392 ng/L in Florida, up to 67 ng/L in the Gulf Stream, up to 372 ng/L in the Cape Fear River Estuary (NC), and persistent in coastal/marine waters. Significant amounts are not broken down by microbes, and ocean currents may disperse them worldwide.

3.8 *Perchlorate (ClO₄⁻)*

It is a contaminant found in milk, food, surface water, and groundwater and used as solid rocket propellants in fireworks, rockets, and missiles; it was found in some natural sources, including nitrate. It was first discovered in the USA. Almost all 350 food and beverage products from more than 50 countries that were measured contain it. It builds up in plants. The thyroid is impacted by perchlorate, which alters normal growth, development, and metabolism.

3.9 *Algal Toxins*

This comprises cylindrospermopsin, anatoxin-a, and microcystin-LR. The EU and WHO have established a preliminary recommendation for microcystin-LR of between 0.1 g/L and 1.0 g/L. Large fish kills, shellfish poisoning, and human disease are all caused by this. Finished drinking water contains microcystins, nodularins, saxitoxins, anatoxins, and brevetoxins (www.epa.gov/safewater/).

3.10 *Hexabromocyclododecane (HBCDD)*

As a PBT (persistent, bioaccumulative, and toxic) compound, HBCDD has been classified as a compound of very high concern by the European Union (<http://echa.europa.eu/candidate-listtable2014>). According to the Stockholm Convention on POPs, HBCDD was classified as a persistent organic pollutant (POP) in 2013 by the United Nations Environment Programme (UNEP) (UNEP 2011). Building insulation foams have a sizeable reservoir of HBCDDs that will continue to slowly leak into the waste stream (Drage et al. 2018). Water supplies have been contaminated by biological micro-pollutants including viruses and bacteria as a result of human activity. Numerous water-borne diseases are caused by biological micro-pollutants, including enteric bacteria, mycoplasmas, viruses, and protozoa, which continue to be a leading cause of death in the globe (Theron and Cloete 2002; http://www.who.int/water_sanitation_health/emerging/emerging.pdf).

3.11 *Perfluorinated Compounds (PFCs)*

The most important representative PFCs are perfluorooctanesulfonate (PFOS), perfluorooctanoic acid (PFOA), and their salts, which are used in a variety of products like firefighting foams, lubricants, metal spray plating, and detergents, inks, varnishes, coating formulations (for walls, furniture, carpeting, and food

packaging), waxes, and water and oil repellents for leather and paper (Arvaniti and Stasinakis 2015; Ahrens 2011; Miralles-Marco and Harrad 2015). They have been utilized in a wide range of consumer items, including Teflon, stain- and water-resistant textiles, Gore-Tex, nonstick materials, cosmetics, cleaning supplies, paints, and food packaging (pizza boxes, fast food wrappers). medical equipment, and engineered coatings (Brusseau 2019).

3.12 Polycyclic Aromatic Hydrocarbons (PAHs)

More than 100 semi-volatile and lipophilic chemical molecules known as polycyclic aromatic hydrocarbons (PAHs) can be found in almost every environmental matrix. Incomplete combustion of organic materials and fossil fuels, together with other natural processes like forest fires and volcanic eruptions, is the main source of PAHs (Chukwujindu et al. 2019).

3.13 Polychlorinated Biphenyls (PCB) Mixtures

Due to their superior physical qualities for various uses, PCB mixes were purposefully created for use as dielectric fluids, flame retardants, and other applications (Bartlett et al. 2019) (Table 1).

4 Effects of Emerging Pollutants

More research is required since these pollutants, which are found in drinking water at low doses, have not yet been linked to human sickness. We are better informed about how they affect wildlife. One such is the alteration seen in male fish, which shows that unknown endocrine-active compounds in the water have affected their reproductive organs. Other instances include snail masculinization, egg-shell thinning, and immune system modifications (https://mde.maryland.gov/programs/water/water_supply/source_water_assessment_program/pages/emerging_concern.aspx). Laboratory studies on PFOS and PFOA's potential carcinogenicity have shown that these substances cause benign liver adenomas, pancreatic adenocarcinomas, and Leydig cell adenomas in mouse models (Klaunig et al. 2012; Chang et al. 2014; Elcombe et al. 2010). In the Danish population, a study found no correlation between PFC levels and cancer risk, with the exception of prostate cancer (Lei et al. 2015).

Manufactured nanomaterials have demonstrated well-defined carcinogenic potentials in animal studies and in vitro assays, particularly reproductive and developmental toxicity at high doses (Ema et al. 2010). Numerous investigations conducted on lab animals in vitro and in vivo have shown that sunscreen has

Table 1 Some of the emerging pollutants and their concentrations (<https://www.epa.gov/ccl-4>)

Pollutant	Concentration ($\mu\text{g/L}$)	Detection frequency in percentiles
Household		
Bisphenol A	10,000 -1000,000	$\geq 90\%$
Benzotriazole-methyl-1 H	1000–100,000	
Non-prescription		
Cotinine	100–100,000	$\geq 90\%$
Nicotine	1000–100,000	$\sim 50\%$
Pseudoephedrine	100–100,000	
Prescription		
Amphetamine	100–10,000	$\sim 75\%$
Carbamazepine	10–1000	
Carisoprodol	30–100,000	
Tramadol	100–1000	$\sim 50\%$
Warfarin	10–1000	
Atenelol	100–1000	
Meprobamate	100–1000	
Metformin	100–1000	
Plant/animal sterol		
Cholesterol	100–100,000	$\sim 75\%$
3-Beta-coprostanol	1000–100,000	$\sim 50\%$
Hormone		
Estrone	1–100	$\sim 50\%$

endocrine-disrupting effects, including disturbance of the hypothalamic–pituitary–thyroid axis (HPT) and reproductive and developmental function (Krause et al. 2012).

Amorphous silicon dioxide (SiO_2), carbon nanotubes (CNTs), and titanium dioxide (TiO_2) are a few examples of manufactured nanomaterials that, by definition, have a particle size of between one and one hundred nanometers (nm) (Kovacic and Somanathan 2013). These substances are thought to be newly emerging pollutants. A wide range of industries, including agriculture, transportation, healthcare, materials, energy, and information technologies, utilize manufactured nanoparticles (Dreher 2004; Nemenko et al. 2014; Radad et al. 2012; Thomas et al. 2006). According to animal research, MTBE can cause renal, immunological, liver, and central nervous system damage in addition to causing testicular, uterine, and kidney cancer (Mennear 1997; Costantini 1993; McGregor 2006; Ahmed 2001). DBP exposure had a negative impact on normal sperm quantity and morphology, but not on sperm motility %, according to certain investigations on DBPs in tap water and semen quality (Luben et al. 2007; Fenster et al. 2003).

Even though the developing pollutants have modest acute toxicity, even extremely low exposure levels can have a major impact on reproduction. Additionally, it is possible that adults will not notice the consequences of early childhood exposure to aquatic species. Traditional toxicity test endpoints might not be

thorough enough to determine criteria for these chemicals, and the chemicals might also have specific modes of action that might only affect particular aquatic animal species (like vertebrates like fish), potential estrogenic effects on biota (like fish feminization), and potential antibiotic resistance. They may have an impact on drinking water treatment changes and aquatic organism populations (reduced food sources) (<http://echa.europa.eu/candidate-listtable2014>).

4.1 PFCs and Cancer

Laboratory studies on PFOS and PFOA's possible carcinogenicity have shown that these substances cause benign liver adenomas, pancreatic adenocarcinomas, and Leydig cell adenomas in rodent models. In the Danish population, a study found no correlation between PFC levels and cancer risk, with the exception of prostate cancer (Lei et al. 2015). Another investigation examined the relationship between DBPs and the menstrual cycle's operation.

Based on findings from prospective research, it has been hypothesized that THM exposure may impair ovarian function by shortening the follicular phase and cycle (Windham et al. 2003). According to a prospective study, women who drink five or more glasses of cold tap water per day with a total THM concentration of less than 75 g/liter are at an elevated risk of spontaneous abortion (Waller et al. 1998).

Except for average residential concentrations that were higher than the allowed limits, there was no association between DPB exposure and fetal growth (Hoffman et al. 2008). Regarding fetal malformation, Agopian et al. (2013) examined data from the National Birth Defects Prevention Study (NBDPS) conducted between 2000 and 2007 and discovered that gastroschisis may be related to shower length but not bath length or shower frequency. When maternal exposure to chlorite levels was 700 g/L, a case-control study on 1917 distinct congenital abnormalities in Italy found a greater incidence of neonates with kidney problems, abdominal wall defects, and cleft palate. Women exposed to 200 g/L of chlorate had an increased risk of having babies with cleft palates, spinal bifida, and obstructive urinary abnormalities (Righi et al. 2012). Endocrine disruption has obvious effects on people, and they are getting worse. DBP exposure had a negative impact on normal sperm quantity and morphology, but not on sperm motility %, according to certain investigations on DBPs in tap water and semen quality (Luben et al. 2007; Fenster et al. 2003). Only research from the years (Eriksen et al. 2009; Hardell et al. 2014) demonstrated a statistically significant link between PFC levels and prostate cancer.

5 Phytoremediation

Utilizing live, green plants to reduce risk in situ and/or remove toxins from contaminated soil, water, sediments, and air is known as phytoremediation. Phytoremediators are specially chosen or designed plants that are utilized in the procedure. Due to its capacity to remove pollutants through biotic processes with little hazards, it is a plant-based, solar energy-driven, affordable, and environmentally benign solution that has attracted a lot of interest (Cunningham and Ow 1996). Some plants have the ability to store and absorb toxins, while others can degrade hazardous molecules into less dangerous ones. A contaminant can be removed, degraded, contained, or any combination of these methods can be used to reduce risk. Additionally, phytoremediation plants can stop poisons from spreading from a contaminated location to nearby places. A type of bioremediation, the term “phytoremediation” was just introduced in 1991. Further study is necessary to determine whether it can promote the biodegradation of organic pollutants, but it may be a fruitful topic in the future. The removal of both metals and organic pollutants from soil can be accomplished through phytoremediation.

6 Methods of Phytoremediation

Actually, the term “phytoremediation” refers to a variety of techniques that use plants to purge contaminated soils and water. Plants can remove and stabilize metal contaminants as well as degrade or break down organic pollutants. One method or a combination of ways may be used to achieve this. The techniques utilized to phytoremediate sites contaminated with organic toxins and metal contaminants, such as lead and mercury, are slightly dissimilar. According to their mechanism, the six different types of phytoremediation procedures that we use are phytoextraction, rhizofiltration, phytostabilization, phytodegradation, and phytovolatilization.

6.1 *Phytoremediation of Metal Contaminated Sites*

6.1.1 **Phytoextraction (Phytoaccumulation)**

In the process of phytoextraction, metal pollutants from the soil are sucked up by plant roots and transferred to the sections of the plant that are above the soil (Prasad 2003; Kotrba et al. 2009). Different plants can absorb and/or withstand various metals to varying degrees; hence a wide variety of plants can be used particularly in areas where multiple types of metal pollution are present. Hyperaccumulator plants are a class of organisms that absorb substantially more contaminants than the

majority of other species. Because they can survive in extremely contaminated environments, these species are used on numerous sites. After the plants have developed and assimilated the metal, they are harvested and properly disposed of. To lower contamination to acceptable levels, this process is performed numerous times. Although this method is often reserved for use with precious metals, in some circumstances it is possible to actually recycle the metals through a process known as phytomining. Zinc, copper, and nickel have all been successfully phytoextracted, while lead and chromium-absorbing plants are the subject of promising current study. The three main mechanisms are accumulation, translocation, and uptake in the shoot. The roots take up metal pollutants from the soil, which then translocate into the shoots where they are stored. In order to extract the metals, the shoot can be harvested and destroyed.

6.1.2 Rhizofiltration

Similar to phytoextraction, rhizofiltration purifies contaminated groundwater as opposed to polluted soils. The pollutants can adhere to the surface of the roots or are taken up by them (Mesjasz-Przybyłowicz et al. 2004; Gomes 2016). Rhizofiltration plants are not placed directly in the site; instead, they must first become acclimated to the pollution. In place of dirt, plants are hydroponically cultivated in clear water until they have acquired a substantial root system. To acclimate the plant, a clean water supply is substituted once a substantial root system has developed. After acclimating, the plants are planted in the polluted area, where the roots absorb the contaminated water and its toxins. The roots are harvested and carefully disposed of as soon as they become moist. As seen in Chernobyl, where sunflowers were grown in pools that were radioactively contaminated, repeated treatments of the site can reduce pollution to acceptable levels.

6.1.3 Phytostabilization

Toxins can be immobilized in soil and water by using specific plants, a process known as phytostabilization. They are absorbed and accumulated by roots, absorbed onto the roots, or held in the rhizosphere (the area around roots that functions like a small chemistry lab with microbes, bacteria, and microorganisms that are secreted by the plants) in order to stop the contamination from spreading and moving throughout the soil and groundwater (Bolan et al. 2010; Ali et al. 2013, Mahar et al. 2016; Khalid et al. 2017). It lessens or even stops migration into the groundwater or air, as well as the contaminant's bioavailability, halting its spread through the food chain. This method can also be used to reestablish a plant community on sites where high levels of metal contamination have rendered them utterly lethal to plants. Even wind erosion and the leaching of toxins from the soil are decreased once a community of these tolerant plants becomes established and grows.

6.2 *Phytoremediation of Organic Polluted Sites*

6.2.1 Phytodegradation (Phytotransformation)

Phytodegradation is the breakdown of organic pollutants by plant-driven metabolic processes. Organic pollutants in the soil are taken up by the roots, transported up the shoot to the leaves, and then broken down into their constituent parts by plant enzymes (metabolized) (Jabeen et al. 2009). These smaller pollutant molecules are kept in the leaves, where they may be utilized by the plant as metabolites and integrated into its tissues as it grows. It has been shown that certain plants have enzymes that can break down organic chemicals, chlorinated solvents like TCE (trichloroethane), and munitions residues.

6.2.2 Rhizodegradation

Rhizodegradation, often referred to as enhanced rhizosphere biodegradation, phytostimulation, and plant-assisted bioremediation, is the breakdown of organic pollutants in the soil by soil-dwelling bacteria that enjoy the root systems of particular plants (Danh et al. 2009). The rhizosphere, often known as the plant root zone, is where the action takes place. Numerous different microorganisms live in large populations in this soil. This is because plant roots emit compounds that give off carbon and energy for microbial growth. The biodegradation of chemicals seems to be accelerated by the presence of both plants and microbes. Sugars, alcohols, and organic acids found in plant roots serve as glucose sources for soil microorganisms, promoting their growth and activity. Some of these substances might also serve as chemically seductive signals for bacteria that use fuel. There are bacteria in the soil that break down fuels and solvents to create safe by-products. In addition to loosening the soil and bringing water to the rhizosphere, plant roots also encourage beneficial microbial activity.

6.2.3 Phytovolatilization

As plants discharge water from their leaves, they absorb contaminants that are water soluble and release them into the atmosphere (Lim et al. 2016). As the water moves through the plant's vascular system from the roots to the leaves, the hazardous substance may undergo modification. Following that, the pollutants evaporate into the air around the plant. The effectiveness of plants as phytovolatilizers varies, with one study demonstrating that well-known trees can transform and disseminate up to 90% of the TCE they absorb. By rapidly absorbing significant amounts of water, plants are also utilized to regulate the movement of subsurface water. These plants are known as hydraulic control, and they effectively serve as natural hydraulic pumps. These plants can transpire up to 300 gallons of water per day if a deep

root network has grown close to the water table. The migration of contaminants from surface water into groundwater (below the water table) and drinking water supplies has been slowed down as a result of this fact. These two applications for plants include:

- **Riparian corridors and buffer strips**—These are two methods of phytoremediation that are used simultaneously along the banks of rivers or the borders of groundwater plumes. They are essentially extensive areas of plants that serve as a filter and processing system to break down, contain, or extract pollution. While buffer strips are utilized in this way along the perimeter of landfills, riparian strips are used along the banks of rivers and streams.
- **Vegetative cover**—The term “vegetative cover” refers to the employment of plants to cover or cap waste sites. For such sites, the typical caps are typically made of clay or acrylic. They aid in preventing erosion, contaminant leaching, and possibly even the degradation of the landfill beneath.

6.3 Plants in Management of Pollutants (Phytoremediators)

Plants have evolved to tolerate the presence of different metals in variable concentrations in soils for many millions of years. When consumed in moderation by humans, some metals, including zinc, nickel, cobalt, and copper, serve as nutrients. However, when consumed in excess, these metals are hazardous. Mercury, lead, cadmium, silver, gold, and chromium are heavy metals that are dangerous even in minute quantities. Heavy metal contamination has reached unsafe levels in some locations as a result of human activities like mining, disposing of municipal trash, and manufacturing. These substances harm lipids, DNA, and proteins by oxidative damage. Plants that accumulate excessive amounts of heavy metals in the environment are known as hyperaccumulators. There are three ways that they do this:

- (i) Taking them in and securing them in the bubble-like structures called vacuoles in their cells.
- (ii) Chelation, the process of combining a contaminant with another molecule. Organic acids frequently play this part. For instance, malic acid surrounds zinc and detoxifies it, while citric acid surrounds cadmium and does the same for cadmium. Metals can also be bound by phytochelatins, a family of polypeptides, and transported to vacuoles.
- (iii) Making use of metallothioneins, a class of tiny, metal-binding proteins. Phytoremediation is the deliberate use of plants to remove heavy metals from soil using any of these methods.

Some of the plants used as phytomediators (Koptsik 2014; Wang et al. 2012; Marques et al. 2009; Brown et al. 1994) are as follows:

Apocynum cannabinum L. (Apocynaceae), a perennial herbaceous plant known by the names dogbane, Amy root, hemp dogbane, Indian hemp, rheumatism root, or

wild cotton, is utilized to sequester lead in its biomass. In addition, syphilis, rheumatism, intestinal worms, fever, asthma, and dysentery are all treated with it in herbal medicine. The plant's toxins have been utilized for lowering the pulse, as well as being a sedative and mild hypnotic, despite the fact that they can also cause nausea and catharsis.

***Brassica juncea* (L.) Czern. & Coss.** is an amphidiploid with *Brassica nigra* (L.) Koch ($2n = 16$) and *Brassica rapa* L. ($2n = 20$) as parents. It is an erect, annual to biennial herb up to 160 cm tall, often unbranched, sometimes with long ascending branches in upper part, almost glabrous to scattered hairy, slightly glaucous; taproot sometimes enlarged.

A variety of lupine endemic to western North America called *Lupinus microcarpus* Var. *densiflorus* (Fabaceae), sometimes known as wide-bannered lupine or chick lupine, is capable of absorbing arsenic from the soil.

***Hydrilla verticillata* (L.f.) Royle** (Hydrocharitaceae), known as Esthwaite Waterweed or Hydrilla, is an aquatic plant and hyperaccumulator of mercury, cadmium, chromium, and lead.

***Lupinus microcarpus* Var. densiflorus** (Fabaceae), commonly known as chick lupine and also called wide-bannered lupine, is a type of lupine that is native to western North America and has the ability to absorb arsenic from the soil.

***Salsola soda* Weinm** (Amaranthaceae), the Barilla plant, also known as opposite leaf Russian thistle or opposite leaf saltwort, is a tiny (to 0.7 m tall), annual succulent shrub that is indigenous to the Mediterranean Basin. *Salsola soda* has also been investigated as a "bio desalinating companion plant" for crops like tomatoes and peppers that are cultivated in salty soils as a bioremediation method. Despite the two plants competing for the remaining minerals in the soil, the *Salsola soda* absorbs enough sodium from the soil to promote the growth of the crop plant, leading to improved agricultural yields.

***Tradescantia pallida* (Rose) D.R. Hunt** (Commelinaceae) is a type of spiderwort that goes by the name Wandering Jew, along with the species *T. fluminensis* and *T. zebrina*, which it is closely related to. Purple Queen and Purple Heart are two additional common names. It is indigenous to eastern Mexico's Gulf Coast, exceptionally good in removing volatile organic compounds, a class of typical pollutants and respiratory irritants, from indoor air.

***Pteris vittata* L. (Pteridaceae)**, the Chinese brake, Chinese ladder brake, and plain old ladder brake are all common names for this device. It is an arsenic-accumulating fern that is native to Asia, tropical Africa, and Australia.

***Salix viminalis* L. (Salicaceae)**, a multi-stemmed shrub with the common name "willow," can reach heights of 3–6 m (rarely 10 m). With greenish-gray bark and long, erect, straight branches, it is a well-known hyperaccumulator of cadmium, chromium, lead, mercury, zinc, petroleum hydrocarbons, organic solvents, MTBE, TCE, and by-products, as well as selenium, silver, uranium, and zinc.

***Pistia stratiotes* L.** (Araceae) is a genus of aquatic plants often known as water lettuce, Nile cabbage, or water cabbage. It was initially found from the Nile near Lake Victoria in Africa; its natural location is unknown but most likely pantropical. It is currently found in almost all tropical and subtropical freshwater ways, either

naturally or as a result of human introduction. In the water, it outcompetes algae for nutrients, avoiding large-scale algal blooms.

***Ambrosia artemisiifolia* L.** (Asteraceae), the species of *Ambrosia* with the widest distribution in North America, is the common ragweed. Other names for it include American wormwood, blackweed, carrot weed, hay fever weed, Roman wormwood, stammerwort, stickweed, and annual ragweed. North America is where it originated. Heavy metals like lead are removed from soil using *Ambrosia artemisiifolia*.

***Moringa oleifera* Lam.** (Moringaceae), moringa, benzolive tree, and West Indian ben are some of its common names in English. It also goes by the name “drumstick tree.” It is a very nutrient-dense vegetable tree with a wide range of applications. The moringa tree may help with sustainable land management, food security, rural development, and nutrition. It is regarded as one of the most beneficial trees in the world because practically every part may be utilized to make food or has some other useful quality. In many nations, moringa micronutrient liquid, a natural anthelmintic (kills parasites) and adjuvant (to aid or enhance another treatment), is used as a metabolic conditioner to aid against endemic diseases in developing countries. In the tropics, it is used as feed for animals. PCBs and other chlorinated substances are absorbed.

***Pennisetum purpureum* Schumach** (Poaceae), a kind of grass from the tropical grasslands of Africa popularly called elephant grass, Napier grass, or Uganda grass, is used to remove lead and mercury.

***Hydrangeas* Gronov. ex L. (Hydrangeaceae)** are common ornamental plants grown for their abundant flower clusters, which come in a variety of colors, including pink, blue, purple, creamy white, and other hues in between. They extract aluminum from the ground.

***Melastoma affine* D. Don** (Melastomataceae) is a pretty flowering shrub found in tropical and subtropical woods in India, South-east Asia, and Australia that goes by the popular name “blue tongue.” It is a plant that grows along the edges of rainforests; it has leathery, dark-green foliage that is evergreen in warm regions; purple blooms; and tasty, purple fruits that stain your tongue blue, hence the name. The soil’s aluminum is removed by it.

***Bacopa monnieri* (L.) Pennell** (Plantaginaceae), commonly referred to as water hyssop, cleans bogs and wetlands of not only lead but also mercury, cadmium, and chromium and forms an attractive ground cover for muddy beaches. It has delicate white flowers and tiny succulent leaves.

***Eichhornia crassipes* (Mart.) Solms** (Pontederiaceae), known as water hyacinth, naturally draws cadmium, chromium, mercury, lead, zinc, cesium, strontium-90, uranium, and pesticides from the water. It has beautiful blooms, typically lavender to pink, and grows quite quickly. It was first discovered in South America but has since spread elsewhere.

***Thlaspi caerulescens* (Brassicaceae)**, a blooming plant known as Alpine Pennygrass, can be found in Western Europe, Scandinavia, and the USA. It absorbs cadmium and, in some cases, is also thought to have absorbed zinc.

***Vicia faba* L.** (Fabaceae) originates in North Africa and Southwest Asia and is sometimes referred to as the broad bean, fava bean, field bean, bell bean, or tic bean.

The alkaloids vicine, isouramil, and convicine found in raw broad beans can cause hemolytic anemia in people with the inherited disorder glucose-6-phosphate dehydrogenase deficiency. L-dopa, a compound used to treat Parkinson's disease, is abundant in broad beans. Additionally, a natriuretic, L-dopa may aid in the management of hypertension. The removal of volatile organic molecules is well known.

Helianthus annuus L. (Asteraceae), commonly known as sunflowers, effectively remove uranium and strontium-90 from contaminated soil in Ukraine following the Chernobyl tragedy, the worst nuclear power plant accident in history. They also absorb lead, arsenic, zinc, chromium, copper, and manganese.

7 Conclusion

Emerging contaminants raise concerns because they are being released into freshwater systems and the environment at a growing rate, even in very small amounts. Some of these pollutants have the potential to disrupt human and aquatic species endocrine systems and lead to the emergence of bacterial disease resistance. There is currently little scientific knowledge about the accumulation of new pollutants in the environment, their fate, transit, and risk. Only minimally has the impact of individual developing contaminants been assessed on environment and human health. Although each chemical employed in a minute quantity may be thought to be innocuous, there are growing worries about the combined impact of this variety of compounds when they infiltrate the environment and the food chain (European Union 2012). Therefore, it is essential to research the prevalence and hazards of EPs so that they may, if necessary, be incorporated into water-quality monitoring programs. It is also necessary to think about redesigning and/or modernizing treatment systems (Becerril 2009). It is now possible to quantify these substances in extremely low quantities thanks to improvements in detection techniques. A simple, inexpensive, yet very successful and environmentally benign method for environmental remediation.

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Microbial Fuel Cell as an Approach for Bioremediation of Emerging Contaminants



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Abstract Incessant industrialization, unconstrained urbanization, and an environmentally unsustainable lifestyle have exacerbated the unwarranted release of emerging contaminants (ECs) into aquatic ecosystems across the globe. Depending on their source of origin, ECs encompass a range of pollutants, including pharmaceuticals and personal care products, pesticides, industrial chemicals, surfactants, etc. In aquatic environments, ECs demonstrate bio-refractory characteristics and can thus induce acute as well as long-term health issues to the exposed biota, even if present in trace concentrations. Conventional biological treatment techniques are ineffective in eliminating ECs from wastewater due to the limited biodegradability of these micropollutants. Besides, contemporary physicochemical treatment processes are economically and environmentally taxing. In this context, microbial fuel cell (MFC), the first derivative of bioelectrochemical systems (BES), has been widely exploited in recent years to attenuate ECs via biotic (anodic) and abiotic (cathodic) routes. However, such systems are incipient and require significant modifications to overcome operational limitations and fulfill field-scale requirements. This chapter focuses on this aspect, among others, to collate the latest progress in MFC application for the abatement of ECs from environmental matrices sustainably. Specifically, it emphasizes the MFC-mediated removal and degradation mechanisms of ECs. In addition, the chapter critically examines the factors influencing the performance of MFC in degrading these refractory pollutants, including microbial catalyst, cathode catalyst, substrate, and imposed potential. Finally, it distinguishes the key gaps in the specific domain knowledge and lays out novel strategies to abet the commercialization of MFC.

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1 Introduction

Emerging contaminants (ECs) comprise synthetic and organic compounds suspected or confirmed to endanger aquatic environments and humans. These ECs are intricate organic compounds that contain a variety of toxins, including phenols, dyes, medicines, herbicides, insecticides, surfactants, personal care items, and artificial sweeteners. Environmental agencies have not yet developed defined regulatory standard limits because of their incomprehensible behavior, occurrence, outcome, and ecotoxicological nature (Scaria et al. 2021). Conventional treatment plants are ineffective in mitigating ECs, making the wastewater treatment plant effluent the main source of discharge of ECs into the aquatic environment (Chakraborty et al. 2020; Zamora-Ledezma et al. 2021).

Attributing to their bio-refractory nature, ECs can induce bioaccumulation, carcinogenicity, genetic mutation, biotoxicity, antibiotic resistance, and chronic diseases in humans and aquatic organisms, even at low concentrations (Tran et al. 2018). Therefore, it is imperative to eliminate these pollutants from wastewater before releasing them into natural water bodies. (Chakraborty et al. 2020). This can be accomplished by implementing cutting-edge treatment procedures rather than traditional ones. On the other hand, the detrimental impact of using unprecedented fossil fuel catering to the increasing population demands has motivated researchers to focus on sustainable and carbon-neutral technologies for wastewater treatment (Power et al. 2018).

For abatement of EC, usually, advanced technologies, like chemical oxidation, adsorption, ultrasonication, membrane filtration, precipitation, advanced oxidation processes, biological treatment, and electrochemical treatment, have been investigated (Chaturvedi et al. 2021; Raj et al. 2023). However, the downside of these methods is the requirement of significant amounts of chemicals, energy, and expensive equipment to drive the treatment operation. Further, the waste generated from these treatment technologies needs additional processing. Moreover, the complete mineralization of organic pollutants is not always accomplished, which can result in the formation of more toxic intermediates than the parent compound itself (Crini and Lichtfouse 2019). Hence, energy-effective water decontamination platforms that can successfully degrade and bioremediate EC from wastewater are a priority.

Consequently, microbial fuel cell (MFC), the first iteration of bioelectrochemical systems (BES), has attracted immense interest in removing ECs from wastewater. Employing mature and acclimated microbial consortia in the anodic chamber of MFC has effectively removed most bio-refractory pollutants from wastewater (Bajracharya et al. 2016). In addition, the ability of the cathode to generate highly reactive species, like hydroxyl radicals ($\cdot\text{OH}$), via Fenton and Fenton-like reactions, has made it possible to mineralize ECs in the cathodic chamber of MFC while yielding bioelectricity (Feng et al. 2010a).

Therefore, the current chapter encapsulates the progress made in the remediation of trace organic contaminants via MFC. The chapter elaborates on the biotic as well as abiotic mechanisms for contaminant removal through MFC. In addition, the key operating parameters determining the performance of MFC have been discussed in detail. Moreover, the disadvantages of conventional MFC configuration and different MFC-based hybrid systems that display improved removal efficiency while producing bioelectricity have also been incorporated. A separate section on the long-term and pilot-scale investigation has been included in the chapter to speculate the suitability of the MFC-based technologies for on-site applications. Finally, strategies and perspectives that promote the commercialization aspect of these neoteric systems have been suggested as a blueprint for future research.

2 Mechanism of Electricity Generation and Pollutant Removal Through MFC

2.1 Fundamentals of MFC and Power Generation

A bioelectrochemical wastewater treatment system utilizes electrochemically active bacteria as biocatalysts to degrade organic matter and parallelly convert the organic chemical's energy into electricity (Peera et al. 2021). A typical MFC configuration features a two-chambered electrochemical reactor bifurcated using a separator, such as a proton-exchange membrane (PEM) (Fig. 1). The anaerobic anodic chamber

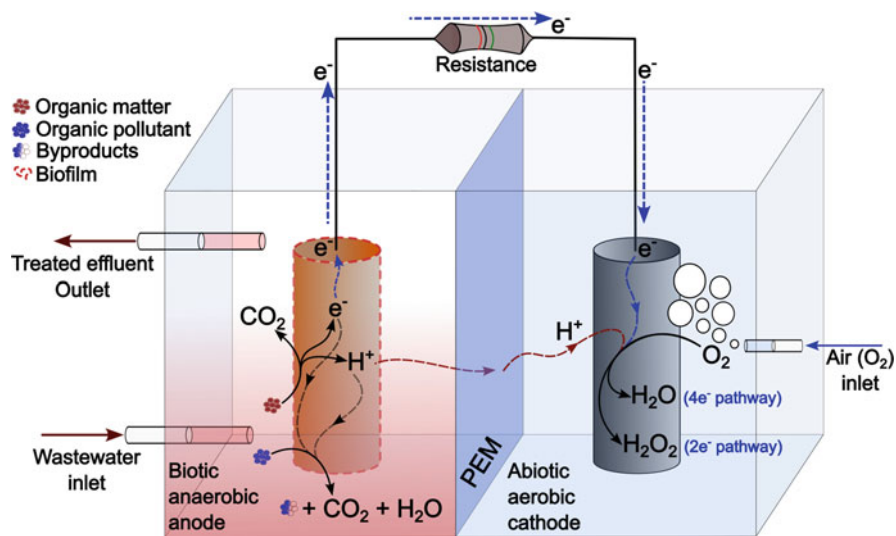


Fig. 1 Schematic demonstrating simultaneous organic matter and emerging organic pollutants degradation along with bioelectricity production in a microbial fuel cell

receives the organic substrate in the form of wastewater, which is biodegraded by electroactive microbes colonizing the sessile anodic biofilm. The bio-oxidation of organics results in the release of electrons (e^-), protons (H^+), and carbon dioxide (CO_2) in the anolyte. These H^+ and e^- are transported to the cathodic chamber through PEM and via an external circuit, respectively. Subsequently, the transported H^+ and e^- combine with oxygen (O_2) at the cathode to produce water (H_2O), thus producing electricity.

The main constituents of MFC include electrodes (anode and cathode), electroactive bacteria, organic substrate, PEM, oxygen (or any other terminal electron acceptor), and an electron transport system carrying electrons through an external circuit (Tsekouras et al. 2022). Traditionally, carbon-based materials such as carbon felt, carbon paper/cloth, and graphite plate are employed as electrodes (anode and cathode) owing to their low-cost fabrication, chemical stability, and biocompatibility. However, these electrodes have high overpotential that dampens the power output of MFC. Hence, metal, metal oxides, and carbon-metal composite nanoparticles are often modified to catalyze otherwise sluggish electrochemical reactions. The biotic component of MFC, that is, electroactive bacteria, is pivotal to efficient wastewater treatment and bioenergy production. Both pure strains and mixed consortia of indigenous and/or engineered strains of electroactive species are employed in the MFC as biocatalysts (Al-Ansari et al. 2021). Nevertheless, a mixed culture is preferred for wastewater treatment applications, as sustaining pure culture is tedious due to the complex nature of waste effluents.

Organic compounds, mainly glucose or acetate, are fed as a substrate and are easily degraded by electrogenic bacteria, though organic pollutants in wastewater can also act as fuel (Munoz-Cupa et al. 2021). In a traditional dual-chambered MFC, PEM physically separates the anodic and cathodic compartments while keeping them ionically conjugated by facilitating the passage for movement of protons. The anodic chamber, the biological half-cell of MFC, is maintained under anaerobic conditions to allow the proliferation of the electrogenic bacteria. The PEM prevents diffusion of O_2 into the anodic compartment from the cathodic side, which otherwise could hamper the growth of electrogenic bacteria and significantly lower the Faradaic efficiency by competing to access the electrons (Peera et al. 2021). On the other hand, a constant O_2 (air) availability is ensured in the cathode chamber so that the oxygen reduction reaction (ORR) can occur continuously.

The performance of an MFC can be gauged by bioelectricity output and organic matter removal efficiency. Factors such as the type of electrode catalyst employed, targeted organic pollutants, supporting electrolytes in the cathodic chamber, biocatalysts, and operational conditions affect the performance of MFC. Moreover, MFC has also been employed to remove specific contaminants from wastewater, such as antibiotics, polyaromatic hydrocarbons, chlorinated aromatics, insecticides, pesticides, and herbicides. The advantages catered by MFC as a wastewater purification technology include (i) conversion of chemical energy of organic pollutants to valuable electricity and pollutant mineralization resulting in the liberation of H_2O and CO_2 ; (ii) it is independent of external energy source; (iii) it is an eco-friendly technology that exploits anaerobic electrogens and O_2 (air) for its function; (iv) it can

target and achieve high removal rates of organic, inorganic, and organometallic pollutants (Xiao et al. 2021; Yong et al. 2017; Lim et al. 2021); (v) the treatment process involves less quantity of sludge generation (Li et al. 2014); (vi) it is capable of remediating contaminated soil as well as gaseous pollutants (Abbas and Rafatullah 2021; Zhang et al. 2020); and (vii) obtaining value-added products from wastes primarily through MFC-based hybrid system (Arun et al. 2020). These salient features give MFC an edge over contemporary treatment technologies and can be the potential solution to sustainable wastewater management.

2.2 Types of ECs and Anodic Degradation in MFC

2.2.1 Organic Dyes

Textile, food, paint, printing, plastic, and paper are a few industries that release untreated wastewater containing synthetic organic dyes into surface waters (Samsami et al. 2020). Owing to their carcinogenic, mutagenic, and toxic effects, these pollutants must be eliminated before discharging the wastewater into the natural water bodies (Khan et al. 2015; Myslak et al. 1991). Besides, dyes induce color in receiving waters, which declines the photosynthesis activity of aquatic flora (Samsami et al. 2020). In addition, some dyes, like azo dye, can be carcinogenic due to their aromatic moieties with azo linkages (N=N) (Zheng et al. 2015). Bio-decolorization of dyes through a conventional anaerobic reduction mechanism is relatively slow and necessitates reductive conditions (Solanki et al. 2013).

In comparison, MFC is a better alternative in terms of reaction kinetics. The addition of substrates such as glucose, acetate, ethanol, molasses, and other organic waste materials acts as an electron donor in the anodic chamber of MFC (Eq. 1) (Pandey et al. 2016; Oon et al. 2018a). The co-metabolism results in the oxidation of substrates, delivering reducing equivalents which then reduce organic pollutants such as azo dye (Table 1) and support simultaneous bioelectricity generation (Eq. 2). The two reactions of oxidizing substrate and organic pollutant reduction compete as they depend on electrons supplied by electrochemically active bacteria (EAB) (Khan et al. 2021). Also, the presence of sulphate-reducing bacteria in the anodic chamber may enhance dye degradation by facilitating sulfite reduction to elemental sulfur, which releases surplus electrons for substrate oxidation (Miran et al. 2018).

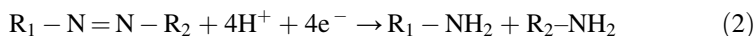
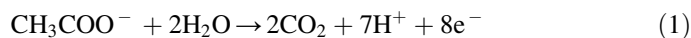


Table 1 Degradation of wastewater containing azo dye in the anodic chamber of MFC

Inoculum	Anode	Organic pollutant (initial conc. in mg L ⁻¹)	Operational duration (h)	Degradation efficiency (%)	Power density (mW m ⁻²)	References
Anaerobic sludge	Unpolished graphite	Methyl orange (10–20)	24	73.4	0.13	Liu et al. (2009)
Aerobic sludge	Porous carbon paper	Active brilliant red X-3 B (300)	12	90	213.93	Sun et al. (2011)
<i>Geobacter sulfurreducens</i>	Granular activated carbon (GAC)	Dye (150)	72	91	610	Fang et al. (2013)
Mixed-waste sludge	Graphite brush	Azo dye (260)	720	85	–	Long et al. (2017)
<i>Proteobacteria</i> , <i>Deltaproteobacteria</i> and <i>Desulfovibrio</i>	Graphite felt	Textile diazo dye (100)	24	90	258	Miran et al. (2018)
Mixed-culture sludge	Carbon felt	Azo dye (500)	463 days	95	8.67	Oon et al. (2018b)
<i>Proteus hauseri</i> ZMq44	Carbon cloth	Thionine-based textile dye (40)	120	–	83.39	Xu et al. (2019)
Anaerobic sludge	Graphite fiber brush	Congo red (200)	24	88	23.50	Dai et al. (2020)
Marine sludge	GAC	Methylene blue (500)	96	93.15	15.73	Di et al. (2020)
<i>Proteus hauseri</i>	Porous carbon cloth	Thionine-based Textile Dyes (40)	48	50	83.4	Chen et al. (2016)

2.2.2 Pharmaceutical Products

Recent years have witnessed an enormous spike in the consumption of antibiotics, and the onset of pandemics like COVID-19 has further aggravated the situation. Various antibiotics are frequently used to treat human and veterinary illnesses and eventually reach the environment through human and animal discharges (Van Boeckel et al. 2014; Lyu et al. 2020). Past research has reported the presence of antibiotics in treated effluent of wastewater treatment facilities, which indicates the inability of the conventional treatment unit to eliminate these recalcitrant chemicals (Gao et al. 2012). Consequently, antibiotics are discharged into the natural water sources, thus jeopardizing the existence of fragile aquatic ecosystems. For instance, almost 70% of the antibiotic tetracycline used in medicinal practices, animal husbandry, and aquaculture to inhibit bacterial infection eventually ends up in the environment and can have endocrine-disrupting effects upon persistent exposure (Wang et al. 2018).

Investigations have revealed that a shock exposure to antibiotics at higher concentrations can hinder bacterial growth in the anodic chamber of MFC, leading to a sudden decline in the power output (Topcu and Taşkan 2021). However, with gradual dosing of antibiotics, anodic microbes of MFC can get acclimatized and effectively remediate pharmaceutical effluents. In fact, once electrogenic bacteria adapt to such an environment, the power efficiency of MFC may also get boosted. For instance, Cheng et al. (2020a) employed a pomelo peel-based biochar-loaded (surface area = $2457.37 \text{ m}^2 \text{ g}^{-1}$) anode to treat swine wastewater containing sulfonamide antibiotics (500 mg L^{-1}) in a dual-chambered MFC. The MFC treatment resulted in significant removal of sulfamethoxazole (82.44–88.15%), sulfadiazine (53.40–77.53%), and sulfamethazine (61.12–80.68%). It was observed that increased biochar concentrations from 100 to 500 mg L^{-1} increased the daily average voltage generated from 550 to 650 mV. This improved performance was due to antibiotic absorption via π - π electron donor-acceptor interactions on biochar surface. Additionally, it was found that adding sulfamonomethoxine encouraged the proliferation of microorganisms such as *Cupriavidus*, *Rhodococcus*, *Sphaerochaeta*, and *Cloacibillum*, causing a considerable increase in pollutant removal efficiency and power output (Zhang et al. 2021).

Likewise, Cheng et al. (2020b) observed a high-power output of 0.336 W m^{-2} while degrading salinomycin in a single-chambered MFC system. Salinomycin has an antibiotic characteristic that alters the osmotic pressure across the membrane of a microbe, eventually disrupting the cell. It is widely utilized in the livestock industry. The improved power generation could be attributed to the binding of salinomycin with the channel proteins on the bacterial surface, which enhanced the electron transfer rate.

In a similar type of investigation, Wu et al. (2021) demonstrated almost complete removal of 80 mg L^{-1} of chloramphenicol in the anodic chamber of MFC with a high-power density of 414.0 mW m^{-2} . The acclimation approach of continuously replacing the anolyte once in every 3 days and gradually increasing the

chloramphenicol concentration from 1 to 80 mg L⁻¹ in 75 days improved the pollutant degradation. Additionally, the electrochemical activity of the anode was accelerated by the development of highly porous biofilm with cobweb-shaped proteins facilitating mass and e⁻ transfer. Meanwhile, Al-Ansari et al. (2021) reported the degradation of antimicrobial sulfadiazine in MFC within an operation of 60 h, where the voltage attained and removal efficiency were 1.28 ± 0.1 V and 89.2 ± 2.1%, respectively. However, sulfadiazine concentrations greater than 350 mg L⁻¹ decreased microbial activity, diminishing the degradation efficiency.

Similarly, a single-chambered Fe-Co-C/N-coated air cathode MFC degraded 60.64% of sulfamethoxazole (6 mg L⁻¹) within 48 h of operation (Li et al. 2021c). These investigations reveal the importance of acclimatizing anodic microbes to the target organic pollutant for extracting the optimum overall performance from the MFC. On the other hand, despite proper acclimation, anodic pollutant degradation is possible up to a certain concentration.

2.2.3 Pesticides

Pesticide usage has increased dramatically in modern agriculture, reaching over 2.5 million tons annually (Fenner et al. 2013). It ultimately makes its way into water bodies through agricultural runoff, leaching, and spray (de Souza et al. 2020). Exposure to pesticide residue has been linked with many adverse health effects, including lung cancer, Alzheimer's disease, and headaches (Hassan and El Nemr 2020). In an air cathode MFC, Cao et al. (2015) used granular activated carbon (surface area = 500–900 m² g⁻¹) as an anode to degrade hexachlorobenzene (40 mg kg⁻¹). This novel system attained 71.15% removal of hexachlorobenzene and a power output of 77.5 mW m⁻², which was attributed to the reductive dechlorination pathway under anaerobic conditions. In another investigation, 200 mg L⁻¹ sulfamethoxazole was degraded in the anodic chamber of MFC with a degradation efficiency of 70%, which highlights the ability of MFC to handle high dosages of antibiotics (Wang et al. 2015).

Clearly, electrogenic-mediated bio-oxidation plays a significant mechanism in antibiotic removal in MFC; however, the dominant species may vary depending upon the characteristics of the antibiotic present in the wastewater. For example, Zhang et al. (2018) observed that during the elimination of the pesticide oxyfluorfen (50 mg L⁻¹) in MFC, the major microbial species constituted *Arbacter*, *Acinetobacter*, *Azospirillum*, *Azonexus*, and *Comamanas*. In contrast, Li et al. (2019a) documented that the degradation of the pesticide metolachlor in MFC was predominantly executed by microbial species such as *Trichosporon*, *Mortierella*, *Chaetomium*, *Kernia*, *Debaryomyces hansenii*, and *Mortierella polycephala*. Interestingly, other than bacteria, fungi have also been known to disrupt pollutants and produce bioelectricity parallelly. However, Zhang et al. (2019a), who achieved 70% degradation of 30 mg L⁻¹ pesticide fipronil in a dual-chambered MFC, utilizing bacterial species like *Pseudomonas*, *Sphaerochaeta*, *Azoarcus*, *Chryseobacterium*, and *Azospirillum*. Hence, MFC has showcased a satisfactory performance in

degrading different pharmaceutical pollutants compared with traditional biological treatments. Nevertheless, more research is needed to improve the removal efficiency and create anodic consortia capable of withstanding fluctuating pollutant concentrations and shock loads.

2.2.4 Other Organic Compounds

The refractory compounds formed by phenol and its derivatives are stable structures that are difficult to biodegrade. These are primarily employed in producing organic compounds like colors and polymers and in the food, pharmaceutical, and oil refining sectors. Nevertheless, they react with other pollutants to generate harmful contaminating entities. These eventually end up in aquatic ecosystems with toxic effects such as carcinogenicity and genotoxicity (Chen et al. 2013).

Many investigations on the degradation of these refractory compounds via MFC have reported promising results. A persistent and mature biofilm formed in a long-term operated MFC acclimated with low concentrations of organic pollutants can effectively remove organic contaminants. This was observed when p-nitrophenol was degraded in the anodic chamber of a MFC, with an efficiency of 81% within 24 h (Zhao and Kong 2018). The matured microbial consortia could degrade other pollutants such as chloramphenicol, benzofluorfen, fluoxastrobin, and flubendiamide. The major bacterial species in the anodic biofilm were *Corynebacterium*, *Comamonas*, *Chryseobacterium*, and *Rhodococcus* (Zhao and Kong 2018). To elaborate, in a *Pseudomonas monteilii* LZU-3 biocatalyzed MFC, 99.89% p-nitrophenol (initial concentration = 100 mg L⁻¹) was removed while producing a maximum voltage of 183 mV (Khan et al. 2019).

In another study, Hassan et al. (2016) degraded 2,4-dichlorophenol in MFC using a pure strain of the exoelectrogenic bacterium *Bacillus subtilis* in the anodic chamber. The investigation emphasized the effect of catholyte on bioelectrochemical activities and the performance of MFC. Potassium persulphate (50 mM) at pH of 3.0 exhibited the highest current generation of 64.0 mA m⁻². The maximum power output generated along with 2,4-dichlorophenol degradation efficiency were 9.5 mW m⁻² and 60%, respectively. Further, in a comparative investigation, the degradation of pentachlorophenol in terms of chemical oxygen demand (COD) removal suggested that dual-chambered MFC (1468.85 mW m⁻²) performed better than single-chambered MFC (872.7 mW m⁻²). It was observed that the degradation of pentachlorophenol was favored in the aerobic condition in the cathodic chamber of dual-chambered MFC when compared to the single-chambered MFC, where the pollutant degradation occurred in the anaerobic anodic chamber (Khan et al. 2018).

Apart from reactor design, pollutant degradation efficiency can also be enhanced by the type of substrate used. An investigation by Li et al. (2019b) demonstrated that supplementing 4-hydroxybenzoic, syringic, and vanillic acid in the anodic chamber enhanced the degradation of phenolic moieties. Moreover, an improvement in degradation rate (146.15–392.31%), as well as current production efficiency (36.18–63.91%), was observed when the substrate concentration was increased

from 0.3 to 3.0 g L⁻¹. It is clear that factors such as the type of electrolyte used in the cathode, catholyte pH, reactor design, and the type of substrate supporting co-metabolism are essential in improving the power performance and pollutant degradation in MFC.

Petroleum hydrocarbons are another important class of stable and toxic compounds toward marine and soil ecosystems (Lamichhane et al. 2016). These constitute a mixture of aromatic, polyaromatic, and saturated hydrocarbons, asphaltenes, and resins, which are usually found in petrochemical effluents and need to be treated to safeguard the environment from their deleterious effects (Varjani and Upasani 2016). In this context, a diesel-degrading *Vibrio* sp. electrogenic strain E2 was employed in an MFC by Li et al. (2019c), which was able to degrade 50% of diesel (initial concentration = 3.26 mg L⁻¹) and attained a power output of 31.37 mW m⁻² within 8 days of operation.

Further, Zhao et al. (2019) considered a single-chambered MFC to understand the influence of carbon substrate and surfactant concentration on polyaromatic hydrocarbon (phenanthrene and pyrene) degradation from the soil. Increasing concentrations of β -cyclodextrin (5.67 g kg⁻¹) that acted as substrate and surfactant enhanced the removal rate of phenanthrene and pyrene by 96.4% and 101.7%, respectively. (Zhao et al. 2019). Similarly, Chakraborty et al. (2021) investigated sodium dodecyl sulphate removal in the presence of L-cysteine, employed as a carbon substrate in MFC. Although the degradation efficiency rose to 70%, the power generation subsided due to the adverse effects of the pollutants on microbial growth at the anode.

Caffeine (1,3,7-trimethyl xanthine) is an emerging pollutant due to its widespread use as a stimulant in beverages, particularly coffee and tea (Raj et al. 2021). It is persistent in surface waters resulting in antibiotic-resistant bacterial strains that affect reproduction in aquatic communities and disrupts the endocrine system in humans (Beauchamp et al. 2017; Li et al. 2020). Yap et al. (2021) adopted CuO-loaded carbon plates as electrodes in MFC, achieving a maximum power density of 28.75 mW m⁻² and a caffeine elimination efficiency of about 97.67%.

3 Hybrid and Integrated Systems

Organic pollutants often induce toxicity on microbial consortia in the anodic chamber, reducing the substrate degradation/utilization efficiency. To tackle this issue, researchers have shown interest toward integrating the existing MFC technology with other treatment systems, such as constructed wetlands, photocatalysis, Fenton oxidation, and aerobic treatment. These hybrid systems can treat contaminants even at high concentrations compared to stand-alone MFC with a better and more stable removal efficiency and output power density (Suresh et al. 2022). As a result, the integrated systems have shown promising results in degrading organic pollutants and generating electricity (Table 2).

Table 2 Degradation of organic pollutants in MFC-based hybrid reactors

MFC-based hybrid system	Electrode	Organic pollutant conc. in mg L ⁻¹	Operation duration (h)	Degradation efficiency (%)	Power density (mW m ⁻²)	References
MFC-Fenton	Carbon felt ^c (scrap iron)	P-nitrophenol (139.11)	12	~100	143	Zhu and Ni (2009)
MFC-aerobic bioreactor	Carbon fabric ^{a,c}	Acid Orange 7 (210 g m ⁻³ day ⁻¹)	12	90	51.9	Fernando et al. (2014)
MFC-Fenton	Graphite plate ^c (FeSO ₄)	Paracetamol (10)	9	70	217.27	Zhang et al. (2015)
MFC-aerobic bio-reactor system	Carbon felt ^{a,c}	Acid Orange 7 (150)	24	96	–	Thung et al. (2018)
MFC-CW	Granular activated carbon ^{a,c}	Sulfadiazine (4.8 mg day ⁻¹)	72	99	15.41	Song et al. (2018)
MFC-photocatalytic system	Granular activated carbon ^a (Bi ₂ MoO ₆)	Aniline (50)	6	96	81.89 W m ³	Zhang et al. (2019b)
MFC-photocatalytic system	Granular activated carbon ^a (TiO ₂ nanotube arrays)	Phenol (400)	6	70	106.40 W m ³	
MFC-photocatalytic system	Carbon felt ^a (mpg-C ₃ N ₄)	2,4,6-trichlorophenol (200)	10	79.3	19.8 W m ³	Wang et al. (2019c)
MFC-CW	Granular activated carbon ^{a,c}	Brilliant red X-3B (270)	36	64.65	0.88 W m ³	Fang et al. (2017)
MFC-CW	Carbon rod ^{a,c}	Acid red 18 (200)	24	96	1.58	Oon et al. (2020)
MFC-Fenton	Carbon felt ^c /powdered activated carbon/Fe ₃ O ₄	Acid Orange 7 (200)	24	67	1.13	
		Cingo Red (200)	24	60	1.02	
		Sodium dodecyl Sulphate (10)	4	87.4	105.67	Sathe et al. (2021)

^aanode material, ^ccathode material

3.1 *Microbial Fuel Cell Constructed Wetland (CW-MFC)*

Constructed wetlands (CW) are a green wastewater treatment method and are fundamentally an engineered replica of the natural wetland environment (Zhuang et al. 2019). Macrophytes (aquatic plants), substrates, and mixed complex microorganisms in CW treat wastewater through biological, chemical, and physical processes. Macrophytes are employed in the CW due to their efficient O₂ transfer rate, ability to adapt to the local climate, and rapid growth (Li et al. 2021a, b, c). Traditionally adopted macrophytes include *Phragmites australis* (common reed), *Canna indica* (purple arrowroot), *Cyperus papyrus* (Nile grass), *Elodea nuttallii* (western waterweed), and *Typha latifolia* (bulrush) (Li et al. 2021a, b, c; Gulamhussein and Randall 2020).

However, CW has a few disadvantages, such as enormous land requirements and clogging of the support matrix resulting in reduced life span and contaminant removal efficiency of the system. Overcoming these drawbacks is imperative to achieve a better and efficient performance of CW. One viable solution is integrating CW with other treatment technologies (Wu et al. 2018).

Since CW possess aerobic (upper portion) and anaerobic (lower part) zones, they can be easily reconfigured to retrofit a typical MFC with cathodic and anodic compartments (Yadav et al. 2012). The retrofitted MFC and CW hybrid assembly are often referred to as CW-MFC (Fig. 2).

Investigations have demonstrated variations in CW-MFC in dye decolorization efficiency and electricity production with different cathode diameters (20.0–27.5 cm), which have been found to influence anode performance. At 25 cm cathodic diameter, the maximum decolorization volume and power density noticed were 271.53 mg L⁻¹ and 0.88 W m⁻³, respectively (Fang et al. 2017). On the other hand, past investigations have shown that dye removal and power generation in upflow CW-MFC are also influenced by parameters like nitrate, salinity, and dye concentrations, as observed by Oon et al. (2018a, b). This was seen when the power density was hampered in cases of an increase in dye concentration and a threefold (428 mg L⁻¹) increase in nitrate concentration (Oon et al. 2018b). Notably, optimum levels of aeration and salinity (3.5 g L⁻¹) maximized the power output (8.67 mW m⁻²). Investigations have also focused on other influencing parameters such as microphytes, filter media, microbial consortia, and pH of the electrolyte (Oon et al. 2018b).

3.2 *Microbial Fuel Cell-Photocatalytic System*

The microbial fuel cell-photocatalytic (MFC-PC) system comprises a photoactive anode that absorbs light energy with a suitable wavelength. It allows the electrons in the valance band to jump instantly to the conduction band, resulting in the development of holes in the valance band. The cathode extracts the photoelectrons and the

Fig. 2 Schematic depicting the fundamental working principle of microbial fuel cell constructed wetland (CW-MFC) system

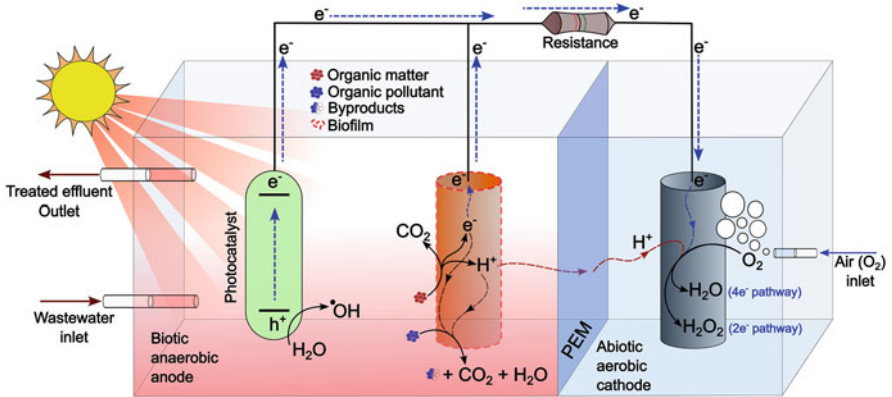
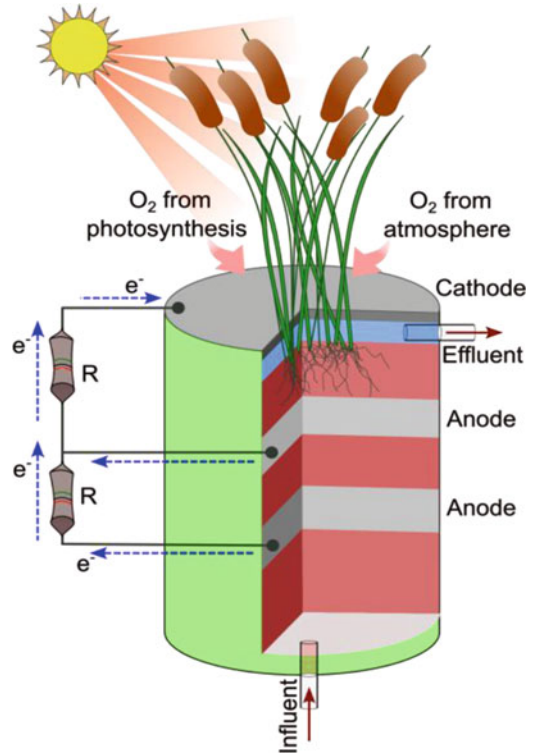


Fig. 3 The MFC-PC system involves the integration of the photocatalysis phenomenon in the anodic chamber of an MFC

electrons generated via the bio-oxidation process via an external circuit, thus enhancing electron-hole pair separation. The resulting holes facilitate the oxidation of pollutants, thereby improving the overall degradation efficiency (Fig. 3).

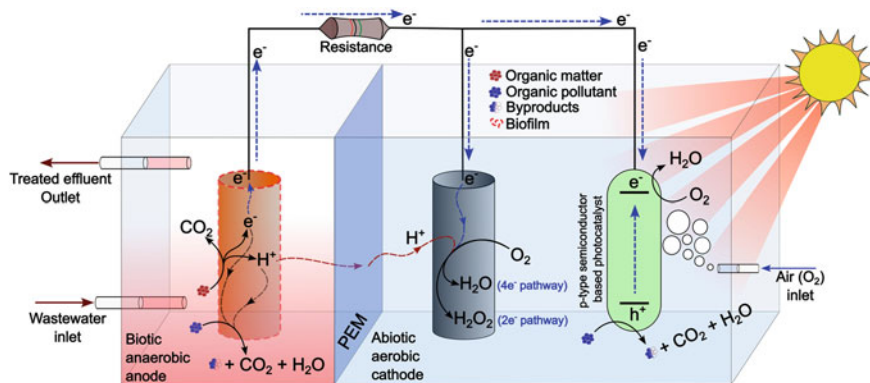


Fig. 4 The MFC-PC system involves the integration of the photocatalysis phenomenon in the cathodic chamber of an MFC

For instance, Long et al. (2017) exhibited 85% degradation of an azo dye, that is, active brilliant red X-3B, of 300 mg L^{-1} in an MFC-PC using TiO_2 photoanode and UV as a light source. The photoanode-fitted MFC resulted in 1.12 times higher decolorization owing to the generation of holes in the anolyte compared to the MFC without photoanode. Additionally, the current output in the MFC-PC hybrid system was 14.2% higher, which could be ascribed to the generation of photoelectrons that enhanced the ORR activity (Long et al. 2017).

In another configuration of MFC-PC, a photocathode is employed in which a p-type semiconductor catalyzes the reduction reactions instead of a photoanode (Fig. 4). The bioanode, when coupled with the photocathode, causes the migration of the e^- generated at the anode to the photocathode through the external circuit. The migrated e^- then combines with the holes generated at the photocathode to reduce organic pollutants in the cathodic chamber (Rahman et al. 2023). This configuration was utilized by Wang et al. (2019a), wherein Mo/W-coated graphite felt acted as a photocathode and achieved complete removal of metronidazole (2-methyl-5-nitroimidazole-1-ethanol). Likewise, Zhang et al. (2019a) demonstrated phenol degradation efficiency, and COD removal as high as 95% and 96%, respectively, in an MFC-coupled photo-electrocatalysis reactor. In comparison, the photo-electrocatalytic treatment alone exhibited 16.5% phenol removal. Similarly, Wang et al. (2019b) conducted the degradation of 2,4,6-trichlorophenol (200 mg L^{-1}) in MFC. When Mpg- C_3N_4 -coated carbon felt was employed as the photocatalytic anode, the removal efficiency was almost 79.3%. *Pseudomonas* was the most prevalent microbial species at the anode of the MFC-based hybrid reactor.

3.3 MFC-Biofilm Electrode Reactor

The MFC-biofilm electrode reactor (MFC-BER) is a hybrid configuration where the electricity from MFC is supplied to the BER for degrading organic pollutants without further external supply. Additionally, the effluent from BER is used as an influent to the anodic chamber of MFC for further degradation (Fig. 5). Therefore, BER can be considered as a pretreatment process for degrading pollutants such as azo dye in a hybrid system (Suresh et al. 2022). The investigation by Cao et al. (2017) demonstrated the removal of brilliant red X-3B dye with an initial concentration of 200 mg L^{-1} in the MFC-BER. The MFC-BER system showed higher degradation than MFC alone, with the highest power density obtained in hybrid systems as 0.257 W m^{-3} . The two-stacked MFC coupled with BER demonstrated stable performance even at high current densities without showing any voltage reversal phenomenon. This was achieved by connecting to a smaller external resistance to obtain a high current in the acclimatization stage and then increasing the resistance while coupling the MFC and BER.

3.4 MFC-Aerobic Bioreactor System

The MFC-aerobic bioreactor hybrid system facilitates the aerobic biological treatment of the effluent treated in the anodic chamber of MFC. It proves advantageous in removing aromatic amines present in wastewater that are difficult to degrade completely in a stand-alone MFC. The decolorization of azo dye in the anodic chamber of MFC is accomplished through azo bond cleavage with the support of the azoreductase enzyme releasing aromatic amines. On the other hand,

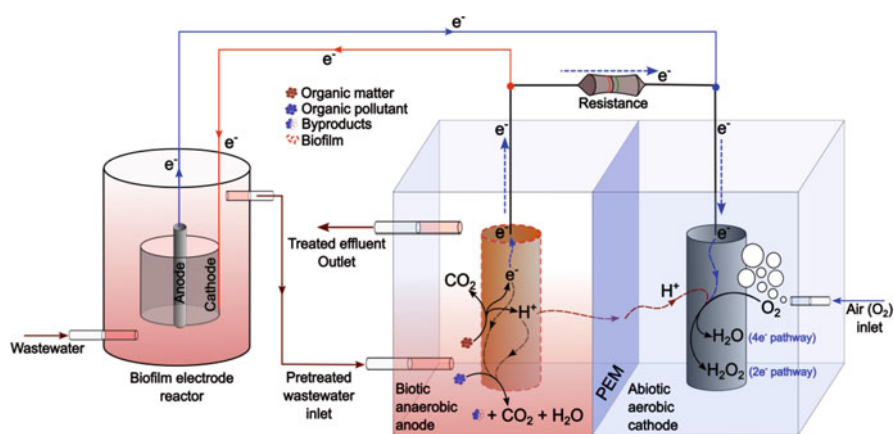


Fig. 5 Schematic of the MFC-biofilm electrode reactor (BER). It ensures a pretreatment of wastewater in BER before introducing it in the anodic chamber of MFC

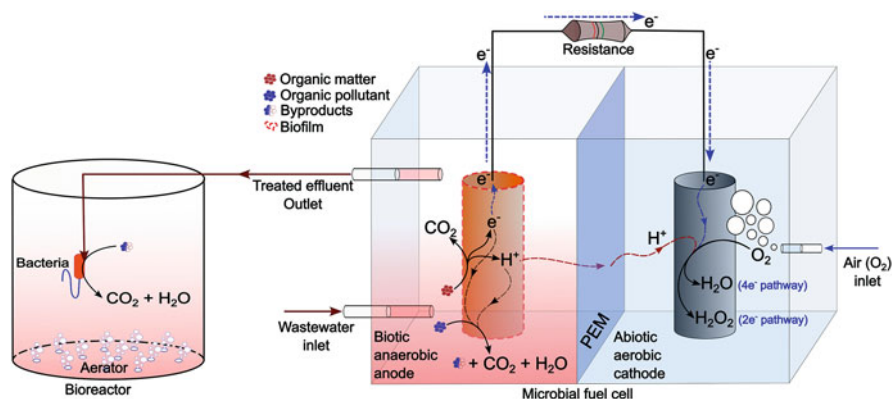


Fig. 6 Introducing the treated effluent from the anodic chamber of microbial fuel cell to an aerobic bioreactor to facilitate the degradation of by-products such as aromatic amines. It results in the MFC-aerobic bioreactor system

the anaerobic anode environment hardly supports further biodegradation of aromatic amines into lower-molecular-weight compounds (Fernando et al. 2014; Thung et al. 2018). Hence, it can be accomplished by integrating with a dual-stage anaerobic-aerobic treatment process (Fig. 6). The investigation by Khan et al. (2021) demonstrated high decolorization and COD elimination of 94 and 85%, respectively, while decomposing the azo dye acid blue 29 (initial concentration = 200 mg L⁻¹) in the MFC-aerobic bioreactor system. A similar investigation showed the degradation of reactive orange (RO16) (400 mg L⁻¹), where the COD removal efficiencies reached as high as 90% in the integrated air cathode MFC-aerobic bioreactor (Sultana et al. 2015).

3.5 MFC-Fenton Process System for Cathodic Removal

The MFC-Fenton system allows dye degradation in the cathodic chamber alongside bioelectricity generation. Electrons released during the oxidation of organic pollutants at the bioanode contribute to the formation of $\cdot\text{OH}$ at the cathode (Fig. 7). The $\cdot\text{OH}$ formation in the cathodic chamber depends on the reaction between O_2 , e^- , and H^+ ions at the cathode that produces the precursor H_2O_2 (mentioned in Eqs. 3, 4, 5). Eventually, in the presence of Fe^{2+} , H_2O_2 is catalyzed to form $\cdot\text{OH}$ via the so-called Fenton reaction mechanism (Eq. 6) (Fu et al. 2010). It is aided by adding iron salt in the catholyte or coating a heterogeneous iron-based catalyst on the cathode surface (Xiong et al. 2021). The exhausted Fe^{3+} ions are reduced to Fe^{2+} simultaneously, which avoids external replenishing of Fe^{2+} at regular intervals (Eq. 7) ($E_{\text{Fe}^{3+}/\text{Fe}^{2+}} = 0.77 \text{ V vs. SHE}$). The $\cdot\text{OH}$ have high oxidizing power, allowing nonselective oxidation of contaminants at the cathode while maintaining good current efficiency.

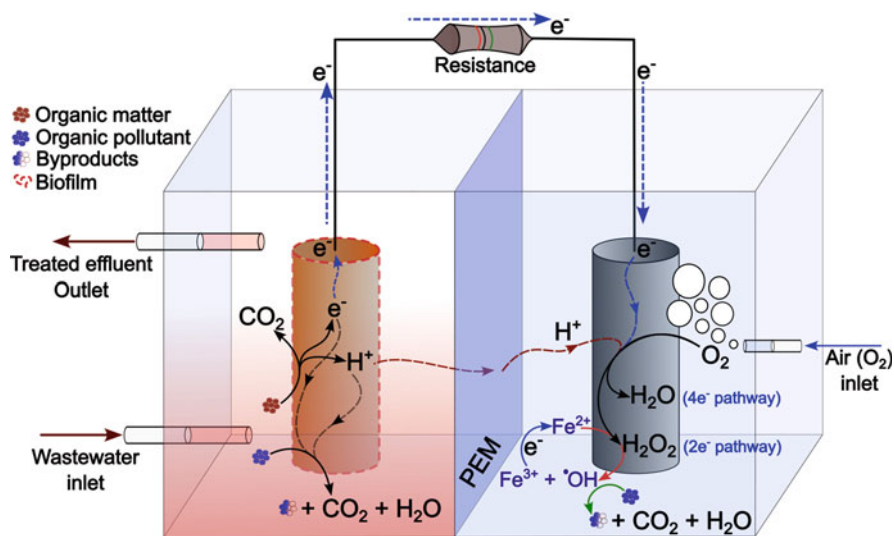
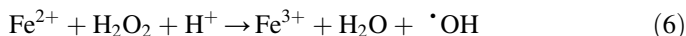
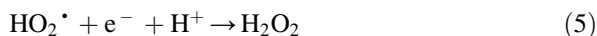
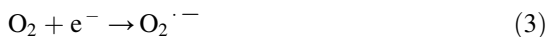


Fig. 7 Schematic depicting the principle of the microbial fuel cell-Fenton system

The cathodic reaction occurring in MFC-Fenton systems are as follows:



In an MFC-photo-Fenton investigation, Wang et al. (2019b) demonstrated 96.83% decomposition of methyl orange with an initial concentration of 20 mg L^{-1} while generating a power density of 43.4 mW m^{-2} . The photo-assisted bioelectro-Fenton reaction had Fe^{3+} loading of about 10 mg L^{-1} , and the presence of W/Mo oxides coated on the graphite felt electrode accelerated the transfer of electrons and improved the removal of methyl orange dye (Wang et al. 2019b). In another bioelectro-Fenton investigation, Long et al. (2021) demonstrated the degradation of tetracycline ($10\text{--}40 \text{ mg L}^{-1}$) with about 99% degradation efficiency in 8 h in the H-type MFC-coupled electro-Fenton reactor. Interestingly, a single-chambered MFC reactor achieved only 74% removal efficiency. The reduction in the removal was due to the inhibitory effects of methyl orange on anodic biofilm, even at low concentrations of 10 mg L^{-1} .

Investigations have reported the degradation of metronidazole under aerobic reduction (cathode) and anaerobic oxidation (anode). High antibiotic metronidazole degradation efficiency ($94.5 \pm 1.4\%$), mineralization efficiency ($89.5 \pm 1.1\%$), and

output power (251 mW m^{-2}) were demonstrated in the MFC-Fenton reactor by Wang et al. (2019a). The optimized catalyst ratio loadings reported were 0.17:1.0 (Mo: W), 0.18 mg cm^{-2} (Mo: W loading), and 10 mg L^{-1} (Fe (III)), respectively. Similarly, Zhao and Zhang (2021) adopted a dual-chambered electro-Fenton-coupled MFC system for mesotrione degradation. When the pollutant was degraded simultaneously at both chambers, under the optimized conditions, the removal rate of the herbicide mesotrione at the anode and cathode reached as high as 0.83 and $1.39 \text{ mg L}^{-1} \text{ h}^{-1}$, respectively. The dominant microbial species responsible for pollutant degradation in the anodic chamber were *Mycobacterium*, *Desulfovibrio*, and *Petrimonas*. Similarly, electron transfer was promoted by *Cloacibacillus* and *Azospirillum* (Zhao and Zhang 2021).

3.6 MFC-Catalytic Oxidation Reaction System

The homogeneous Fenton process produces iron sludge, necessitating additional sludge handling and management. In comparison, heterogeneous catalysts like limonite (Tao et al. 2013) and $-\text{FeOOH}$ (Feng et al. 2010b) have been used to reduce the amount of catalysts employed. These catalysts can be used to generate H_2O_2 to oxidize organic pollutants. The flaw in this method is that surplus dissolved oxygen is not fully utilized for pollutant degradation (Yuan et al. 2017).

Iron phthalocyanine (FePc) mimics the active sites of enzymes involved in catalytic aerobic oxidation and destruction with peroxides. It can destroy recalcitrant organic contaminants by activating H_2O_2 and O_2 in the MFC-catalytic oxidation reaction (MFC-COR) system (Pérollier et al. 2005). In contrast to the Fenton process, the catalytic process creates nucleophilic iron (III) peroxy-complexes and high-valent metal-oxo compounds as reactive species (Sorokin and Meunier 1996). Even though this is efficient at treating wastewater, eliminating catalysts such as FePc is a great challenge from the effluent, leading to secondary pollution and catalyst loss. To overcome this limitation, the use of the catalyst on support materials such as cellulosic fiber (Chen et al. 2007), chitosan (Shen et al. 2010), and carbon nanotubes (Lu et al. 2009) have recently been used (Fig. 8). Organic contaminants such as trichlorophenol (Sorokin et al. 1996) and dyes (Chen et al. 2007) degrade to low-molecular-weight organic acids or mineralized to innocuous CO_2 and H_2O . According to Yuan et al. (2017), using a FePc catalyst produced H_2O_2 in the cathodic chamber, which resulted in the effective oxidation (90%) of red dye in 72 h and a maximum power output of 808.3 mW m^{-3} .

P-nitrophenol is a phenolic derivative commonly treated as an aquatic pollutant. The degradation of P-nitrophenol demonstrated by Zhang et al. (2016) ensured complete removal efficiencies at concentrations below 50 mg L^{-1} . Low electrical resistance in the catholyte increased the reduction efficiency ($31.7 \pm 2.1\%$ to $76.4 \pm 4.1\%$) of P-nitrophenol when sodium acetate in the electrolyte concentration was increased (2000 to 4000 mg L^{-1}). With the utilization of H_2O_2 , the degradation of refractory pollutants in an integrated MFC-COR system is greater when compared

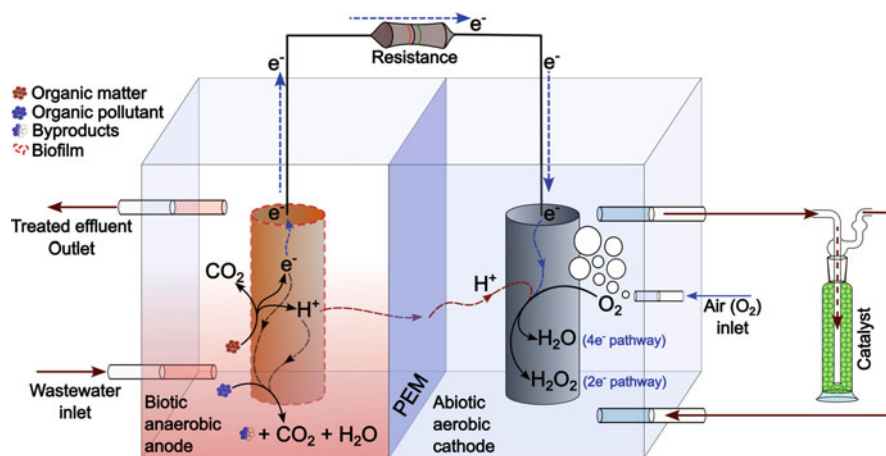


Fig. 8 Schematic depicting the basic working principle of the MFC-catalytic oxidation system

to a conventional MFC-Fenton system. Compared to conventional MFC-Fenton systems, the H_2O_2 is utilized more efficiently for reactive species generation in the integrated MFC-COR system, resulting in accelerated removal of refractory pollutants. In addition, H_2O_2 and O_2 both can be used as oxidants for oxidative degradation in MFC-COR, making this integrated system equally effective in eliminating biodegradable as well as refractory organic pollutants (Suresh et al. 2022).

4 Field-Scale Applications and Future Prospective

Commercialization and field-scale application of these hybrid technologies require consideration of aspects like chemical and mechanical stability, consistent performance, and low maintenance cost over the long run. A 10 L serpentine-type MFC reactor operated by Zhuang et al. (2012) for over 180 days observed a deterioration in the performance of the cathode. The efficiency of the air cathode was recovered entirely by rinsing it with water due to the decrease in cathode alkalization and increase in humidity of the cathode side. The stability of the electrodes plays a major role in determining the performance of MFCs.

The long-term (180 days) stability of carbon fiber brush employed as an anode for treating brewery wastewater was investigated by Brunschweiler et al. (2020). The clogging of the anode decreased the accessible area for microorganisms to adhere, which increased the internal resistance by 18% ($896 \pm 216 \Omega$). On the other hand, when two brushes of 5 cm replaced the carbon fiber brush of 10 cm diameter, power density increased by two times (240 mW m^{-2}) due to the usage of thicker and more robust fibers. It helped in enhanced stability and maintained the surface area by avoiding clogging. To highlight further, Zhang et al. (2013) reported the long-term performance of tubular MFC for treating municipal wastewater for more than

400 days. During this operation, a gradual reduction in the performance of MFC was observed due to corrosion or fouling of electrodes, microbe deactivation, and PEM clogging over the operation period (Kardi et al. 2017).

Despite the considerable progress in MFC-based technology for removing ECs, a few critical issues still need to be addressed. For instance, increasing pollutant concentration in MFC hampers pollutant removal efficiency due to inhibition of microbial consortia at the anode. On the other hand, when it comes to MFC-based hybrid systems such as MFC-photocatalysis and MFC-biofilm electrode reactors, their dependence on external energy (light) sources may undermine the sustainability aspect of MFCs. Moreover, past investigations on MFC are limited to sophisticated, laboratory-scale investigations in a controlled environment that optimize the MFCs to a specific concentration for a particular pollutant, which is rarely encountered during field-scale treatment. Hence, the following lacunas must be appropriately tackled in future research to make MFC-based technology more robust and reliable: (i) synthesis of electrode materials with improved conductivity and stability over longer operating times in MFC reactors, (ii) consideration of a range of operational factors responsible for the complete mineralization of organic pollutants has to be reported, (iii) extensive studies on MFC configurations supporting scaled-up MFC reactors, (iv) exploring the possibility of treating micro and nanoplastics using the MFC-based technology, (v) MFC integration to treat air pollutants and solid waste, (vi) emphasis on optimizing the operational parameters that ensure the continuous production of maximum power density, and (vii) focusing on MFC-based investigations that consider the treatment of organometallic compounds and metal recovery. Considering these suggestions in future investigations would provide a better understanding of the operation of field-scale MFC reactors that would promote a scaled-up MFC operation.

5 Conclusion

MFC-based technologies are a sustainable alternative for effectively removing ECs and harnessing bioelectricity simultaneously. Recent research has demonstrated the effective elimination of organic pollutants such as pharmaceutical compounds, synthetic organic dyes, pesticides, and phenolic and poly hydrocarbons via MFC. The critical factors affecting the performance of MFC are microbial consortiums and electrode catalysts. Nevertheless, other considerations like the concentration and structural complexity of the organic pollutant, electron donors and acceptors, and the electrical connection type (series or parallel) in the event of multiple MFC setups can also affect the operational efficiency of MFC to a certain extent. On the other hand, while degrading recalcitrant pollutants in MFC, operational parameters should be considered, like temperature, offered external resistance, nature of catholyte, pH, and the synergetic effect of the carbon substrate.

When it comes to the biotic anode in MFC, the selection of microbial strains gives a direct advantage concerning degradation efficiency and maximizing power

density. Further, factor such as reactor design also plays a major role in improving the performance of MFC. The dual-chambered MFC has shown greater efficiency when compared to a single-chambered MFC while oxidizing organic matter from wastewater. On the other hand, regarding MFC-based hybrid systems, researchers have demonstrated better pollutant degradation efficiency and power density than stand-alone MFC. The performance of an MFC-based hybrid system depends on influencing parameters such as the size of the cathodic chamber, catholyte salinity, cathodic aeration, coexisting microbial species, and the impact of degradation by-products.

Nonetheless, these systems still need to be optimized to create a perfect synergy for a cost-effective operation. Hence, further investigations must be performed to explore different hybrid combinations and assess the long-term performance of these hybrid treatment systems. In conclusion, MFC-based technologies have shown great potential for sustainable wastewater management. However, significant improvement in understanding the role of material science and biotic–abiotic interactions in MFC is required to aid these neoteric technologies to realize their full potential.

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Microbial Endophytes: A Novel Approach for Emerging Pollutants



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Abstract Over the years, pollution has turned into a major environmental concern. Pollution is generated by various anthropogenic, agricultural, and industrial activities. Different biotechnological methodologies are being employed to remove pollutants present in the environment. The process of bioremediation is one of the safest approaches used to counter environmental problems. In recent years, it has become increasingly prevalent to use microbial endophytes to remove such contaminants. Endophytic microorganisms associated with plants have turned out to be efficacious in degrading organic and xenobiotic compounds present in agricultural and industrial soil. Microbial endophytes capable of resisting inorganic pollutants aid in heavy metal remediation in contaminated soil. So, endophytic phytoremediation is a promising in situ bioremediation approach for environmental pollution. This chapter summarizes microbial endophytes and their role in the remediation of various environmentally hazardous elements.

Keywords Microbial endophytes · Phytoremediation · Xenobiotics · Heavy metals

1 Introduction

Pollution of the environment is among the most exigent and challenging issues over the past decades. The rapid pace of urban development and industrialization have prompted the abasement of environmental standards (Vasilachi et al. 2021). Agricultural practices highly rely on the usage of chemicals namely fertilizers and pesticides in order to improve crop yields and meet the expectations of the ever-growing world population (Prasad et al. 2020; Gupta et al. 2020). These chemicals pose a serious impact on the natural environment of soil leading to soil pollution and have detrimental repercussions on living organisms including flora and fauna (Gavrilescu et al. 2015; Gupta et al. 2020). There have been diverse categories of

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pollutants that significantly harm the environment at the global level such as persistent organic and inorganic pollutants, xenobiotics, and greenhouse gases (Vasilachi et al. 2021).

Emerging pollutants (EPs) are characterized as chemical compounds that can be naturally occurring or synthetically created and have the potential to infiltrate the environment and cause serious adverse impacts on both environment as well as humans by virtue of their toxicity (Geissen et al. 2015; Vasilachi et al. 2021). These surging pollutants encompass a diverse range of chemicals such as pharmaceuticals, cosmeceuticals, pesticides, herbicides, toxins, hormones, endocrine-disrupting agents, and plastics. PPCPs (pharmaceutical and personal care products) are emerging pollutants with substantial ecotoxicological and detrimental effects on human well-being (Kurade et al. 2021). Environmental pollutants also include persistent inorganic compounds including heavy metals like cadmium, arsenic, mercury, lead, etc. (Caliman and Gavrilescu 2009; Bunke et al. 2019). In addition, there are some biological pollutants such as bacteria and viruses, that act as micropollutants in soil (Geissen et al. 2015). Another class of pollutants comprises xenobiotics which contain distinct structural elements that are rare in nature or rather unknown (Datta et al. 2020). These xenobiotic compounds are exogenous chemicals that are artificially synthesized such as drugs, cosmetics, food additives, and pollutants (Maurya and Malik 2016; Datta et al. 2020). Xenobiotics have eminent recalcitrant properties that attribute to their extremely toxic nature (Godheja et al. 2016). Most of these EPs are persistent in nature and not easily degradable, hence they proceed within various environmental matrices via air or water route and thus can be discovered in even those places where they never used to exist (Rasheed et al. 2019).

Phytoremediation is a biotechnological tool to cope with environmental pollution related to emerging pollutants. Green biotechnology using plants and their associated microbes (endophytes) is a sustainable approach for mitigating emerging pollutants and rehabilitating the environment (Kurade et al. 2021). Different plant species can absorb pollutants, so exploiting this absorption prospect, phytoremediation holds the potential for reclaiming polluted soils and waters (Kamusoko and Jingura 2017). Microbial endophytes are life forms that colonize the internal structures of plants, creating a mutually beneficial relationship with the host plant without impairing its physiological activity (Kusari et al. 2012; Gunjal et al. 2018). The most common endophytes associated with numerous plant species are *Pseudomonas*, *Bacillus*, and *Azospirillum* (Gunjal et al. 2018). The efficacy of phytoremediation can be intensified by exploiting plant-microbe interplay (Afzal et al. 2014). Certain endophytic microbes are known to function as vectors for instigating different strains that can degrade pollutants (Kaur et al. 2018). Several microbial endophytes are capable of deteriorating xenobiotic compounds (Singh et al. 2017), and also show extreme tolerance against numerous inorganic metals with relatively high density (Yamaji et al. 2016). Endophytes are prominent producers of various enzymes that result in the degeneration of organic pollutants, thus enhancing the phytoremediation of these hazardous elements (Singh et al. 2016). So, the collaborative approach of using plants and their associated microbes is a propitious prospect for environmental cleanup.

Considering the potential of endophytes, the main objective of this chapter is to view, assess, and discuss phytoremediation, microbial endophytes, and their role in mitigating emerging organic pollutants, heavy metals, xenobiotics, and greenhouse gases.

2 Phytoremediation by Endophytes: A Sustainable Approach

Phytoremediation can be described as the removal process of harmful pollutants or impurities from the environment with the help of photosynthetic organisms, that is, plants. This is a feasible technique because plants are present almost everywhere on the planet. This technique has drawn a lot of interest as it is a sustainable method for the elimination and degeneration of pollutants/contaminants (He et al. 2020; Kurade et al. 2021; Song et al. 2021; Anand et al. 2023). The potential and widespread presence of emerging pollutants such as PPCPs in the environment results in adverse ecological effects even at insignificant concentrations because of their highly reactive biological properties (Underwood et al. 2011; Xiong et al. 2021). On account of the persistent nature of EPs, their biomagnification and accumulation occur at different trophic levels in a food chain resulting in a negative influence on the ecosystem (Kelly et al. 2007). Conventional treatments such as wastewater treatment plants (WWTPs) for eliminating EPs like PPCPs have been proven to be inefficient and unsatisfactory. More efficient bioremediation techniques including microbial degradation and enzymatic catalysis could be employed. However, these advanced approaches are not cost-effective which is a negative factor for large-scale commercial applications (Bartrons and Peñuelas 2017; Xiong et al. 2018). Phytoremediation of emerging pollutants is a plant-based simple bioremediation technique that is sustainable and very effective in eliminating pollutants via spontaneous biotic processes (Rane et al. 2016; Gikas et al. 2018; Kurade et al. 2021). Plants are exploited for the remediation of varied pollutants from the environment including heavy metals uptake (Wang et al. 2017), polychlorinated biphenyls (PCBs) rhizodegradation and uptake (Passatore et al. 2014), dye degradation by ornamented plants namely *Aster amellus*, *Petunia grandiflora*, *Portulaca grandiflora*, etc. (Khandare and Govindwar 2015). Phytoremediation of different contaminants is usually executed by distinctive mechanisms (Fig. 1) including phytodegradation, phytovolatilization, phytoextraction, phytostabilization, phytoaccumulation, rhizofiltration, and rhizodegradation (Van Aken 2008).

Although, the phytoremediation technique also has some disadvantages, which include low cell mass, the release of gaseous pollutants, and negative effects on the growth of plants, their physiology, and metabolism (Gerhardt et al. 2009; Beans 2017; Waigi et al. 2017). However, these limitations can be subdued by microbe-assisted phytoremediation. Phytoremediation can be enhanced by plant-microbe associations namely plant-endophyte interactions or plant-rhizospheric interactions.

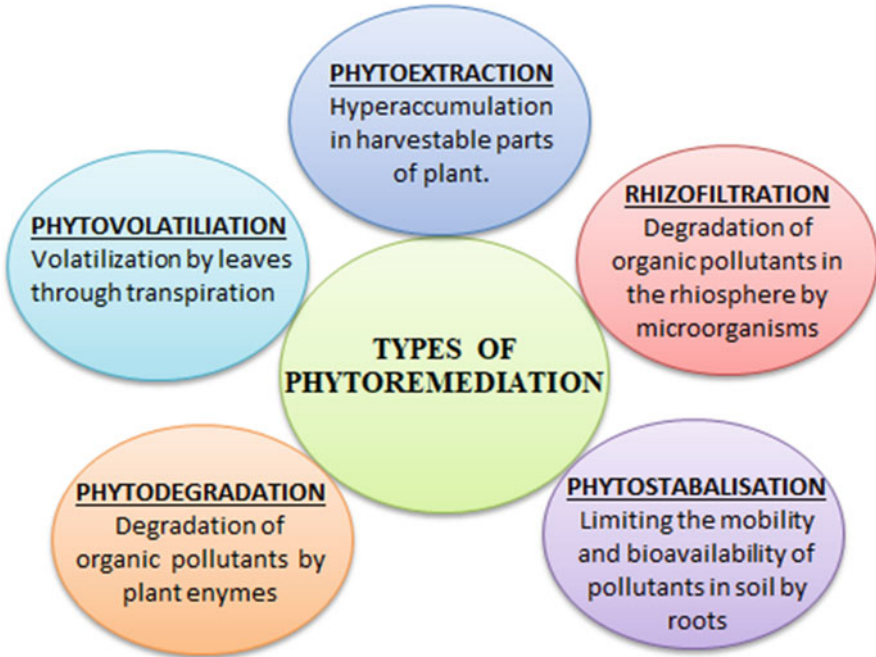


Fig. 1 Types of phytoremediation

Rhizoremediation can upgrade the process of phytoremediation and facilitate the growth of rhizosphere-associated microbial communities by root exudation and possible enzyme induction (Didier et al. 2012). But endophytic microbes were found to be more efficient in phytoremediation than the microorganisms present in the rhizospheric region (Rajkumar et al. 2010; Weyens et al. 2015; Gunarathne et al. 2019; Zuzolo et al. 2021). Endophytic microbes including bacteria, actinomycetes, and fungi are omnipresent in the visceral tissues of plant species and these microbes do not manifest any negative or inimical consequences on their host plant. Such microorganisms are present in collegial association with many plant species (Anand et al. 2023). Thus, this is a more economical, environmentally safe, and sustainable approach to pollution control (Kong and Glick 2017; Mitter et al. 2019).

2.1 Role of Endophytes in Phytoremediation

Endophytic microorganisms greatly help the host plant in adapting to the polluted environments, deteriorating or immobilizing pollutants present in the surroundings, encouraging plant growth, increasing metal tolerance, etc., as a result, it further strengthens the phytoremediation property (Germaine et al. 2009; Zhang et al. 2011; Li et al. 2012).

Endophytes improve the growth of plants in polluted environments by two different mechanisms:

1. Direct method in which endophytes produce growth-promoting elements including phytohormones, enzymes, and organic molecules such as IAA (indole-3-acetic acid), siderophores, and ACCD (1-Aminocyclopropane-1-carboxylate deaminase).
2. Indirect method in which they activate resistive properties of plants in defiance of pathogens.

Other than this they also modify the plant's metal augmentation capability by eliminating metal-disarming interstitial polymeric material, plus metal-activating natural acids and microbial surfactants (Ma et al. 2016). Moreover, endophytes are found to be helpful in decreasing phytotoxicity. Endophytes possess multiple traits that have shown the ability to alter the toxicity of contaminants by producing siderophores, natural acids, iron chelators, and several contaminant-reducing enzymes (Saravanan et al. 2007; Soleimani et al. 2010; Yousaf et al. 2010).

3 Endophytic Microorganisms

The word “endophyte” is procured from the Greek terminologies “endon” and “phyton” meaning “occurring inside” and “plants,” respectively (Lata et al. 2018; Singh et al. 2020). Endophytic microorganisms colonize the internal tissues of plants without causing any obvious harm to the host plant. Due to their potential to enhance the growth of plants, improve health, and tolerance to abiotic and biotic challenges, these microbes have attracted a lot of research. There have been many bioactive compounds found in their manufacture, including secondary metabolites production aiding in agricultural sustainability (Le Cocq et al. 2017); producing certain plant-growth promoting enzymes/plant growth regulators to facilitate vegetation (Ryan et al. 2008); enhancing biological nitrification and denitrification processes (Ji et al. 2014); releasing antibiotics, antimicrobial (Yu et al. 2010), and antifungal (Rodriguez et al. 2009) metabolites and serving as biological control agents against various pathogenic organisms infecting plants (Hong and Park 2016), nemathelminthes (Tian et al. 2007), and insects (Suryanarayanan et al. 2016); forming intrinsic associations and benefiting plants by procuring nutrients (Santos et al. 2018).

Microbial endophytes are associated with different plant species as biotrophic symbionts. These organisms are ubiquitously inhabiting numerous plant species either latently or actively (Gunjal et al. 2018). Entry of endophytes into plant tissue is similar to that of pathogens (Santoyo et al. 2016). Endophytic microbes colonize plant tissues passing different stages namely host finding or recognition, entry into host tissue through openings (stomata, lenticels, hydathodes, abrasions, and micro-pores), and colonization in the host plant tissue or surface (Singh et al. 2020). Besides the various roles of endophytes in plant development discussed earlier,

Table 1 Plant-associated bacterial and fungal endophytes with their bioactive influence

S. no.	Endophytes	Plant (host)	Bioactive role	References
1.	<i>Bacillus amyloliquefaciens</i> EPP90 (bacterial endophytes)	<i>Pennisetum glaucum</i>	Abiotic stress tolerance ability to plants	Kushwaha et al. (2020)
2.	<i>Bradyrhizobium</i> sp. SUTNa-2, <i>Enterobacter cloacae</i> RCA25, <i>Herbaspirillum huttiense</i> RCA24 (bacterial endophytes)	<i>Oryza sativa</i>	Promote plant growth	Andreozzi et al. (2019), Greetatorm et al. (2019)
3.	<i>Mucor</i> species (fungal endophytes)	<i>Arabidopsis arenosa</i>	Provides metal toxicity tolerance to plants	Domka et al. (2019)
4.	<i>Penicillium aurantiogriseum</i> 581PDA3, <i>Trichoderma harzianum</i> 582PDA7 (fungal endophytes)	<i>Triticum aestivum</i>	Promote plant growth and provide abiotic stress tolerance ability	Ripa et al. (2019)

these microbes also perform a remarkable role in the deterioration and remediation of different pollutants (Gunjal et al. 2018).

Microbial endophytes generally include bacterial endophytes, fungal endophytes, and endophytic actinomycetes (Raghukumar 2008). Based on the life strategy of these microbes, they can be obligate or facultative. The former ones are true endophytic microbes that completely depend on their host for growth and survival, whereas the latter ones have at least a single phase in their life process outside their host plant. Transmission of obligate parasites occurs vertically among plants or by means of vectors (Raghukumar 2008; Su et al. 2010). Obligate endophytic diazotrophs colonize the internal tissues of roots and aerial parts, whereas facultative ones occupy the surface and root interior of nonleguminous plants. These include bacteria such as *Azospirillum brasilense*, *A. diazotrophicus*, *H. rubrisubalbicans*, and *Azoarcus* spp. (Gunjal et al. 2018). Table 1 represents potential endophytes utilized for phytoremediation.

4 Microbial Endophytes in Organic Pollutants Degradation

Organic pollutants arise on account of the unendurable use of natural resources and also as a consequence of many anthropogenic activities such as substantial utilization of chemical pesticides, PPCPs, and other emerging pollutants. These pollutants are hazardous to man as well as to nature because of their toxicity, hydrophobicity, and persistence (Afzal et al. 2014). Polluted soil contains organic compounds like polycyclic aromatic hydrocarbons (PAHs), phenolic compounds, polychlorinated biphenyls, pesticides or herbicides, pharmaceuticals, and toxins which slow down the proliferation and metabolism of microorganisms present in soil (Sun et al. 2014; Birolli et al. 2021). Owing to the toxic nature of organic pollutants, they act as mutagens or carcinogens and might infiltrate the food chain and afflict humans as

well as animals (Havelcová et al. 2014). The existence of hydrocarbons in surroundings negatively affects the growth of plants and the seed germination process (Smith et al. 2006). It also affects the absorption of water and minerals by plants and microorganisms (Nie et al. 2009). Thus, the expulsion of such organic impurities present in the environment is mandatory. Biodegradation, bioadsorption, and bioaccumulation are major biotic mechanisms responsible for the remediation of organic contaminants (Kurade et al. 2021). Table 2 represents various endophytes able to degrade organic pollutants.

There are numerous bacteria and plants which exist in close association and cooperatively degrade organic pollutants. These microbes are generally present in the rhizospheric or endospheric parts of plants and possess certain pollutant-degrading genes which convert organic contaminants into mineral nutrients known as mineralization (Afzal et al. 2011). Root interior of plants contains more endophytic microbes in contrast to the bulk soil region (MacKinnon and Duncan 2013) and the number of organic pollutant degraders is proportionate to the occurrence and quantity of organic pollutants present in the surroundings. Endophytes are capable of degrading several hydrocarbons namely benzene, xylene, toluene, and volatile organic compounds like trichloroethylene (TCE), and also show resistance to heavy metals (Moore et al. 2006). Certain strains of microbial endophytes which colonize the plant tissue have alkane degrading genes such as *alkH* (alkane hydroxylase), *CYP153* (cytochrome P450-type alkane hydroxylase), *alkB* (alkane monooxygenase), and these genes are commonly present in the bacterial genus *Pseudomonas* and *Bacillus* (Yousaf et al. 2011; Kukla et al. 2014; Liu et al. 2014). A group of toxic and persistent organic pollutants which include PAHs, phenol and its derivatives, insecticides, pesticides, and polyhalogenated organic compounds are ubiquitous in the environment (Peng et al. 2013).

Bacterial endophytes like *Burkholderia fungorum* DBT1 is able to break down harmful PAHs including dibenzothiophene and phenanthrene (Andreolli et al. 2013). These low-molecular-weight compounds are easily degraded by endophytic bacteria but for high-molecular-weight PAH degradation, endophytes require carbon which is provided by plants (Chaudhry et al. 2005). Endophytic species *Klebsiella terrigena* E42 in close association with the *Spirodela polyrhiza* plant own the capability to degenerate fenopropathrin (Feng et al. 2017). The insecticide widely used in agriculture is Chlorpyrifos [O, O-Diethyl O-(3,5,6-trichloro-2-pyridinyl) phosphorothioate] (CP). CP is toxic for humans as it causes breast cancer, kidney, and liver damage. *Pseudomonas* sp. BF1-3 obtained from *Platycodon grandifloras* has the enzyme organophosphorus hydrolase which helps in the breakdown of CP (Barman et al. 2014). Pea plant having *Pseudomonas* capable of degrading 2,4-dichlorophenoxyacetic acid (2,4-D) which is an organochlorine herbicide (Feng et al. 2017). The persistent organic pollutants (POPs) include hazardous polychlorinated biphenyls (PCBs) with exorbitant toxicity. Among them, bisphenol A (BPA) can impede the human endocrine system and it is toxic and show carcinogenic properties (Suyamud et al. 2020).

Table 2 Overview of organic pollutant degrading endophytes

S. no.	Endophytes	Host plants	Pollutant degradation	References
1.	<i>Pseudomonas</i> sp. P3, <i>Pseudomonas</i> sp. Ph6 <i>P. putida</i> PD1, <i>Stenotrophomonas</i> sp. P1	Canadian horse-weed (<i>Conyza canadensis</i>) and red clover (<i>Trifolium pratense</i> L.)	PAHs such as naphthalene and fluorene	Khan et al. (2014), Zhu et al. (2016)
2.	<i>Alcaligenes</i> sp. (AIEB-6), <i>Pseudomonas</i> sp. (AIEB-4), and <i>Achromobacter</i> sp. (AIEB-7)	Hemp (<i>Cannabis sativa</i>)	Phenols and its derivatives	Iqbal et al. (2018)
3.	<i>Bacillus megaterium</i> strain RRB, <i>Sphingobacterium siyangensis</i> strain RSA, and <i>Pseudomonas aeruginosa</i> strain RRA	Rice plants and grain	CP degradation in rice and wheat	Feng et al. (2017)
4.	<i>Pseudomonas putida</i> strain VM144	<i>Pisum sativum</i>	(2,4-Dichlorophenoxyacetic acid)	Germaine et al. (2006)
5.	<i>Pantoea anantisi</i>	<i>Dracaena sanderiana</i>	Bisphenol A (BPA)	Suyamud et al. (2020)
6.	<i>Pseudomonas aeruginosa</i> L10, <i>Massilia</i> sp. Pn2	<i>Phragmites australis</i> , wheat	C ₁₀ -C ₂₆ <i>n</i> -alkanes in diesel oil, and phenanthrene	Wu et al. (2018)
7.	<i>Exiguobacterium profundum</i> strain N4	<i>Amaranthus spinosus</i>	Diazo dye, reactive black 5	Sharma and Roy (2015)
8.	<i>Burkholderia cenocapacia</i> 869T2	Vetiver grass	2,3,7,8-TCDD (2,3,7,8-tetrachlorodibenzodioxin)	Nguyen et al. (2021)
9.	<i>Bacillus thuringiensis</i>	Indian ginseng	Pyrethroids such as cypermethrin and cyhalothrin	Birilli et al. (2021)
10.	<i>Methylobacterium populi</i> BJ001	Poplar tissues (<i>Populus deltoidesnigra</i> DN34)	Methane and nitro-aromatic compounds like 2,4,6-trinitro-toluene	Van Aken et al. (2004)

5 Microbial Endophytes in Inorganic Pollutants Remediation

Inorganic contaminants like heavy metals, radioactive elements, and mineral salts are very harmful to humans and the environment due to their toxic nature (Yang et al. 2014). Human-induced activities including fossil fuel burning, effluent from various

industries, and mining are the principal cause of tainting of soil, oceans, and atmosphere with inorganic pollutants (Simmons et al. 2010; Kopittke et al. 2017). A variety of natural processes also contribute to inorganic pollution namely geological weathering, volcanic activity, soil erosion, metal corrosion, evaporation of metals from soil, and sediment resuspension (Masindi and Muedi 2018).

Unlike organic pollutants, inorganic pollutants like heavy metals cannot be degraded (Rosestolato et al. 2015). Cd, Hg, Cu, Ni, Zn, and Pb are examples of such minerals that are nonbiodegradable and adversely affect the environment via bioaccumulation and biomagnification due to their persistent nature (Narendrula-Kotha et al. 2020). These metals interfere with the growth and proliferation of plants, microbial growth, and metabolic reactions such as the breakdown of organic pollutants. Radioactive elements are also present in the soil as pollutants due to the development of nuclear power (Miao and Pan 2015). Micronutrients including Cu, Co, Zn, and Fe are present in trivial amounts in plants but they perform a substantial role in plant development (Rahman and Singh 2019). Nevertheless, elevated concentrations of these minerals are noxious to plants which leads to alterations in gene expression, variations in proteins, and metabolite constitution, and these changes activate the coping mechanism in plants under toxicity of these metals (Berni et al. 2019). Chlorosis in young leaves and inhibition of plant growth are symptoms of high metal concentrations (Yang et al. 2020). In this regard, removing these pollutants is of uttermost importance.

Despite the toxicity of heavy metals toward plants, there are certain varieties that demonstrate metal tolerance and few of them are even metal hyperaccumulators, that is, they grow in metal-contaminated soil or water and translocate or accumulate metals in their tissue by absorption from the soil via roots (Li et al. 2012). Endophytes which are associated with hyperaccumulators also have the ability to show resistance to metals (Idris et al. 2004). Plants accumulate these minerals/metals under the domination of endophytes and the concentration of these minerals present in the rhizosphere also changes (Xu et al. 2015). Endophytes increase the plant's capability to stabilize/accumulate the inorganic pollutants as they produce several factors like siderophores (Rajkumar et al. 2010), exopolysaccharides, biosurfactants, phosphorus solubilization, auxins, and organic acids which increase plant growth (Chen et al. 2014; Ahmad et al. 2014). *Klebsiella* sp. and *Enterobacter* sp. in association with *Brassica napus* increase the growth of host plant and accumulation of metals like cadmium, zinc, and lead (Jing et al. 2014). The potential of the plant named *Elsholtzia splendens* to accumulate Cu is enhanced by CZ1 strain of *Pseudomonas putida* (Xu et al. 2015). *Burkholderia cepacia* VM1468 has pTOM-Bu61 plasmid which degrades trichloroethane (TCE) and has *ncc-nre* (*ncc*: nickel-cobalt-cadmium resistance genes; *nre*: nickel resistance) locus for Ni resistance (Weyens et al. 2010). Bacteria corresponding to the roots of *Cirsium arvense* produce certain factors like ACCD enzyme, IAA, and siderophores that contribute to lowering the toxicity of arsenic (As) by promoting plant growth (Cavalca et al. 2010). Several microbial endophytes are competent in producing organic acids like oxalic and citric acid resulting in the enhancement of mobility and bioavailability of heavy metals. So, phytoremediation of heavy metals is augmented by metal-resistant endophytic

Table 3 Various endophytes for heavy metal remediation

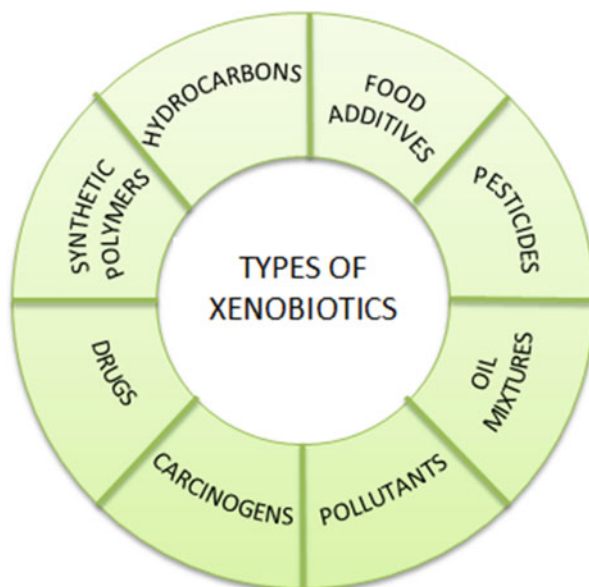
S. no.	Endophyte	Host plant	Target pollutant	References
1.	<i>Bacillus</i> sp., <i>Enterobacter</i> sp., <i>Clostridium aminovalericum</i> , <i>Ralstonia eutropha</i>	<i>Zea mays</i> , <i>Nicotiana tabacum</i>	Cd	Mastretta et al. (2009), Moreira et al. (2014), Ahmad et al. (2016)
2.	<i>Pseudomonas putida</i> , <i>Bacillus</i> sp.	<i>Elsholtzia splendens</i> , <i>Alnus firma</i>	Cu	Shin et al. (2012), Xu et al. (2015)
3.	<i>Pseudomonas</i> sp., <i>Psychrobacter</i> sp.	<i>Ricinus communis</i> , <i>Brassica juncea</i>	Ni	Ma et al. 2015)
4.	<i>Salix schwerinii</i> , <i>Salix viminalis</i>	<i>Bacillus pumilus</i> , <i>Paenibacillus lactis</i> , <i>Pantoea agglomerans</i>	Zn	Weyens et al. (2013)
5.	<i>Acinetobacter</i> sp., <i>Bacillus</i> sp., <i>Steganosporium</i> sp., <i>Aspergillus</i> sp.	<i>Commelina communis</i> , <i>Rabposia eriocalyx</i> , <i>Arenaria serpyllifolia</i>	Pb	Zhang et al. (2011), Li et al. 2012b)
6.	<i>Pseudomonas korensis</i> , <i>Rhodococcus aetherivorans</i>	<i>Zea mays</i> , <i>Pteris vittata</i>	As	Shagol et al. (2014), Lampis et al. (2015)
7.	<i>Bacillus</i> sp., <i>Pantoea</i> sp., <i>Pseudomonas</i> sp.	<i>Stanleya pinnata</i> , <i>Astragalus bisulcatus</i>	Se	Sura-de Jong et al. (2015)

microorganisms which promote plant growth, lowers metal toxicity, and improve translocation and agglomeration of these metals in plants (Li et al. 2012). Table 3 shows several plant-associated endophytes for metal remediation.

6 Microbial Endophytes in Xenobiotic Degradation

The term “xenobiotic” refers to anything that is “foreign to life,” where “Xeno” means foreign and “biotic” means living/live (Datta et al. 2020). Xenobiotics contain chemical substances which are new/unrecognized by nature (Rieger et al. 2002). These substances are toxic and are not recognized by the organisms as they are foreign to life such as pollutants, drugs, cosmetics, and food additives (Chen et al. 2007; Godheja et al. 2016; Kumar et al. 2017). Xenobiotics are mostly made up of organic compounds such as carbon halogen elements (Qadir et al. 2017), alkyl-benzyl sulphates (Brandt et al. 2001), PCBs (Top and Springael 2003), pesticides/insecticides (Baun et al. 2003), fabricated polymeric compounds (Magan et al. 2010), medicinal drugs, and oil mixtures (Qadir et al. 2017). These substances have the tendency to enter the food chains directly and affect the human population in adverse ways (Koppel et al. 2017). Types of xenobiotics are displayed in Fig. 2.

The obstinate property of the xenobiotic compounds depends on their structural complexities (Godheja et al. 2016). Many of these chemical substances are

Fig. 2 Types of xenobiotics

considered to be carcinogens. Compounds such as fabricated polymers, pesticides, and hydrocarbons can cause cancer in human beings (Damstra et al. 2002). Exposure to xenobiotics can result in DNA damage (da Silva 2016), sexual dysfunctions (Bonde and Giwercman 2014), and psychological disorders (Genuis 2009). These pollutants can also affect the health of the fetus and mother by crossing the blood-placental barrier (Myllynen et al. 2007). Relying on the structural complexities of these xenobiotic compounds, they can either be broken down into simpler forms (Rieger et al. 2002) or can be converted into a more hazardous form (Magan et al. 2010). The xenobiotic compounds can be converted into small organic or inorganic components by both biotic and abiotic processes (Jeon et al. 2016). Primary mechanism for deterioration of xenobiotic compounds involves the oxidation of hydrocarbons, reduction of halogenated hydrocarbons, and hydrolysis of fabricated aromatic compounds such as anilines and phenols (Atashgahi et al. 2018).

Xenobiotic compounds such as complex hydrocarbons, specifically aromatic compounds, were found to be degraded by bacterial endophytes indigenous to poplar trees (Taghavi et al. 2011). Several endophytic microbes help in pollutant degradation and simultaneously promote plant growth activities. These endophytes can break down xenobiotic compounds and can potentially benefit plants by secreting growth promoters such as auxins and aid in the nitrogen fixation process (Becerra-Castro et al. 2011). *Burkholderia* sp. PsJN, *Microbacterium arborescens*, and *Bacillus pumilus* are endophytes associated with onion roots, shoots of *T. domingensis*, and *Pistia* roots, respectively, are known to degrade textile effluents (Shehzadi et al. 2014). DS24 and DS4 strains of *Streptomyces griseorubiginosus* associated with *Miscanthus giganteus* hybrid of *Miscanthus sinensis* and *Miscanthus sacchariflorus* results in the degradation of certain PPCPs namely diclofenac and

sulfamethoxazole (Sauvêtre et al. 2020). Endophytes draw on xenobiotic compounds as an energy source which helps them to effectively perform the process of bioaugmentation. Additionally, the amino acids, carbohydrates, and nutrients present in the host plant facilitate the pollutant-degrading properties of these endophytes (Bacon and Hinton 2007).

7 Microbial Endophytes in Bioremediation of Greenhouse Gases

Certain gaseous chemical compounds in the atmosphere of our planet act as greenhouse gases which absorb and reemit IR radiations and heat up the earth's atmosphere. However, if the concentration of these gases increases, it leads to various global environmental issues such as global climate change, depletion of the ozone layer, and sea-level rise. Greenhouse gases result from both natural and anthropogenic activities and majorly comprise of CO₂, CH₄, N₂O, water vapor (H₂O), and halogenated compounds (Stepniewska and Kuźniar 2013). Potential of endophytic microorganisms in greenhouse gas bioremediation has been recognized in a number of research. For instance, certain species of microbial endophytes namely *Bacillus* and *Methylobacterium* are known to promote growth of the plant and enhance the carbon dioxide uptake, as well as facilitate the oxidation of methane and nitrous oxide reduction (Kumar et al. 2016; Liu et al. 2017). Similarly, filamentous endophytic fungal species like *Trichoderma* and *Aspergillus* have been known to sequester carbon, produce enzymes that degrade methane, and convert nitrous oxide into harmless nitrogen gas (Araujo et al. 2018; Liu et al. 2020).

One mechanism that triggers reduction of greenhouse gas emissions by fungal endophytes is by enhancing plant growth and carbon sequestration. Fungal endophytes can improve plant biomass production, increase the efficiency of photosynthesis, and enhance carbon fixation (Choudhary et al. 2018; Pimentel et al. 2019). They can also contribute to the reduction of greenhouse gas emissions by enhancing plant tolerance to stress factors like heavy metal contamination and salinity. These stress factors can lead to the production of greenhouse gases, but fungal endophytes can help alleviate stress and reduce emissions. Additionally, the potential production of complex organic compound-degrading enzymes by fungal endophytes can help in reducing the effluence of greenhouse gases from agricultural and industrial processes (Kour et al. 2020).

In accordance with recent research by Taurisano et al. (2020), the plausible potential of algal endophytes in the bioremediation of CO₂ was evaluated. The study showed that such endophytes can significantly enhance the photosynthetic efficiency of the main plant, leading to higher carbon fixation and reduction of CO₂ concentration in the atmosphere. The significance of algal endophytes in reducing methane gas emissions, a potent greenhouse gas, from paddy fields was also investigated (Singh et al. 2019). The study revealed that certain algal endophytes

could inhibit the activity of methanogenic archaea, which are responsible for CH₄ production in rice paddies, leading to a reduction in CH₄ emissions.

7.1 Prominent Mechanisms of Greenhouse Gas Bioremediation by Microbial Endophytes

It has been exhibited that microbial endophytes are crucial to greenhouse gas remediation. In recent years, research into how microbial endophytes can lessen the effects of greenhouse gases has grown significantly. Some of the recently highlighted mechanisms for enhancing the process of bioremediation of greenhouse gases by endophytes are as follows:

7.1.1 Carbon Sequestration

The process of taking CO₂ from the air and storing it in long-term sinks, such as soil, oceans, or forests, is known as carbon sequestration. Microbial endophytes accomplish this by enhancing plant nutrient absorption and promoting the formation of root systems, which results in increased biomass production and ultimately leads to greater carbon storage (Kumar et al. 2019).

In a recent study, fungal endophyte, *Phomopsis liquidambar*, has been reported to upgrade plant growth and increase carbon sequestration in poplar trees by improving nutrient uptake and enhancing secondary metabolite synthesis (Ma et al. 2018). Bacterial endophytes, like *Methylocystis* sp., also perform a critical function in the carbon sequestration of wetland ecosystems by converting methane into biomass (Chen et al. 2018).

The application of microbial endophytes in the sequestration of carbon has significant potential for alleviating the negative effects of greenhouse gas emissions on climate change. By enhancing the plant capacity and assisting with carbon retention in the soil, microbial endophytes can reduce the amount of CO₂ in the atmosphere (Sahu et al. 2021).

7.1.2 Methane Oxidation

Methane oxidation is a process that converts methane to less harmful compounds, which include water and carbon dioxide. According to studies, endophytic microbes including bacteria and fungi can oxidize methane in plants (Ho et al. 2019). Diffusion first moves the methane from soil to the roots of plants, where it gets subsequently ingested by microbial endophytes present in the plant tissues (Singh et al. 2019b). Rice, wheat, and sugarcane are only a few of the plant species from which endophytic methane-oxidizing bacteria (MOB) have been isolated (Kim et al.

2016). These MOBs have the capability to oxidize methane in an aerobic manner, and it is believed that they significantly reduce methane emissions from agricultural soils such as rice paddies (Ding et al. 2014). Moreover, endophytic fungi are reported to boost the growth of methane-oxidizing bacteria, thereby enhancing the methane oxidation rate (Ho et al. 2019). Furthermore, endophytic fungus *Penicillium funiculosus* was found to consume methane under aerobic conditions in vitro (Lopez-Mondejar et al. 2016). Nevertheless, advanced research should be conducted for understanding the mechanisms underlying this process and to develop effective bioremediation strategies.

8 Conclusion

Phytoremediation assisted by microbial endophytes is an emerging and promising technology to mitigate hazardous emerging pollutants. These abiding pollutants are the result of numerous anthropogenic and natural factors leading to environmental pollution. In nature, endophytic microorganisms exist in close symbiotic alliance with plants aiding them in growth and development, and physiological functions by producing growth hormones, protecting against pathogens, fixing nitrogen, boosting crop yields, and removing contaminants. These microbes have specific genes for degrading and transforming toxic pollutants including xenobiotics and other organics into nontoxic forms. Heavy metal tolerance/resistance property of microbial endophytes helps in lowering heavy metal phytotoxicity and also aids in the augmentation and translocation of these metals into plants thus contributing to heavy metal bioremediation. In addition, endophytes tend to be quite impactful in reducing greenhouse gas emissions and climate change. They can gradually decrease the accumulation of greenhouse gas concentration by processes like carbon sequestration and methane oxidation. Thus, microbial endophytes have the potential to be extremely helpful in decreasing the adverse effects of anthropogenic activity on the environment and promoting more sustainable future for humanity if properly utilized. However, further technological advancements need to be investigated in order to flourish the utilization of these microbes in various bioremediation techniques.

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Nano-Bioremediation: An Emerging Weapon for Emerging Pollutants



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Abstract Every year, various sectors especially production and processing organizations involved in pesticides, pharmaceuticals, and dyes emit harmful toxic substances into the atmosphere which infests the ecosystem. However, environmentalists and conservation organizations adapt physical, chemical, and biological approaches to eradicate pollution and toxic substances from the environment, but these are challenging ones. Nanotechnology-based bioremediation is an emerging and promising approach that plays an imperative role in the confiscation of pollutants on cost-effective grounds. Recent advancements in nanotechnology especially nanoparticles have taken bioremediation to the next level. These techniques in general provide a broader variety of options for controlling pollutants in aquifers and wastewater as well as heavy metal and hydrocarbon-polluted sediments. Bacterial, fungal, and [algal cultures](#) and their components, extracts, or biomolecules as catalytic agents are widely emerging as a trend for the imperishable production of nanomaterials. This chapter explores the potential roles of bioremediation in counteracting environmental pollutants.

Keywords Bioremediation · Nanotechnology · Pollutants · Environment · Nanoparticles, Hazards

1 Introduction

Nowadays, environmental pollution is one of the major challenges worldwide because of its greatest threats to the health and well-being of humanity. The major sources of environment pollution are urbanization, industrialization, burning of fossil fuels, mining, and agriculture activity (Manisalidis et al. 2020). As a result, various chemicals including elements and toxic compounds have been released into the air, water, and soil. Uncontrolled use of hazardous compounds in consumer

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products, industrial waste discharge into water bodies, and the indiscriminate use of pesticides and veterinary drugs are some of the major causes of environmental pollution (Gangwar et al. 2019).

In nature, nonbiodegradable systemic pollution is a major threat to living organisms when they enter the food chain and accumulate in higher species through biomagnification (Bari and Kindzierski 2017). These hazardous substances may remain in environmental matrices for a very long time due to their elemental composition. The issue has consequently caused significant concern throughout the world, requiring in-depth investigation to create practical mitigation plans for polluted areas (Gosset et al. 2017).

Nanotechnology is an advanced and innovative technology that has tremendous potential for providing inventive solutions to a wide range of environment issues. Currently, nanotechnology has already been used in various industrial sectors such as food production, water purification, medical products, energy technology, as well as biodegradation (Ibrahim et al. 2016). Researchers from all over the world have focused a lot of interest on nanomaterials because of their distinctive physicochemical properties in a variety of environmental science fields, particularly in bioremediation. This is because nanomaterials owing to their unique physical and chemical properties such as larger surface per unit area produce plasmon resonance and easily penetrate and diffuse contamination sites (Sikiru et al. 2022).

On the other hand, bioremediation has received significant attention due to their vital role in the biological system for removal and reduction of contamination from water, soil, and air. It also has a significant role in the preservation of several ecological processes like nutrient uptake, improved food production, and biodegradation (Mondal et al. 2023). Bioremediation has many advantages over physiochemical methods such as high competence, cost and energy effectiveness, minimal generation of chemical and biological sludge, and supplementary nutrient requirements. However, bioremediation has a drawback as well, namely, it takes a long time, usually several months to over a year, to carry out the elimination of a hazardous molecule. Additionally, when areas are extensively contaminated with highly toxic and hazardous pollutants, their application is restricted (Chaudhary et al. 2023).

Since each approach has advantages and disadvantages of its own, integrating remediation methods could be seen as a way to handle remediation issues. Recently, nano-bioremediation is one of the techniques that has attracted a lot of attention. It is utilizing the advantage of nanotechnology as well as bioremediation. Nano-bioremediation exhibits several advantages over traditional remediation techniques. Firstly, the high surface area and reactivity of nanomaterials enhance the contact between pollutants and degrading agents, improving the degradation efficiency or transformation of contaminants. Secondly, the incorporation of biological agents allows utilization of natural microbial processes, facilitating the degradation of complex pollutant mixtures. Thirdly, nano-bioremediation can be applied to various environmental matrices, including soil, water, and air, making it a versatile approach. Additionally, ease of improvement/modification in surface properties of

nanoparticles entitles them for selective removal of specific pollutants (Madima et al. 2020).

Even though nano-bioremediation has promising prospects in environmental pollution control, long-term residence and mobility of nanoparticles can have probable toxicological effects on ecosystems and human health (Del Prado-Audelo et al. 2021). Therefore, safe implementation of nano-bioremediation techniques needs comprehensive risk assessments along with development of relevant approaches. However, additional research and development is required for complete understanding of potential risks and optimize the efficiency of nano-bioremediation techniques (Wang et al. 2022). The ultimate purpose of this chapter is to examine unique concept concerned with identification of nanomaterial-assisted bioremediation processes and possible interactivity among pollutants, microorganisms, and nanomaterials to abolish pollutants from the environment.

2 Emerging Pollutants

Emerging pollutants, also known as emerging contaminants or novel pollutants, refer to a diverse group of chemicals or substances that have recently been identified as potential environmental contaminants (Escher et al. 2014). These pollutants are not typically monitored or regulated, but they are gaining attention due to their potential adverse effects on ecosystems and human health. Industrial activities, pharmaceuticals, personal care products, pesticides, and other human-related activities are usually the source of pollutants (Kümmerer 2008). Some common emerging pollutants are as follows:

1. Pharmaceuticals and personal care products include prescription and over-the-counter drugs, as well as personal care products such as fragrances, cosmetics, and sunscreen agents. These products can enter into environment through improper disposal, wastewater treatment plants, or agricultural runoff which leads to adverse effects on aquatic organisms and ecosystems and can bestow evolution of antibiotic resistant bacteria (Aukidy et al. 2014).
2. Per- and polyfluoroalkyl substances are synthetic chemical moieties commonly utilized in numerous industries and consumer applications, including firefighting foams, nonstick coatings and water-repellent fabrics. These materials can exist for a very long period in the environment and usually shows bioaccumulation in water sources, soil, and wildlife (Bhatt et al. 2022).
3. Microplastics are originated from the collapse of bigger plastic items, microbeads in personal care products, or synthetic fibers released during laundry. They usually have size less than 5 mm and invade into food chain by impacting crucially marine life, fresh water ecosystems, soil, and even the air (Andrady 2011).
4. Endocrine-disrupting chemicals are substances capable of interfering or causing adverse effects on reproductive, neurological, and immune system. Bisphenol A

(BPA), phthalates, and certain pesticides are the common endocrine-disrupting chemicals (Gore et al. 2015).

5. Industrial discharges and municipal wastewater (Deblonde et al. 2011).
6. Agricultural activities like use of pesticides, fertilizers, and veterinary drugs (Boxall et al. 2009).
7. Urban runoff and storm water carrying various pollutants, including heavy metals, microplastics, and chemicals from urban infrastructure and activities (Guerra et al. 2020).
8. Atmospheric deposition of emerging pollutants over long distances into soil and water bodies through airborne particles and gases (Geissen et al. 2015).
9. Improper disposal of waste, including landfill leachate and incineration residues (Ndou and Rampedi 2022).

3 Nano-Bioremediation: Concepts and Principles

Nanotechnology is a fast-advancing area addressing the manipulation and control of material at the nanoscale level, typically in the range of 1–100 nm. Nanotechnology has offered a broad range of applications in removing or mitigating pollutants and contaminants from soil, water, and air to restore ecosystems and protect human health. Nanomaterials have remarkable difference in their properties leading to unique characteristics and functionalities compared to bulk counterparts. Higher surface area-to-volume ratio and porosity (depending upon composition of nanomaterials) of nanomaterials facilitate adsorption or absorption of contaminants onto their surfaces by providing effective pollutant binding sites. Furthermore, nanomaterials can enable redox reactions and accelerate the degradation or transformation of pollutants by microbial or enzymatic processes by working as catalysts. Each kind of nanomaterial own distinctive properties which can be customized according to need for elimination of specific contaminant (Fulekar and Pathak 2019; Singh and Saxena 2022). The important characteristics and properties of nanomaterials making them relevant for pollutant removal applications are as follows:

1. **Large Surface Area:** Nanomaterials own remarkably higher surface area-to-volume ratio compared to bulk materials and provide higher surface area for more active sites for pollutant adsorption or catalytic reactions. For example, nanomaterials like nanoscale metal oxides (e.g., TiO_2 and ZnO) exhibit excellent adsorption capacities due to their high surface area (Liang et al. 2012).
2. **Enhanced Reactivity:** The unique reactivity of nanomaterials at the nanoscale is contributed by quantum confinement effects and surface-related phenomena. These effects enhance catalytic reactions for pollutant degradation. Zero-valent iron nanoparticles exhibit high reactivity and ability to generate reactive oxygen species. Therefore, zero-valent iron nanoparticles have been extensively utilized for the degradation of organic pollutants (Raffa et al. 2021).

3. **Tailorable size and composition:** Nanoparticles or nanocomposites can be fabricated with precise control over their size, shape, and composition for customized target-specific delivery. This tunability permits the development of nanomaterials with improved pollutant removal efficiency. Even size and composition of metallic nanoparticles can be optimized for selective adsorption or catalytic reactions (Phenrat et al. 2008).
4. **Surface Modification:** The surface functionalization of nanomaterials by coating or conjugation with organic or inorganic materials can improve their pollutant removal capabilities, stability, selectivity, and affinity of nanomaterials toward specific pollutants (Xu et al. 2018).
5. **Photocatalytic activity:** Certain nanomaterials, such as semiconductor metal oxides (e.g., TiO_2 and ZnO), exhibit photocatalytic activity when exposed to light. Their ability to generate reactive oxygen species upon light irradiation helps in decomposing pollutants. Therefore, such materials have been extensively explored for water and air purification applications (Ren et al. 2021).
6. **Magnetic Properties:** Nanomaterials exhibiting inherent magnetic properties like iron oxide nanoparticles (e.g., magnetite and maghemite) have found acceptance in environmental remediation process due to their reusability, ease of separation from the treated medium using an external magnetic field, and simplifying the posttreatment process (Gupta and Gupta 2005).
7. **Stability and Regenerability:** The stability and regenerability of nanomaterials are crucial factors for sustainable pollutant removal systems. Nanomaterials should maintain their structural integrity and performance over multiple cycles of pollutant removal or degradation (Ethaib et al. 2022).

Bioremediation is an eco-friendly approach to address environmental pollution by utilizing biological processes to degrade or transform hazardous contaminants into less-harmful substances. In recent years, the combination of nanomaterials and microorganisms has shown promising synergistic effects in enhancing the efficiency and effectiveness of bioremediation strategies. This approach leverages the unique properties of nanomaterials to improve microbial activity, contaminant bioavailability, and overall biodegradation processes (Bhatt et al. 2022). Nanotechnology-based environmental remediation approaches have promisingly addressed the environmental challenges by producing coherent and cost-effective solutions. Some vital applications of nanotechnology in environmental remediation are as follows:

- (a) Nanoscale zero-valent iron (nZVI) particles have acquired notable recognition for their potential to reduce, degrade, and eliminate a wide range of contaminants, including heavy metals and organic pollutants. Higher reactivity and larger surface area of nZVI particles allow effective transformation and immobilization of contaminants via either of mechanisms, that is, reduction, oxidation, and adsorption (Zhang 2003). In addition, palladium nanoparticles can facilitate pollutants degradation via catalytic reactions into less-harmful chemicals like dechlorination of polychlorinated biphenyls (Tripathi et al. 2023).
- (b) Nanosensors: Nanotechnology-based sensors provide tremendously sensitive, selective, and cost-effective detection abilities for early detection, monitoring,

sensing, and effective management of environmental pollutants. Various contaminants, including heavy metals, volatile organic compounds (VOCs), and pathogens can be ascertained with enhanced accuracy and real-time monitoring utilizing nanosensors (Willner and Vikesland 2018).

- (c) Nanostructured materials supplemented with adsorption and filtering capacities have offered efficient removal of heavy metals, organic pollutants, microorganisms, and emerging contaminants like pharmaceuticals and microplastics. Nanofilters, nanomembranes, and nanocomposites are often used for water purification (Qu et al. 2013).
- (d) Soil cleanup can be amplified by enhancing the degradation, immobilization, or transformation of pollutants utilizing nanoparticles functionalized with particular properties to target and treat contaminants effectively. The utilization of nano-remediation techniques enhanced efficacy, minimized treatment time, and lessened environmental impact compared to traditional methods (Peralta-Videa et al. 2011).
- (e) Nanomaterials can be used as carriers for intended conveyance of microorganisms to contaminated sites. Modified nanoparticles are fabricated to encapsulate bacteria, fungi, or enzymes to protect them from harsh environmental conditions and assist their delivery to appropriate locations. The specific targeted distribution guarantees effective and programmed release of microorganisms and enhances their bioremediation efficiency (Thirumalaisamy et al. 2022).

4 Mechanisms of Pollutant Degradation Using Nanomaterials

The unique characters of nanomaterials such as high surface area, size-dependent reactivity, and enhanced catalytic activity make them efficient in pollutant degradation processes. Nanomaterials can degrade pollutants by one or combination of the following mechanisms:

4.1 Photocatalysis

Some of nanomaterials like titanium dioxide, zinc oxide, and graphene oxide manifest photocatalytic activity. The irradiation of such materials at suitable wavelength promotes their photolytic potentiates which can be utilized for degeneration of pollutants. Light-sensitive nanomaterials initiate the generation of electron-hole pairs on exposure with light and take part in redox reactions with pollutants facilitating their degradation (Chen and Mao 2007; Teoh et al. 2012).

4.2 Adsorption

The higher degree of porosity and availability of surface area of nanomaterials offers bigger opportunities to adsorb pollutants onto their surface. Physical adsorption of pollutants onto the nanomaterial surface helps in their removal from the environment (Nasrollahzadeh et al. [2021](#)).

4.3 Oxidation and Reduction Reactions

Nanomaterials having suitable oxidative-reductive potential play a critical role in degradation of pollutants like zero-valent iron nanoparticles. Iron nanoparticles on reaction with chlorinated solvents can convert them into less-toxic or nontoxic compounds (Lampron et al. [2001](#)).

4.4 Catalytic Reactions

Nanomaterials with catalytic properties, such as palladium nanoparticles, can enhance the rate of pollutant degradation through catalytic reactions. These nanoparticles can promote the breakdown of organic pollutants, such as chlorinated hydrocarbons by providing an active surface for the reaction to occur (Shah and Li [2019](#)).

4.5 Advanced Oxidation Processes

Nanomaterials utilized in advanced oxidation processes like Fenton and photo-Fenton processes initiate the generation of reactive oxygen species under specific conditions of light, temperature, dielectric constant, etc. The reactive oxygen species generated react with pollutants and degrade them into less-harmful substances (Jadhav and Jadhav [2021](#)).

5 Synergistic Effects of Nanomaterials and Microorganisms in Bioremediation

The utilization of nanomaterials and microorganisms has synergized the bioremediation process by

5.1 Enhancing Microbial Activity

Nanomaterials such as activated carbon, graphene oxide, or magnetic nanoparticles bestow physical support or immobilize microorganisms to protect them from harsh environment which lead to improved stability and activity of microbial communities during the biodegradation of organic pollutants. The immobilization/attachment of microorganisms permit them to increase microbial population and their metabolic activity along with close proximity to pollutants to increase the degradation efficiency (Sarkar et al. 2018).

5.2 Increased Contaminant Availability

Higher surface area-to-volume ratios of nanomaterials enable the adsorption and desorption of contaminants to make them more accessible to microorganisms. Metallic nanoparticles have been considerably utilized to intensify heavy metal-contaminated sites due to their excellent adsorption capacity. Zero-valent iron nanoparticles can seize contaminants and generate a desirable microenvironment for microbial colonization and degradation of pollutants (Huang et al. 2021).

5.3 Facilitated Electron Transfer

Certain nanomaterials like graphene-based nanomaterials can act as electron shuttles or conductive materials and promote the exchange of electrons between microorganisms and contaminants. The enhanced extracellular electron transfer in microbial fuel cells promotes the degradation of organic pollutants (Colunga et al. 2015). In addition, magnetite nanoparticles can improve the redox activity of microorganisms to accelerate the biodegradation of various organic pollutants (Zhuang et al. 2020).

5.4 Targeted Delivery of Nutrients and Enzymes

Nanoparticles can be utilized as cargoes for conveying nutrients, cofactors, or enzymes directly to microorganisms to enhance their biodegradation capabilities. Composite nanoparticles have been found effective to accelerate the degradation of pesticides (Zhao et al. 2022). This targeted delivery approach ensures the efficient utilization of resources and minimizes their loss in the environment.

5.5 *Monitoring and Sensing Capabilities*

Nanomaterials can be integrated into biosensors or nanosensors to monitor microbial activity and contaminant levels in real time. Several investigations have reported that silver nanoparticles or quantum dots can impact microbial quorum sensing, a cell-to-cell communication mechanism used by bacteria to regulate gene expression. Quorum sensing modulation can enhance the production of extracellular enzymes or metabolites involved in pollutant degradation pathways. This interaction between nanomaterials and microorganisms can promote the overall efficiency of pollutant degradation (Kashish 2021). Quantum dots have been used as fluorescent probes to detect the presence of specific microorganisms or track the biodegradation process (Pavlicek et al. 2023). These monitoring tools enable the optimization of bioremediation strategies and provide valuable insights into the remediation progress.

5.6 *Generation of Reactive Oxygen Species*

Nanomaterials like titanium dioxide nanoparticles or zinc oxide nanoparticles can generate reactive oxygen species (ROS) on activation by ultraviolet (UV) light. The ROS, including hydroxyl radicals ($\bullet\text{OH}$) and superoxide radicals ($\bullet\text{O}_2^-$) exhibit strong oxidative properties and can effectively degrade organic pollutants. Microorganisms are benefited by these ROS to promote and break down complex organic compounds contributing to enhanced pollutant degradation (Borchert et al. 2021).

6 **Integration of Nanomaterials and Microorganisms**

Integration of nanomaterials with microorganisms is a budding domain of research with manifold importance in several fields, including medicine, environmental remediation, energy production, and agriculture. This integration combines the unique properties of nanomaterials with the metabolic activities of microorganisms to develop hybrid systems with enhanced functionalities.

6.1 *Nanomaterials in Microbial Biosystems*

Nanomaterials can be integrated into microbial biosystems to enhance their performance and functionality. Such integration improves the efficiency of microbial bioremediation processes. Literature has reported the degradation of pollutants by microorganisms, such as bacteria and fungi via reductive dehalogenation process utilizing iron-based nanoparticles/nanocomposites. The transformation of toxic

compounds into less-harmful forms is facilitated by electron donor nature of nanoparticles (Lowry et al. 2012). In addition, incorporation of nanomaterials into bioelectrochemical systems improves their performance in energy production, biosensing, and wastewater treatment. Graphene-based nanomaterials have been broadly studied to amplify the electron transfer between microorganisms and electrodes in microbial fuel cells. Such integration ameliorates the power output and efficiency of microbial fuel cells (Goyat et al. 2022).

6.2 *Microorganisms as Templates for Nanomaterial Synthesis*

Microorganisms such as bacteria and fungi can act as templates for the synthesis and assembly of nanomaterials with controlled structures and properties. Biomineralization and biofabrication are important approaches allowing the production of nanomaterials with unique characteristics that cannot be easily achieved via traditional synthesis methods. During biomineralization, microorganisms regulate the genesis and growth of nanomaterials by controlling the deposition of minerals to fabricate nanoparticles, nanowires, and nanostructured materials with tailored properties (Yao et al. 2017). Even though, nanomaterials can be fabricated through the extracellular synthesis of nanoparticles by microorganisms. Depending upon the metabolic activities of microorganisms, metal ions are converted into nanoparticles and then deposited outside the cells. Bacteria such as *Shewanella* and *Bacillus* have been widely used to fabricate metallic nanoparticles, semiconductor nanoparticles, and magnetic nanoparticles (Durán et al. 2011). This field is rapidly advancing to investigate newer applications and approaches for employing the synergistic capabilities of these two components.

6.3 *Bio-Conjugation Techniques for Attaching Microorganisms to Nanomaterials*

Bio-conjugation techniques involve the covalent or noncovalent attachment of biomolecules, such as microorganisms to nanomaterials. Most common chemical method used for bio-conjugation is amine coupling method. It involves covalent bonding between reactive functional groups on nanomaterial's surface and amino functional groups present on the surface of microorganism to form stable amide bonds (Jazayeri et al. 2016). Thiol functional groups present on the surface of microorganism can be exploited to form stable thioether or disulfide bonds with maleimide or pyridyl disulfide functionalized nanomaterials (Hsu et al. 2020). In addition, opposite charges on the surfaces of microorganism and nanomaterial can lead to electrostatic interactions between them to form complex (Li et al. 2019).

Sometimes antibodies, lectins, or other affinity molecules are utilized to establish specific stable interactions between microorganisms and nanomaterials. Immobilization of these affinity molecules onto the nanomaterial surface allows selective binding to target microorganisms (Yu et al. 2021).

6.4 Microbial Activity and Survivability Through Nanomaterials

Nanomaterials can interact with microorganisms at the nanoscale level and influence their growth, activity, metabolism, and overall performance. Metallic nanomaterials such as silver nanoparticles, zinc oxide nanoparticles, and copper nanoparticles have manifested strong antibacterial properties by interacting with bacterial cell membranes, disrupting their structure and causing cell death. Literature has reported inhibitory effect of silver and zinc oxide nanoparticles on growth of various gram-positive and gram-negative bacteria (Sondi and Salopek-Sondi 2004; Brayner et al. 2006). Certain nanomaterials exhibit enzyme mimetic activity and accelerate enzymatic reactions to enhance microbial metabolic activity. For example, gold and graphene oxide nanoparticles have revealed peroxidase-like activity to modulate the oxidation of various substrates. The enhancement of activity of enzymes involved in microbial metabolic pathways by nanomaterials improves their efficiency in the processes like biodegradation or bioremediation (Zhao et al. 2021).

Biofilms are complex structures formed by microorganisms that adhere to surfaces and are embedded in a matrix of extracellular polymeric substances (EPS). Nanomaterials can influence the formation and stability of microbial biofilms. Certain nanomaterials, such as iron oxide nanoparticles, have enhanced the biofilm formation. They can serve as nuclei for biofilm development, promoting the attachment and growth of microorganisms. This can be particularly useful in applications such as wastewater treatment or bioremediation, where biofilms play a crucial role in microbial activities (Klaus et al. 1999). Harsh environmental conditions often restrict activity of microorganisms and survival. The use of nanomaterials like carbon-based nanomaterials can help to enhance microbial tolerance under such stress conditions. Such materials can scavenge reactive oxygen species and protect microbial cells from oxidative damage (Ahmad et al. 2015).

7 Challenges and Considerations in the Application of Nano-Bioremediation Techniques

Nano-bioremediation involves the application of engineered nanoparticles or nanomaterials to enhance the biodegradation and transformation of pollutants. Even though nano-bioremediation presents several advantages, that is, enhanced

pollutant accessibility, higher reaction rates, and improved efficiency, there are lots of challenges and considerations that need to be addressed to ensure its safe and effective application. The commonly encountered challenges and considerations in the application of nano-bioremediation techniques are

7.1 Characterization of Nanomaterials

The foremost challenge is found in accurately characterizing the nanomaterials used in nano-bioremediation. Physicochemical properties of nanomaterials like size, shape, surface charge, aggregation behavior, and stability play a critical role in influencing their transport, reactivity, and potential toxicity in the environment. Various characterization techniques, such as transmission electron microscopy (TEM), dynamic light scattering (DLS), and zeta potential measurements, can be employed to assess these properties (Yin et al. 2011).

7.2 Environmental Fate and Transport

The fate and transport of nanoparticles in the environment is a crucial factor to assess their potential risks and effectiveness in bioremediation. Their aggregation, sedimentation, adhesion to soil or sediment, and interaction with organic matter can influence their distribution and mobility. Therefore, predictive models and experimental investigations can help in measuring the transport behavior and deposition patterns of nanoparticles (Xin et al. 2021).

7.3 Ecotoxicity and Human Health Risks

Ecotoxicity referring to potential of nanomaterials to bioaccumulate in food chains is a major concern to effect human health. Physicochemical characteristics of nanoparticles like size, shape, surface charge, and composition can influence their toxicity. Therefore, toxicity tests including cell-based assays and animal studies should be conducted to assess the safety of nanoparticles (Sano et al. 2020).

7.4 Long-Term Effectiveness and Sustainability

Long-term effectiveness and sustainability of nano-bioremediation techniques need to be evaluated before their practical application. Factors such as the stability and reactivity of nanoparticles, microbial adaptation, and potential development of

resistance mechanisms need to be considered. Additionally, the potential release of nanoparticles into the environment should be minimized to prevent unintended ecological consequences (Navarro et al. 2008; Yadav et al. 2020).

7.5 *Scale-Up and Cost Considerations*

Various factors like cost, availability of nanoparticles, and integration with existing remediation technologies affect the scaling up of nano-bioremediation techniques from laboratory to field applications (Navarro et al. 2008; Yadav et al. 2020).

8 Environmental Fate and Safety Considerations

Environmental fate and safety considerations are crucial aspects in the evaluation of chemicals, pesticides, and other substances to ensure their potential impact on the environment and human health. These assessments emphasize on to know-how the chemicals move, transform and persists in various environmental compartments, such as air, water, soil, and organisms (Rajput et al. 2022; Yunus et al. 2012). The potential adverse effects of substances on organisms and ecosystems are determined by performing acute and chronic toxicity tests on different species residing in water (fish, invertebrates, and algae) and land (earthworms, birds, and plants) (Spurgeon et al. 2020). However, exposure assessment involves estimation of the potential exposure of humans and the environment to a substance by estimating the concentrations of substances in different environmental compartments based on their usage patterns, release scenarios, and environmental monitoring data (Guardo et al. 2018). The potential exposure of individuals to substances via various routes such as inhalation, dermal contact, and ingestion is usually assessed considering scenarios of occupational exposure and consumer use (Tudi et al. 2022).

9 Current Challenges and Future Directions

Bioremediation has shown success in many cases. It still faces certain challenges and has several future directions for improvement (Jabbar et al. 2022; Saleem et al. 2022).

9.1 *Challenges in Bioremediation*

1. **Recalcitrant compounds:** Some pollutants, known as recalcitrant compounds, are highly resistant to degradation by natural microorganisms. These include certain

chlorinated solvents and polychlorinated biphenyls (PCBs). Breaking down these compounds requires specialized microbial communities or genetic modifications to enhance degradation capabilities.

2. **Nutrient limitation:** Microorganisms involved in bioremediation require specific nutrients, such as nitrogen, phosphorus, and trace elements for their growth and activity. Contaminated sites often lack these nutrients, which limit the effectiveness of bioremediation. Nutrient supplementation strategies such as adding fertilizers or optimizing nutrient ratios can help to overcome this challenge.
3. **Co-contamination and synergy:** Environmental sites are often contaminated with multiple pollutants simultaneously, which can have interactive effects on bioremediation processes. Some pollutants may inhibit microbial activity or degrade more slowly in the presence of others. The comprehension of possible interactions and evolving strategies to mitigate the negative effects of co-contamination is crucial (Kour et al. 2022).
4. **Environmental conditions:** The efficacy of nano-bioremediation processes depends upon the environmental factors, that is, temperature, pH, moisture, and oxygen availability. The alteration in these conditions from optimum can affect microbial activity and pollutant degradation rates. Therefore, need exists to develop strategies to optimize environmental conditions or adapt microbes to wide range of environment conditions is for successful bioremediation.
5. **Scale-up and cost-effectiveness:** Scaling up of nano-bioremediation from laboratory scale investigations to field applications is often challenging. It depends considerably on factors like site heterogeneity, pollutant distribution, and the ability to distribute and sustain microbial populations over large areas. Bioremediation processes require monitoring and maintenance and often time consuming which enhances their cost of application (Farooq et al. 2010).

9.2 *Future Directions in Bioremediation*

In order to overcome the limitations of current nano-bioremediation, following approaches can be explored (Lv et al. 2022; Bala et al. 2022):

1. **Advanced genetic engineering:** It is an important technique which can be employed to enhance the capabilities of microorganisms involved in bioremediation. It involves introduction of genes from different microbial species to create synthetic consortia or modify the existing microbes to enhance their degradation efficiency. Genetic engineering can also aid in developing the microbes capable of degrading recalcitrant compounds.
2. **The application of metagenomics and microbial ecology** can be useful for a comprehensive understanding of microbial communities involved in bioremediation. Novel microbial species can be identified with valuable bioremediation capabilities and improve our understanding of microbial interactions and community dynamics.

3. **Bioaugmentation and biofilm technologies:** Bioaugmentation involves the addition of specific microbial strains or consortia to enhance bioremediation. The selection and optimization of microbial inoculants for different contaminants can improve degradation rates and overall efficiency. Biofilm technologies, such as immobilizing microorganisms in matrices or carriers, can enhance their survival, protect them from adverse conditions, and improve their interaction with pollutants.
4. **Nanotechnology and bioremediation:** Nanotechnology offers exciting possibilities for bioremediation. Engineered nanoparticles with suitable microorganisms can act as catalysts, adsorbents, or carriers for focused delivery of microbes or enzymes to contaminated sites. These nanomaterials can improve degradation rates, enhance pollutant capture, and facilitate controlled release of nutrients or growth factors to support microbial activity.
5. **Integrating nano-bioremediation with phytoremediation (using plants) or chemical approaches** can help to develop more effective and sustainable remediation strategies. Integrated approaches leverage the strengths of multiple techniques to tackle complex contamination scenario.

10 Conclusion

Nano-bioremediation has remarkable potential for addressing emerging pollutants. The distinctive characteristics of nano-bioremediation, that is, nanoparticles having inherent capabilities of microorganisms offer a promising solution for the removal and detoxification of diverse contaminants. Furthermore, integration of nanoparticles and microorganisms in nano-bioremediation can create synergistic effects. Nanoparticles can improve microbial activity by enhancing surface area for microbial attachment and facilitating electron transfer processes. Similarly, microorganisms can provide a favorable environment for nanoparticles, protecting them from aggregation or deactivation and promoting their stability and longevity in the contaminated sites. Nano-bioremediation techniques have been used for different environmental matrices including soils, sediments, groundwater, and wastewater for removal of diverse pollutants, including organic compounds, heavy metals, and emerging contaminants. However, area of nano-bioremediation is still in budding stage and several challenges need to be addressed. Further research and development in nano-bioremediation along with rigorous risk assessment and regulatory frameworks is essentially required to harness its full potential in addressing emerging pollutants and ensuring the protection and restoration of our environment.

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Mechanism of Interaction of Nanomaterial and Microbes to Treat Emerging Pollutants



Swati and Hiba Parveen

Abstract The emerging pollutants (EPs) have become ubiquitous in the environment. These pollutants are chemically identified as dangerous compounds to the total environment (soil, water, and air) and also a probable threat to human beings. A number of these emerging pollutants are not yet synchronized at national and international levels. Ancient techniques have failed in emerging these toxic pollutants from the air, water, and soil as a consequence a very intensive area of research has originated in the last few years for the complete mitigation of pollutants by several means. Nanomaterials and microbes interaction deals to treat emerging pollutants. The interaction of nanomaterials is been found very effective due to their distinctive properties, for example, greater surface area and ability to work at low concentrations. Nanotechnology and nanoengineered materials possess excellent effectiveness suitable for pollutants found in water soil and air (some readily accessible nanomaterials include carbon nanotubes, carbon nitride graphite composites, graphene-based composites, and metal oxides). As nano remediation is drawing a beneficial bridge in eliminating emerging pollutants, another effective technique that is gaining popularity is “bioremediation.” Microbes have been known for their scavenger properties so, in recent advancements, microorganisms are meant for the elimination of different contaminants in the environment by various approaches namely bioaugmentation, rhizoremediation, phytoremediation, miscoordination are very helpful in degradation, eradication, and immobilization of diverse chemical wastes from the contaminated environment. Further in this chapter, we will review the approaches made for the reduction of these EPs in virtue of “nanotechnology” and “microbial” methods.

Keywords Nanomaterial · Bioremediation · Pollutants

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1 Introduction

Planet Earth is now on the verge of an extreme environmental tragedy that will affect our affluence. The existing state of the current environs is repeatedly worsening. Issues of flora and fauna have been flooded all over the globe, and we should get prepared for an alternative outcome on the globe. It is time to indulge in new perceptions and methods of mishaps in advance with recent approaches and policies with our complete awareness and implications. Contamination in the surroundings, as in soil, air, and water, undertakes tons of decades to eliminate. Manufacturing and automobile drain releases are the exact causative features for nearly all environmental degradation (Roy et al. 2021). The environment suffers from the same problems due to the widespread usage of pollutants such as particulate matter (PM), heavy metals, pesticides, weedkillers, compost, oil spills, hazardous gases, sewers, and materials composed of carbon. Fig. 1 shows some causes of ecological causes of emerging pollutants. The major causes of water contamination are the ejection of chemicals as heavy metals from manufacturing units and various other automobiles. It has been known as the biggest causes of this unprocessed sewage, releases into water bodies that eventually disturbs the atmosphere and thus, lastly human beings (Singh et al. 2020).

All of this hazardous trash eventually pollutes rivers, lakes, and soils, rendering them unusable. In certain instances, even ordinary tap water catches fire, and pollution is a major issue in major cities today (Ningthoujam et al. 2022). Nano-technology has the ability to help, subtly improve moral, environmentally friendly technologies that primarily benefit the ecology and benefit human beings. Because of

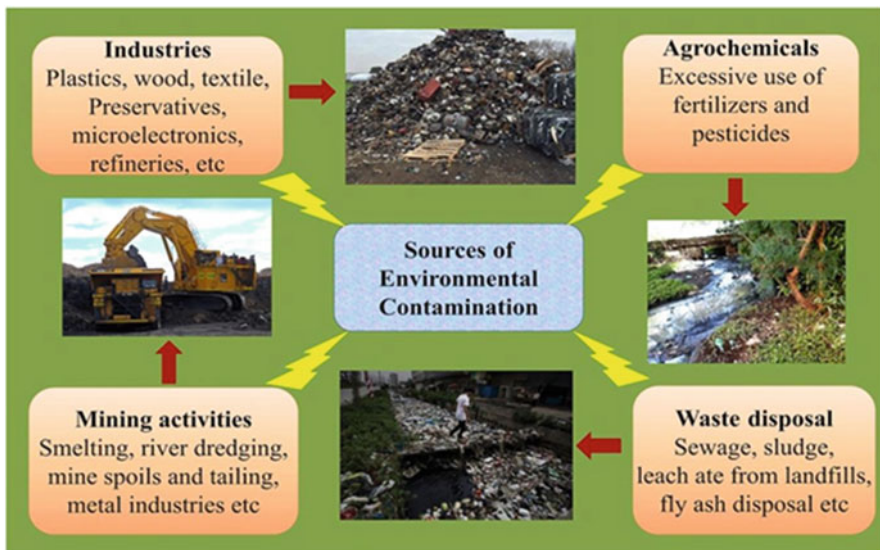


Fig. 1 Causes of ecological pollution (Malla et al. 2018)

their presence, high volatility, and low reactivity, these chemicals are challenging to mitigate. However, it is possible to break down complicated compounds with the aid of nano catalysts. Nano catalysts, which act as catalysts, are a component of nanomaterials (Ahmed et al. 2021). Both homogeneous and heterogeneous catalysis can be accomplished using them. In scientific terms, a nanomaterial is a substance that has an external dimension between 1 and 100 nm and cannot be seen with the human eye (Ningthoujam et al. 2022). These particular materials stand out as of their superior surface-volume ratio and high response characteristics. Additionally, the size, shape, and porosity of nanomaterials—as well as their chemical and physical makeup—have positive effects on the elimination of impurities (Luo et al. 2021). Depending on the constituents they are made of, nanomaterials can be generally categorized into three groups. They are inorganic nanomaterials (metal and metal oxide nanomaterials), carbon-based nanomaterials (fullerene C60 and C540, single-walled nanotubes, multi-walled nanotubes, and graphene), as well as polymer nanomaterials. When compared to the other two, polymer-based nanoparticles have proven to be the most effective in identifying and getting rid of pollutants like the metal manganese, nitrates metals, lead, heavy metals, etc. Additionally, it is efficacious in separating gases like carbon dioxide, sulfur dioxide (SO₂), and nitrogen oxides.

Nanotechnology holds an outlook to suggestively confer the advancement of uncontaminated, greener expertise that has major ecological and health benefits. Nanotechnology methodology has been examined for its possibility to provide a way out for pollution supervision and remediation process, also to take initiatives for upbringing the methods of traditional eco-friendly cleaning methods (Roy et al. 2021).

In another way, the aids that are using for the mitigation of emerging pollutants should be nontoxic so that their residual should also not harm human well-being. Biodegradable materials are best to be used. Materials that decompose naturally are more advantageous since they are more secure and may be used in any situation as they do not produce any waste leftovers that are harmful after usage. Thus, its many stupendous profits, the expansion and relevance of nanomaterials and microbes have engrossed attention all over the globe.

There are many techniques known nowadays for the remediation of pollutants and these techniques are very popular because of their positive and fruitful outcomes. Some of these techniques discussed further in detail as treatment of emerging pollutants by nanomaterial and microbes as depicted in Fig. 2.

2 Why Nanotechnology?

On comparison of their bulk counterparts, nanomaterials exhibit surprising features. They have unique physiochemical properties due to their high surface-to-volume ratio, including a variety of functionalities and enhanced reactivity or selectivity. The unique features of nanotechnology may be used to a variety of products, procedures,

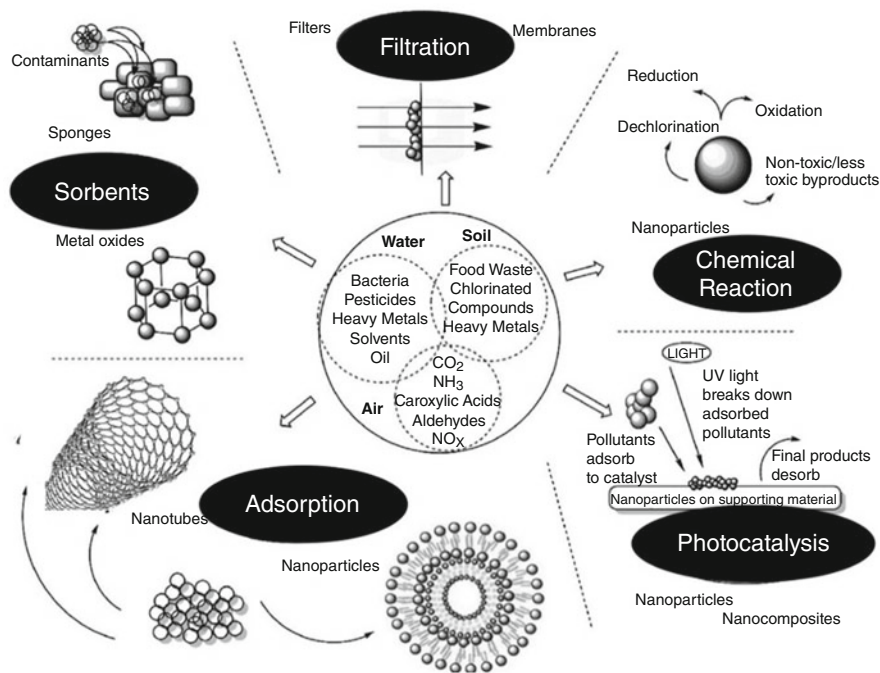


Fig. 2 The various techniques that can be used for environmental cleanup

and uses that undoubtedly promote climate and sustainable development by reducing emissions of greenhouse gases and hazardous waste while conserving energy, water, and raw materials (Guerra et al. 2018). This overview's goal is to highlight current developments in the creation of nanomaterials for the elimination of developing pollutants from the atmosphere.

3 Why Bioremediation?

Microbes have been known as scavengers from ancient times. They are the purifier of our environment so why not to use these techniques for purifying our environment from emerging pollutants (Kumar et al. 2018).

Bioremediation is the method of eliminating impurities from the air, water, and soil by using microbes like fungi, bacteria, as well as specific enzymes like monooxygenase, oxidoreductases, oxygenases, dioxygenases, and laccases. Depending on the site, a bioremediation method may be applied on- or off-site. In accordance with the type, quantity, and severity of the emerging contaminants, various bioremediation strategies can be utilized to eliminate the contaminants (Azubuikie et al. 2016). A number of chemical, physical, and biological strategies

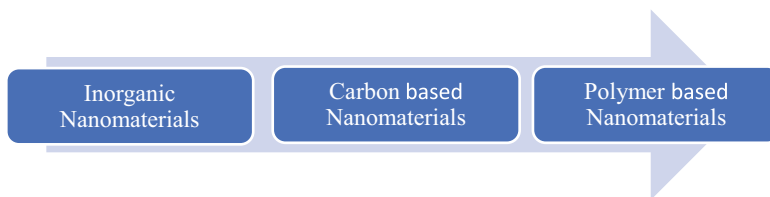


Fig. 3 Emerging pollutants can be remediated by the three main categories of nanomaterial for heavy metals in soil, air, and water

are recommended to locate and eliminate emerging pollutants from the environment (Rodriguez-Narvaez et al. 2017). Membrane filtrations and adsorption by substances like carbon nanotubes and activated carbon were also incorporated in the physical approaches. Some instances of chemical reactions include oxidation, ozonation, catalysis, and UV photolysis (Nishat et al. 2022). Bioremediation has additional benefits over physiochemical approaches in terms of cost, minimal or no by-products, reduced energy requirements, and reuse ability.

The different types, applications, and mechanisms of interaction of nanomaterials and microbes are further discussed. There are several efficient methods to remove a pollutant, including absorption, adsorption, chemical reactions, photocatalysis, and filtration. According to Guerra et al. (2018), regarding the various kinds of materials that can be used for environmental cleanup, there is no standardized classification. The three primary categories of nanomaterials reported are—inorganic, carbon-based, and polymer-based—therefore emphasized in Fig. 3 of this chapter.

4 Nanomaterial

4.1 *Inorganic Nanomaterials*

4.1.1 Nanomaterials Based on Metal and Metal Oxides

Although the bulk of research has been done on the elimination of heavy metals and chlorine containing organic contaminants from water, several metal-based nanomaterials have been created to decrease a range of pollutants (Santhosh et al. 2016). In accordance to Guerra et al. (2018), metal and metal oxide nanoparticles are enormously effective adsorbents with benefits like high kinetics and quick adsorption capacity. Nanoparticles are widely used for environmental mitigation because they are very adaptive for both in situ and ex situ impacts in aquatic environments. Silver nanoparticles (Ag NPs) are widely used to disinfect water because of their potent antiviral, antibacterial, and antifungal activity. By concentrating on binding to the virus' glycoproteins, they can drop the viruses from attaching to host cells. Smaller particle sizes, such as those between 11 and 23 nm, provide less bactericidal activity. Additionally, compared to Ag nanorods and Ag nanospheres, triangular Ag

NPs had stronger antibacterial effects, highlighting the significance of both the particle's size and shape in producing the desired results. Titanium oxides (TiO_2) are yet another metal-based substance that is frequently studied for environmental cleanup. They are popular for their low-cost and nontoxicity, semiconducting as well as photocatalytic, also electronic, gas sensing, and energy conversion features. TiO_2 NPs have been widely explored for the treatment of waste, purification of air, self-cleansing of surfaces, and in water treatment applications as a photocatalyst. Since light activates TiO_2 NPs, their capacity to remove organic pollutants from diverse media is frequently investigated. TiO_2 NPs have the ability to generate extremely reactive oxidants, such as hydroxyl radicals, which can be used to kill bacteria, viruses, fungi, and other pathogens. TiO_2 has a rather limited photocatalytic capacity; therefore, to improve performance, the material is usually doped with another transition metal ion. When compared to TiO_2 nanofibers, Ag-doped TiO_2 nanofibers showed enhanced photodegradation. Titanates, or inorganic titanium oxide compounds, have likewise been documented for the elimination of impurities in addition to titanium oxide materials. For instance, Chen et al. (2016) reported the hydrothermal method for producing basic, acidic, and neutral titanate nanotubes (TNTs), and these materials were tested for their potential to catalyze the reduction of NO with ammonia.

Furthermore, studies have also been done on mixed oxide materials. Iron and iron oxide NPs have been used to effectively remove a number of heavy metals, including nickel dioxide, copper dioxide, CO^{2+} , or Cd^{2+} , as well as to clean up chlorinated organic solvents. Tetrachloroethene (TCE) contamination at a field site in Germany was remedied using carbo-iron, comprised of colloidal activated carbon and embedded nano iron. The use of metal-based NPs poses yet another problem due to the possible toxicity of the chemicals used to make the material as well as by-products created by the breakdown of contaminants (Karn et al. 2009). In order to successfully remove Ni^{2+} and Cu^{2+} from aqueous solutions, Poguberović et al. (2016) demonstrated the utilization of zero-valent iron nanoparticles (nZVI). The ZVI used in the tests was then created using mulberry and oak leaf extracts. These potent antioxidant extracts' constituents combine with iron (III) to form nZVI. To ease worries about the harmfulness of chemicals and by-products when employing chemical synthesis techniques, it is crucial to use natural products when creating environmental remediation materials. Furthermore, Sofija et al.'s "green" synthesis of nZVI has the benefit of reusing natural resources like leaf extracts while also offering a cost-effective adsorbent for the elimination of heavy metals from water. The list of many metal-based materials and their applications for contamination cleanup in the environment as shown in Table 1.

4.1.2 Silica Nanomaterials

Due to the adaptability of mesoporous silica materials, adsorption and catalysis are two applications that have received attention (Tsai et al. 2016). Materials made of mesoporous silica are advantageous for environmental cleanup applications because

Table 1 The possible uses of metal-based nanoparticles in the eradication of emerging pollutants from the air, water, and soil

Material (metal-based nanomaterials)	Environmental remediation using metal-based nanoparticles
Ag NPs/silver ions	Water purifiers, removal of— <i>Escherichia coli</i> from water
Titanium dioxide NPs	Water purifier, removal from soil of these contaminants, <i>E. coli</i> , hepatitis B virus, aromatic hydrocarbons, biological nitrogen, phenanthrene
Metal-doped TiO ₂	Water pollutants action on 2-chlorophenol, endotoxin, <i>E. coli</i> , rhodamine B, <i>Staphylococcus aureus</i>
Titanate nanotubes	Removal of gases like nitric oxide from air
Binary mixed oxide	Removal of dyes like—Methylene blue dye from water and soil
Iron-based	Elimination of chlorine and bromine impurities from soil and water
Bimetallic NPs	Elimination of chlorine and bromine contaminants from water and soil

they have a large surface area, are simple to modify on the surface, have enormous pore volumes, and have variable pore sizes. Numerous researches have advised employing these resources for toxin cleanup in the gas phase due to their high adsorption properties. Numerous research have also gone into great detail into the surface changes of mesoporous silica materials (Son et al. 2008). Another well-known method for creating novel adsorbents and catalysts is to graft functional groups onto the pore walls (Huang et al. 2003). Huang described removing CO₂ and H₂S from natural gas using amine surface-modified silica xerogels and mesoporous silica (MCM-48). The considerable availability of amine groups on the surface of the silica materials was linked to the observed efficacy in the removal of CO₂ and H₂S. Nomura and Jones (2013), Bollini et al. (2011), Drese et al. (2011), Choi et al. (2011), and Hicks et al. (2008) demonstrated the efficiency of amine-modified alumina silicates for the capture of CO₂ and other carbonyl chemicals such as aldehydes and ketones. Silica-based compounds have been developed for the removal of organic dyes from wastewater in addition to gaseous capture. The functionalization of mesoporous silica with –COOH groups was studied by Tsai et al. (2016) because carboxylic acid may create hydrogen bonds with a variety of substances, including metal ions, dyes, and pollutants (Table 2).

4.2 Nanomaterials-Based on Carbon

Comparing carbonaceous materials to metal-based nanomaterials, carbonaceous materials exhibit distinct electrical as well as chemical and physical properties because of the organizational structure of elemental carbon and its variable hybridization statuses. According to Mauter and Elimelech (2008), mutable hybridization states can produce a variety of structural topologies, including fullerene C60, fullerene C540, single-walled nanotubes, multi-walled carbon nanotubes, and

Table 2 Applications of silica nanomaterials in the eradication of emerging pollutants from the air, soil, and water

Material (silica nanomaterials)	Application in environmental remediation of contaminants
Amine-modified xerogels	Removal of gases like carbon dioxide, H ₂ S from air
Amine-modified alumino silicates and porous silica	Gaseous removal of carbon dioxide, aldehydes, ketones from air
Carboxylic acid-functionalized mesoporous silica	Removal of—Cationic dyes, heavy metals from wastewater
Amino-functionalized mesoporous silica	Elimination of heavy metals from wastewater
Thiol-functionalized mesoporous silica	Elimination of heavy metals from contaminated water

graphene. The pure carbon material must first go through surface activities, activation, or functionalization, according to several studies examining the feasibility of carbon nanotubes and graphene for ecological remediation uses. Numerous studies have focused on both multi-walled and single-walled carbon nanotubes (MWCNTs and SWCNTs). These materials are very helpful for removing organic and inorganic pollutants from the atmosphere and from huge volumes of aqueous solution due to their adsorption characteristics. Additionally, photocatalytic methods are used to remove pollutants using carbon-based nanomaterials. In order to reduce heavy metal impurities, the electrons create superoxide radicals. Graphene can be used to create photocatalytic nanocomposites (Guerra et al. 2018). Because of an increase in conductivity, graphene composites containing TiO₂ NPs exhibit greater photocatalytic activity when compared to bare TiO₂ NPs (Zhang et al. 2010).

4.2.1 Carbon Nanotubes (CNTs)

Significantly, a lot of work has been done to improve the adsorption capabilities of virgin CNTs by opening the closed ends (Lithoxoos et al. 2010). SWCNTs are typically arranged in bundles of aligned tubes with a heterogeneous, porous structure, each one surrounded by six other nanotubes in a hexagonal configuration. The four adsorption sites that can be used for an open-ended CNT bundle can be divided into two groups: those with higher adsorption energies that are localized between two adjacent tubes or inside a single tube, and those with lower adsorption energies that are localized on the exterior surfaces of the external CNTs that make up the bundle. Adsorption on external sites approaches balance substantially more quickly than adsorption on interior sites because the exterior sites are in direct contact with the adsorbing material. MWCNTs seldom occur in bundles, unless specific preparation techniques are used to create such arrangements. Yang et al.'s research on nitrogen adsorption from 2001 shown that different pore types, such as inner and aggregation, result in a multistage adsorption process. The adsorption characteristics of these materials were revealed to be much more attributable to aggregated pores than to the more difficult-to-access inner pores.

The oxygen content of carbon nanotubes is also a component that may have an impact on its ability to adsorb substances. Carbon nanotubes may contain $-\text{OH}$, $-\text{C}=\text{O}$, and $-\text{COOH}$ groups that can favorably affect adsorption capabilities, depending on the precise synthesis, the actions and the related purifying operations. CNTs can be oxidized using a variety of chemicals, among them are hydrogen nitrate KMnO_4 , hydrogen peroxide sodium chloride, sodium hydroxide, potassium hydroxide, and sodium hydroxide. Although the adsorbate properties of the CNTs are crucial to the effectiveness of contaminant adsorption. In conclusion, unaltered, pristine carbon-based nanomaterials are frequently passive toward environmental pollutants. They frequently need to be altered or coated with other reactive materials with the proper functional groups or charges in order to increase their efficiency. Thus, in order to increase the intended performance, these hybrid materials combine numerous properties into one template.

4.3 Polymer-Based Nanomaterials

The existence of aggregation, nonspecificity, and lesser stability can limit the use of these nanotechnologies due to their lack of functionality, despite the fact that the high surface area-to-volume ratio of nanoparticles leads to an increase in reactivity and hence superior performance. Another strategy to increase the solidity of nanoscale objects is to custom a host material, whose role is to serve as a matrix or support for other types of materials (such as NPs). Polymers are generally employed for the detection and removal of contaminating gases, such as CO , SO_2 , and NO_2 , organic pollutants, such as pharmaceuticals, and a variety of biologics, such as bacteria, parasites, and viruses. Examples of polymeric hosts that are frequently used to improve stability, circumvent some of the limitations of pure NPs, and impart other desirable properties like improved mechanical strength, thermal stability, durability, and recyclability include surfactants, emulsifiers, stabilizing agents, and surface-functionalized ligands.

For the remediation of polynuclear aromatic hydrocarbons, polyurethane has been developed for remediating pollutants from soil (Tungittiplakorn et al. 2004) has shown the idea that organic NPs can be made with desired properties. While the substance's hydrophobic inside gives hydrophobic organic contaminants affinity, the hydrophilic surface of the nanoparticles makes it easier for them to flow through the soil. Using APU NPs, phenanthrene was recovered (with an 80% recovery rate) from tainted aquifer sand. In addition, decreasing APU particle aggregation in the presence of polyvalent cations was facilitated by adding additional ionic groups to the precursor chain (Tungittiplakorn et al. 2004). Although the use of these materials in the environment might help with pollutant remediation, there is little information on how quickly they degrade.

Wastewater has been treated using poly (amidoamine) or dendrimers (PAMAM) for water samples that are polluted with metal ions like Cu^{2+} . These dendritic nano polymers have primary amines, carboxylates, and hydroxamates as functional

Table 3 Polymer-based constituents for remediation of pollutants from air, water, and soil

Polymer-based materials	Application
Amphiphilic polyurethane NPs	Remediation of soil by removal of polynuclear aromatic hydrocarbons
PAMAM dendrimers	Removal of heavy metals from wastewater
Amine-modified PDLLA-PEG	Removal of gases—VOCs from air or gaseous substance
Polyamine-modified cellulose	Elimination from gases—VOCs from air or gaseous substance
Polymer nanocomposites (PNCs)	From water and soil removal of metal ions, dyes, and microorganisms are done by PNCs

groups, they enable them to sum up a range of water-soluble solutes, as well as cations (such as Cu^{2+} , Ag^+ , Au^+ , Fe^{2+} , Fe^{3+} , Ni^{2+} , Zn^{2+} , and U^{6+}). They are used as chelating agents and ultrafilters to form bonds with metal ions and filter water. Additionally, all these compounds have been used as antiviral and antibacterial agents. Dendritic nano polymers are less likely to pass through the pores of ultrafiltration membranes than linear polymers with equivalent molecular weight due to their reduced polydispersity. By altering the pH of the solution, they can be separated from one another. After that, the concentrated recovered contaminant solution is collected for disposal, and the nano polymers may be recycled (Biricova and Laznickova 2009). Some polymer-based nanomaterials used for the remediation of emerging pollutants are shown in Table 3.

Ge et al. (2012) created a different version of Fe_3O_4 magnetic NP that was altered by combining 3-aminopropyltriethoxysilane and acrylic/crotonic acid copolymers. The generated hybrid NPs (diameter 15–20 nm) were used to remove copper, cadmium, lead, and zinc oxides from metal-polluted water. When inserted into cellulose acetate fibers, silver NPs were found to have a strong antibacterial effect (Nair et al. 2009). Additionally, adding silver NPs (1–70 nm) to polysulfone membranes does not change the membrane structure. 99% fewer *E. coli* bacteria were able to grow on the membrane surface when only 0.9 weight percent of Ag NPs were impregnated into the NCs membrane. Additionally, according to Zaman and Chakma (1994), these Ag NPs were able to diminish the attachment of an *E. coli* solution to the surface of the submerged membrane by 94%. The distinct physico-chemical properties of polymer NPs and polymer NCs, which allow them to effectively remove a variety of contaminants via various methods, make it obvious that both play a crucial role in environmental remediation.

5 Bioremediation

Another technique that is very useful for the mitigation of emerging pollutants which is showing blooming as a result is “Bioremediation” removal with the help of *microbes*. Rising in popularity is bioremediation, a powerful cleaning technique

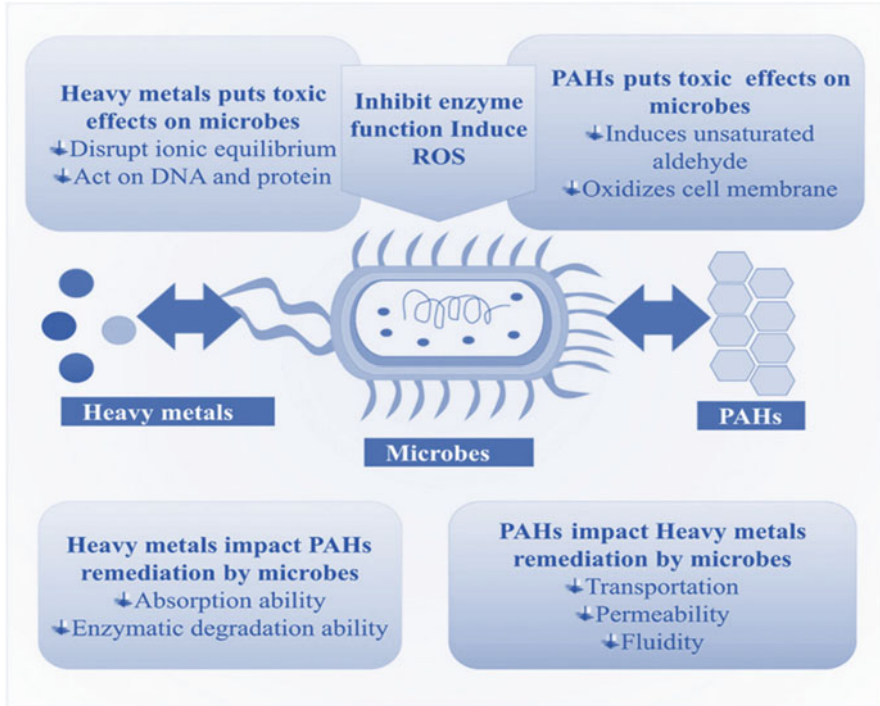


Fig. 4 Bioremediation techniques based on microbes (Malla et al. 2018)

for removing dangerous trash from damaged regions. In the bioremediation process, polluted regions are cleaned up using a range of microorganisms, including aerobes and anaerobes. Microorganisms are crucial to the bioremediation process because it removes, degrades, detoxifies, and immobilizes hazardous wastes and contaminants. Fig. 4 shows a microbes-based bioremediation technique. Depending on the number of dilapidation of contaminants and their change into less hazardous kind are the primary goals of bioremediation. Variables like cost, the kind and concentration of the contaminant, and other considerations, ex situ or in situ bioremediation are perhaps utilized. A suitable bioremediation technique has been selected as a consequence. The most recent advancements in bioremediation methods, how various toxins are broken down by microorganisms, and the use of bioremediation to lessen global pollution are in the near future (Bala et al. 2022).

In order to convert hydrocarbons into less dangerous compounds, a bioremediation method uses microbial enzymes (Bala et al. 2022). Now, research is being done on the widespread application of genetically altered microbes that can also aid in the removal of petroleum, naphthalene, toluene, benzene, and other xenobiotic substances. For improved results, bioremediation is prejudiced by a numeral of variables, including the atmosphere's temperature, the presence of aerobic or anaerobic surroundings, and the availability of nutrients. Emerging contaminants, such as

organic pollutants, heavy metals, poisons, and impurities in air from synthetic or natural source, are a threat to all living things, including humans, animals, and plants. They enter ecosystems mostly through anthropogenic activity. Bioremediation is among the most affordable and ecologically responsible biotechnology innovations. Bioremediation is mostly used in waste management. These organic toxins, which are difficult to degrade and considered to be heterologous biological molecules, can be eliminated. In order to reduce environmental pollution, this study discusses new bioremediation techniques and pertinent information for successful degradation of diverse organic and inorganic pollutants.

5.1 Principle of Bioremediation

The term “bioremediation” is used to describe the controlled biological breakdown of organic pollutants. Hazardous compounds are eliminated or detoxified through bioremediation via provided the microorganisms with the nutrients and other elements they need to function properly. Enzymes are required at every stage of the metabolic process (Chen et al. 2016; Malik et al. 2022). It is related to hydrolases, lyases, transferases, and oxidoreductases in its family. Many enzymes may break down a variety of substrates because of their nonspecific and specific substrate affinities. For bioremediation to be effective, the contaminants must be subjected to enzymatic activity. In order to accelerate microbial evolution and destruction during bioremediation, environmental conditions usually need to be changed (Ren et al. 2018).

The natural and encouraged process of bioremediation can be aided by living things and fertilizers. A crucial aspect of bioremediation technology is biodegradation. It entails the transformation of dangerous organic pollutants, such as CO₂ and H₂O, into naturally existing, nonhazardous inorganic substances that may be used by humans, flora, animals, and marine life (Monika et al. 2021).

5.2 Microbes That Are Engaged in Bioremediation

The addition of microorganisms to food chains maintains biological equilibrium (Hussain et al. 2022). To eradicate polluted constituents from the atmosphere, bioremediation employs bacteria, algae, fungus, and yeast. Microbes may thrive at degrees as low as 196 F and as high as 1200 F when hazardous chemicals or any waste stream are present. Microbes are great candidates for cleanup because of their adaptability and biological functions (Bala et al. 2022). The most crucial nutrient for bacteria is carbon. Processes for bioremediation employed microbes from various settings. Microbes include but are not limited to, *Mycobacterium*, *Achromobacter*, *Alcaligenes*, *Arthrobacter*, *Pseudomonas*, *Xanthobacter*, *Bacillus*, *Corynebacterium*, *Flavobacterium*, *Nitrosomonas*, and other species (Table 4).

Table 4 Multiple microbes utilized in the bioremediation of different environmental pollutants (Malla et al. 2018)

Microbes used in bioremediation	Different kinds of degraded contaminants	Significant conclusions
<i>Brevibacterium epidermidis</i> EZ-K02	Industrial wastes	A bacteria called <i>Brevibacterium epidermidis</i> may break down wastewater that has been polluted by large-scale chemical compound dissolution and nitrocellulose particles.
<i>Bacillus</i> sp. CDB3 <i>Lysinibacillus sphaericus</i>	Arsenic	Arsenic poisoning can be treated with the help of <i>Bacillus</i> sp. CDB3, (<i>Lysinibacillus sphaericus</i>), due to its great resistance to arsenic contamination.
<i>Mycobacterium dioxanotrophicus</i>	Heterocyclic organic compounds (dioxane)	<i>Mycobacterium dioxanotrophicus</i> is able to clean up surroundings that have been polluted with a variety of heterocyclic organic compounds.
<i>Hyphomicrobium</i> sp. strain GJ21	Dichloromethane	Dichloromethane is used by <i>Hyphomicrobium</i> to break down the halogenated contaminants.
<i>Microbacterium oleivorans</i> strain A9	Radionuclides	A radionuclide-resistant actinobacterium with the ability to degrade uranium is called <i>Microbacterium oleivorans</i> strain A9.
<i>Plantibacterflavus</i> strain 251	Hydrocarbon-contaminated environments	Novel biodegradation enzymes are found to exist in the isolate of <i>Plantibacterflavus</i> . It is predicted that the bacteria will offer some cutting-edge insights on taking use of the hydrocarbon degradation pathways.
<i>Bacillus subtilis</i> SR1	Polyaromatic hydrocarbon	In addition to being resistant to heavy metals, the bacterium <i>Bacillus subtilis</i> SR1 is also accomplished with digesting polyaromatic hydrocarbons.
<i>Alkaliphilus metalliredigens</i> strain QYMF	Heavy metals	A metal-reducing bacterium with an uncommon ability for metal respiring microbes: it can thrive in alkaline settings.
<i>Pseudomonas veronii</i> strain 1YdBTEX2	Aromatic solvents, viz., benzene, toluene, ethyl benzene, xylene (BTEX)	The bacteria <i>Pseudomonas veronii</i> has genes which uses a catabolic route to degrade aromatic solvents.
<i>Pseudomonas plecoglossicida</i> TND35	Nicotine	In addition to being a potent degrader of nicotine, <i>Pseudomonas plecoglossicida</i> TND35 also possesses genes with respect to breakdown of the heavy metals, aromatic chemicals, and butanol production.
<i>Microbacterium</i> spp.	Heavy metals	A crucial part in phyto-extraction and the utilization of heavy metals is played by <i>Microbacterium</i> spp.

(continued)

Table 4 (continued)

Microbes used in bioremediation	Different kinds of degraded contaminants	Significant conclusions
<i>Arthrobacter</i> sp. strain SPG23	Degradation of hydrocarbons	Gram-positive hydrocarbonoclastic bacteria called <i>Arthrobacter</i> is a powerful bacterium that may be used to clean up diesel fuels.
<i>Raoultella ornithinolytica-TNT</i>	Trinitrotoluene	The bacteria <i>Raoultella ornithinolytica-TNT</i> is gram-negative. TNT is made less harmful by using nitrate generated from trinitrotoluene in certain strains and is therefore regarded as a powerful microorganism in respect to utilization for bioremediation.
<i>Pseudomonas taeanensis</i>	Hydrocarbons (petroleum compounds)	This bacterium can break down petroleum products including petrol, diesel, and kerosene.
<i>Caulobacter</i> sp. strain OR37	Heavy metals	Has the ability for tolerating high levels of heavy metals, including nickel, Cd, Co, and uranium.

5.2.1 Aerobic

Numerous microorganisms can bioremediate a variety of environmental contaminants in aerobic environments. Numerous complex chemical compounds can be broken down by aerobic bacteria such as *Bacillus*, *Pseudomonas*, *Sphingomonas*, *Flavobacterium*, *Nocardia*, *Rhodococcus*, and *Mycobacterium*. Alkane hydrocarbons, polyaromatic compounds, insecticides, and compounds can all be broken down by these microorganisms. These contaminants are used by many of these bacteria as a carbon and energy source. Microorganisms cannot grow too much during the aerobic bioremediation process because of the oxygen supply (Bala et al. 2022).

5.2.2 Anaerobic

Amphibian bacteria that destroy and change toxins into less dangerous forms are gaining popularity to facilitate the bioremediation of biphenyls that are polychlorinated, chlorine compounds, and the chlorine-based solvents trichloroethylene and chloroform (Chen et al. 2016). *Pseudomonas*, *Aeromonas*, and sulphate-reducing bacteria are only a few of the microorganisms that have been used in the anaerobic bioremediation process. According to Tripathi et al. (2022) paper, azo dyes can become discolored by microorganisms in a variety of environmental settings. Azo dyes can break down anaerobically by utilizing electrons created by the oxidation of the organic substrate(s) in reduction processes. The efficiency of

color removal would be significantly impacted by microbe electrochemical characteristics as a result of such regulated dye decolorization events. For commercial purposes, dyes were anaerobically decolorized in order to gradually accumulate these time-variant decolorized metabolites (DMs). However, for better research and the usage of a precise system, external augmentation of DMs collected under specific circumstances was carried out.

6 Utilizing Nanotechnology for Bioremediation

The lowest unit of dimension in nanotechnology is the nanometer. Due to their extraordinary skills against a variety of stubborn pollutants, many harmful chemicals can be separated with their assistance. Nanotechnology has changed the way we look at technologies like water treatment. Nowadays, eco-friendly methods are categorized as nanofiltration (Sanghvi et al. 2020).

6.1 Nanotechnology and Microbes

When wastewater is treated with efficient microorganisms (EM) technology, the water can then be used for irrigation once the wastewater has been cleaned up (Vázquez-Núñez et al. 2020). Nanotechnology and EM technologies are useful for water purification. Multiple extensive environmental issues are brought on by recalcitrant organic pollutants like polycyclic aromatic hydrocarbons, or PAHs, which are containing multiple benzene rings. According to Mandeep and Shukla (2020), mutagenic substances that are not degradable are polycyclic aromatic hydrocarbons or PAHs. Ramos et al. (2020) created silver nanoparticles in a study by using complete *Trichoderma* spp. fungal cells for the process.

7 Conclusion

Among the many various kinds of resources used effectively intended for a range of ecological remediation purposes are inorganic, carbonaceous, and polymeric nanomaterials. The type of pollutant to be eliminated, availability to the remediation site, the sum of material required to carry out effective remediation, and whether it is advantageous to recover the remediation nanomaterial (recycling) require thorough analysis before choosing the best nanomaterial. We have presented a broad overview of a few nanoparticles that have been used in the area of ecological restoration because each material has unique profits and complications with regard to its application. Despite the fact that numerous research has been conducted to look at the use of nanotechnology, worries regarding. There is further work to be done on

the use of nanotechnology for ecological remediation. Furthermore, although the principles behind the different nanotechnology in the fight are well understood, it is unknown what will happen to the substances once they have been applied utilized for the collection or degradation of pollutants. Although certain materials have been promoted as recyclable, it seems that with time their usefulness diminishes and they become unusable.

The amount of organic and inorganic contaminants has risen sharply in recent years as a result of expanding human influence, and this poses a threat to ecosystems. It is challenging to get rid of these harmful toxins from the environment. Toxic contaminants from the environment are degraded via physical, chemical, and biological techniques. The most promising and economical option for the removal of contaminants using currently available technologies is bioremediation in conjunction with nanotechnology. Studies have repeatedly shown that the distinctive properties of the nanomaterials, which involve improved catalysis and adsorption capabilities alongside a high degree of reactivity, have become the subject of much investigation. A recent development in the use of fungal, bacterial, and algae cultures, including their individual constituents, extracts, or proteins, as accelerators for the long-term invention of nanomaterials. They can function as enhancers in the bioremediation of dangerous compounds by immobilizing or encouraging the production of remediating contagious enzymes. Recognizing the interactions among contaminants, microbes, and nanoparticles (NPs), or nanoparticles, is important. The foremost focus of this chapter is on the utilization of microbial and nanoparticle technologies for the removal of dangerous pollutants in diverse fields. Additionally, we have also gone over the importance and contribution to the sustainability of this unique nano-bioremediation approach.

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Enzyme Immobilization Technology to Treat Emerging Pollutants



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Abstract Human health has been adversely affected by widespread industrialization and urbanization contaminating the environment with xenobiotics. Although there are many physical and chemical methods for managing xenobiotic pollution, bioremediation appears to be a sustainable solution from an environmental perspective. An inexpensive, environmentally friendly method of converting xenobiotics into less hazardous or nontoxic forms is to use microorganisms, plants, or their enzymes. Compared to microorganisms or phytoremediation, enzyme-based bioremediation is more effective at breaking down pollutants with less waste generated. However, enzymes have a number of drawbacks, including low stability (storage, pH, and temperature), limited reuse potential, and difficulty separating them from reaction media. It may be possible to solve the issues and increase reusability by facilitating the separation process and immobilizing enzymes without compromising their activity by immobilizing enzymes without impeding their activity under various environmental conditions. This chapter discusses the benefits and drawbacks of enzyme immobilization and its future in bioremediation, as well as carrier selection, immobilization techniques, as well as immobilization techniques and their application to bioremediation. For the immobilized systems to maximize their potential for extensive industrial wastewater treatment, this assessment identifies upcoming trends and problems that must be addressed quickly.

Keywords Enzyme immobilization · Bioremediation · Hazardous pollutants · Wastewater treatment

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1 Introduction

As a result of human activities, ecosystems have become contaminated, which has negatively affected humans and other animals (Yaashikaa et al. 2022). Many types of pollutants have been found in most water sources, such as pesticides, dyes, heavy metals, medicines, and other emissions from personal items. Uncertainty surrounds the presence of these contaminants in water sources, but they are quantifiably present, changing the quality of the water and raising the danger to humans and other creatures who ingest polluted water. The aforementioned pollutants may be categorized as emerging pollutants and fall under WHO Category 1 carcinogens due to their lethal characteristics. Lack of current technologies to remove or destroy pollutants from the sources is the main contributor to this problem (Saravanan et al. 2021). Traditional methods for removing these dangerous contaminants have led to the pollutants' development of resistance to these techniques and their ineffective removal. These procedures were less effective since they generated waste byproducts along with additional waste materials. Traditional methods require using a lot of power, which is expensive to produce, to address these restrictions (Chauhan et al. 2012; Kaur et al. 2021).

Secondary waste products are produced as a result of methods such as chemical flocculation and filtering. As a result, it is critical to develop new innovative processes which are environment friendly, feasible, and waste-free. Microorganisms are used in biological treatments to remove pollutants. This approach entails using bacteria, fungi, algae, yeasts, and enzymes for bioremediation (Mahmoodi et al. 2020). Nevertheless, microbiological technologies, while environmentally beneficial, have downsides such as sluggish processing, time consumption, inefficiency in surviving under dangerous pollutant concentrations, and the need for upkeep. Immobilized enzymes are currently employed to remove hazardous contaminants from the environment, which is a significant advancement. Different enzymes, such as peroxidases, laccases, manganese, tyrosinase, and others, performed remarkable good in waste removal because they are easier to handle, monitor, and manage. The use of enzymes has several advantages, including less waste generation, a low energy input demand, decreased toxicity, and the capacity to work at optimal and moderate circumstances. Due to their instability and poor reusability, the employment of flowing freely enzymes is constrained in large-scale industries (Zhang and Wang 2021). Immobilized enzymes are commonly used to increase enzyme stability, catalytic activity, and efficiency. Immobilizing enzymes results in heterogeneous catalysts with improved stability under unfavorable circumstances, leads to better and effective results and a significant reduction in cost (Jenjaiwit et al. 2021). The effectiveness of immobilized oxidoreductases in removing rising contaminants has been demonstrated. However, the choice of substrate and the immobilization method needs to be carefully selected to minimize the negative effects of the process on the enzyme's catalytic function. Biocatalyst deactivation is the main source of dispute in enzymatic treatment procedures. This is brought on by alterations in the enzyme binding site brought on by enzyme denaturation at high temperatures or pH. The

enzyme loses its ability to bind to the substrate when an active site is changed. Both competitive and noncompetitive situations can result in inhibition. When inhibitors bind to allosteric sites, they cause noncompetitive inhibition, while competitive inhibition occurs when the inhibitor competes with the substrate for binding to the enzyme's active site (Ariaeenejad et al. 2021).

This book chapter shows how immobilized enzymes may be used to remove harmful and hazardous contaminants from the environment. Researchers have recently been interested in the removal of environmental contaminants utilizing immobilized enzymes. This study also looks at the many types and classifications of backbone materials to immobilize enzymes. A comparison of the difficulties and developments of immobilized enzymes with unbound enzymes is explored. The elimination of various environmental toxins using immobilized enzymes is also demonstrated. The combination of the aforementioned problems sets this review apart from other pieces of literature.

2 Water Pollution's Origins and Consequences

Both point sources and nonpoint sources of pollution can affect water sources. Point source contaminants can originate from a single location, such as a manufacturing outlet, an oil spill, and the release of industrial waste. Point sources can include industrial and municipal effluents. Pollutants in nonpoint sources originate from a variety of sources and enter water supplies in a variety of ways, where they remain undetected in the ecosystem. Transboundary pollutants (e.g., radioactive waste) are present in the environment and have longer consequences. Organic or inorganic contaminants can be found in ground or surface water (Ferreira et al. 2016). Diseases, chemical substances, bacterial communities, pesticides, herbicides, and other substances fall within the organic pollutants category. Heavy metals, dyes, fertilizers in agricultural runoff, and chemical leakage from industrial wastes are other examples of inorganic pollutants. Urbanization is another source of pollutant discharge, resulting in increased quantities of phosphorous deposition, particularly in metropolitan areas. The major causes of this emission include industrial and municipal discharges, as well as urban runoff.

Solid waste is another problem (Delgado-Povedano and De Castro 2015). The large output of organic and biodegradable wastes resulted in inefficient solid waste management. As a result, most rubbish is not properly disposed of, resulting in the release of significant amounts of harmful contaminants into the environment. Sewage may sometimes be used as fertilizer since it contains a large number of nutrients such as phosphorus and nitrogen, which are essential for plant and animal growth. Chemical fertilizers and pesticides are also a factor in the infiltration of minerals into the ground in agricultural areas, which promotes the growth of algae and reduces the oxygen content of the water, ultimately killing aquatic life forms (Kujawa et al. 2021). Paper, leather, and steel are examples of industrial sectors located on the banks of water sources.

Industries use a large amount of water for numerous operations and discharge effluents including colors, acidic solutions chemical substances, and bases into flowing water supplies. Chemical businesses that primarily manufacture aluminum discharge significant fluoride levels into water and, in certain cases, into the atmosphere. Similarly, steel plants emit cyanide, while fertilizer plants emit ammonia. There is a change in the release of large amounts of chromium salts into water as these salts are used to make sodium dichromate (Zamel and Khan 2021). These toxins are all released into the water stream from various water sources, harming both people and other living things.

The agricultural sector contributes significantly to the pollution of the rivers. To boost crop output, chemical-based fertilizers, herbicides, and insecticides are utilized. Excessive pollutant concentrations are deposited in water bodies as a result of improper handling and removal procedures for these chemical pesticides from agricultural areas (Pokorna and Zabranska 2015). Several operations, such as runoff from the fields, spraying, and washing, pollute and degrade the quality of the water. There are many pollutants that are persistent, biodegradable, and affect the environment for a long time.

The human food chain is contaminated with toxic substances, which leads to biomagnification. Any variation in temperatures of the water has an impact on water quality and puts aquatic life in peril. Anthropogenic activity is mostly to blame for pollution deposition and water contamination. Industrial boilers, steel melting, electric and nuclear power plants, and petroleum refineries are some of the sources of heat that release high temperatures into water sources and alter their physical and chemical properties (Rahmani et al. 2020). Low oxygen level in hot water affects aquatic species' physiological processes such as breathing, reproduction, digestion, and digestion.

3 Traditional Treatment Methods

Physical, chemical, and mechanical treatments are all used in traditional wastewater treatment systems. Coagulation, sedimentation, and filtration are examples of physical techniques. Precipitation and adsorption are used in chemical procedures, whereas screening and filters are used in mechanical methods. The physical technique includes removing contaminants from wastewater without affecting the biological characteristics of the pollutant. This approach is straightforward, practicable, and produces less solid waste; nonetheless, it necessitates the use of people and energy. For pollution removal, the chemical approach employs chemical substances. Adding target substances separates the dissolved contaminants. Although chemical treatment systems may efficiently handle industrial and agricultural waste, the deposition of large amounts of chemical substances in agriculture area degrades fertility of soil and mixes with flowing water, generating contamination.

4 Microbial Treatment Methods

Utilizing microorganisms to remove toxins is part of the biological remediation process. The creation of by-products and secondary wastes, the usage of hazardous chemical compounds, the expensive cost of equipment, and other issues make physical and chemical cleanup methods less desirable (Peng et al. 2021). As a result, increased emphasis is being placed on biological approaches to address these limitations. Biological treatment technologies are tested in both laboratories and large-scale companies to ensure their efficiency and effectiveness. This treatment strategy can be applied in the following manners: either by employing enzymes to remove toxins or by using microorganisms to treat pollutants. The most frequently utilized microbial populations for remediation are *Streptomyces* and *Pseudomonas*, whereas *Pleurotus* and *Trametes* are the most frequently used fungal populations. The cleanup procedure can either be aerobic in nature or anaerobic, or an amalgamation of both, according to the type of microorganism engaged. When oxygen is not used during the anaerobic phase, poisonous aromatic amines may be produced. In comparison, the aerobic process does not produce extremely hazardous chemicals but takes longer to complete (Wang et al. 2022).

Microorganisms aid in the removal of harmful contaminants found in wastewater; however, they are unsuccessful in the removal of colors, phenolic, medicinal drugs, and other chemicals. This might be owing to the substance's resistance to microbiological treatment procedures. Second, the use of enzymes such as peroxidases, lactases, and tyrosinase as an alternate tool for increasing the efficacy of the biological therapy process. In aromatic molecules, specially phenolic and nonphenolic compounds, these enzymes catalyze an oxidation-reduction process. The catalytic activity of enzymes is primarily responsible for breaking down developing pollutants (Awad and Mohamed 2019). The decrease of extremely dangerous chemicals caused by the catalytic function of enzymes leads to the creation of products with fewer hazards and a significant degree of contaminant removal. The mixture's less dangerous elements are hard to separate from one another. The instability and restricted reusability of free-moving enzymes is a problem that also exists with their utilization. The solution selected to solve these drawbacks is immobilization. This method increases the reliability and versatility of the enzyme over multiple cycles (Primožič et al. 2020).

In addition to membrane bioreactors, enzyme immobilization methods can be used to develop biodegradation and bioremediation approaches. The foundation that is used for immobilization determines the procedure efficiency. Materials that are organic, inorganic, hybrid, and composite can be used. Materials should have characteristics like biocompatibility, resistance to mechanical stress, strength, and structural resistance.

4.1 Disadvantage of Microbial Treatment Methods

It has been established that using microbial remediation for dangerous pollutant decontamination has drawbacks, such as preventing microbial growth and possibly eliminating the microbe. Additionally, a number of factors, such as pH levels, amount of nutrients, and the outside temperature, have an impact on microbial development and are crucial for achieving the best possible growth of microorganisms and, as a result, the efficient decontamination of dangerous chemicals. In addition, the kind and chemical content of the waste, its solubility, and its interaction with bacteria all have a significant role in the decontamination of dangerous contaminants by microorganisms (Bharagava et al. 2018).

5 Plant-Based Treatment Methods

In order to reduce pollution in polluted areas, phytoremediation is the process by which plants engage in chemical, biochemical, physical, microbiological, and biological activities. Depending on the type of pollutant, combustion, cleaning, deterioration, and stabilization techniques take place. Pollutants might be organic or elemental. As opposed to organic contaminants like chlorinated compounds and hydrocarbons, which are typically removed using combustion, rhizoremediation, stabilization, and deterioration, elemental pollutants like radionuclides and toxic heavy metals are typically removed using transformation, sequestration, and extraction methods (Thakare et al. 2021). When plants like willow and lucerne are employed, mineralization is also a possibility. A variety of factors must be considered when selecting a phytoremediation, including the type of root system, biomass above ground, plant survival and development rate, environmental conditions, the toxicity of the pollutants, and, most importantly, the length of time required for the bioremediation process. The plants employed are also resistant to diseases and pests. The passive absorption of contaminants by the roots, which are subsequently transferred to the shoot via the xylem, is the basic process of phytoremediation. Subsequent accumulation and transport are affected by xylem and adjacent tissue division, transpiration rate, plant type, and contaminated environment features (Thakur et al. 2016). The success of phytoremediation is dependent on increasing native plant remediation capacity by bio-stimulation or bio-augmentation using exogenous or endogenous plant rhizobacteria. Plants that grow in contaminated environments are typically considered to be superior phytoremediators. Plant growth-promoting rhizobacteria (PGPR) improve plant resistance to heavy metals and edaphic conditions while boosting biomass production. Exogenous plant growth-producing rhizobacteria have also been demonstrated to stimulate stem and root development in *Festuca ovina* L. and *Brassica napus* L. plants, which in turn increases plant length and lowers growth inhibition. Similar to this, *Spartina maritima* plants used in the bioaugmentation of endogenous PGPR in heavy

metal-contaminated estuaries led to an increase in metal accumulation and removal (Azubuike et al. 2016). Plants have been discovered to be the most cost-effective and long-lasting phytoremediation alternatives; however, field research has revealed that the bioremediation process is extremely sluggish and plant tolerance is minimal. To circumvent the limitations of native plants, transgenic plants with higher bioremediation effectiveness were developed (Rai et al. 2020).

5.1 Disadvantage of Plant-Based Treatment Methods

The main disadvantages of plant-based bioremediation methods, according to Shukla et al. (2019), are that only a limited number of compounds are biodegradable, that the end products of the bioremediation processes are occasionally more toxic than the original pollutant, that the reaction processes are specific and thus require specific biological agents, that scaling up plant-based bioremediation is difficult and time consuming, and that issues can arise when bioremediation is not a component of phytoremediation; it mostly includes bioaccumulation. In addition to the right growing conditions, plants need a variety of growth nutrients.

6 Immobilization of Enzymes: Characteristics and Approaches

6.1 Properties

Enzymes are a more effective way to get around the drawbacks of using microorganisms. Enzymes function as effectors in all transformation processes and have a variety of beneficial qualities (Masjoudi et al. 2021). Enzymes can be used as catalysts for a variety of compounds because of their broad or narrow specificity. These enzymes alter the toxicological and structural characteristics of pollutants, aid in the complete transformation of harmful compounds into less dangerous forms, and result in the production of a variety of by-products. Enzymes offer more advantages than conventional and microbiological methods. Figure 1 depicts the mechanism of pollution removal by an immobilized enzyme. Microbial metabolism inhibitors do not block enzymes. In bad conditions, the inhibitors can be used to limit microbial activity. Enzymes are more effective at lower dangerous dosages and are more active when microbial competitors are present. Enzymes can function in free or immobilized form, intracellular (in the presence of originating cells) or extracellular (in the absence or presence of originating cells). The laboratory testing of immobilized enzymes showed that both the temperature, time and stability of immobilized enzyme have significantly impact on xenobiotic compounds transformation. The enzyme activity is kept constant throughout the process. When enzymes are immobilized,

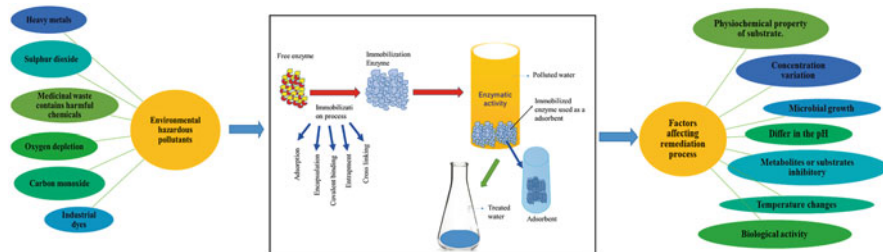


Fig. 1 Mechanism of pollutant removal by immobilized enzymes (Adapted from Yaashikaa et al. 2022)

the support material affects how the enzymes behave. These modifications in the properties of the immobilized enzyme may result from an interaction between the enzyme and the support material that is distinct from the reaction between the substrate and the enzyme in bulk solution. The multidimensional configurations of the protein, which are linked to the support material, may also be to blame for the modifications. Enzyme immobilization improves both the stability and ability to load of the enzymes, leading to controlled diffusion. The stability is improved by the number of bonds that are formed between the support material and the enzyme (Kahoush et al. 2021). Enzyme activity is destroyed when immobilized enzymes bind to substrates because their active sites are unable to bind to the substrate. It is claimed that throughout the process, the free enzyme's activity is maintained at normal conditions. On the other hand, the enzyme may lose its activity if it is immobilized on the support material. An enzyme's interaction with the support substance may be the cause of this.

6.2 Methods

Traditional approaches are excellent at removing toxins in large amounts, but unsuccessful at removing pollutants at ppm or ppb concentrations. During the immobilization process, enzymes connect to the support material in two ways: first, by binding to the surface of the support material, and second, by trapping (Zhu et al. 2020). The polymer materials used to bind the enzymes to the matrices in the first scenario can include biopolymers (such as agarose, chitosan, gelatin, and albumin), organic and inorganic polymers (such as alumina, silica, and zeolite), synthetic polymers (such as acrylic resins and beads), smart polymers (thermally stable and biocompatible), hydrogels, and others. The entrapment operation in the second method commonly employs solgel (metal alkoxide). Enzymes can diffuse over porous solid matrices without interacting with other molecules (Martínková et al. 2016). This approach of immobilization improves enzyme structural stability without sacrificing functional, thermal, or pH tolerance.

Ionic bonding, trapping, metal-linked, covalent bonding, adsorption, encapsulation, and other methods can be used to immobilize enzymes. Adsorption is the most adaptable, fundamental, and straightforward strategy for achieving outstanding results. This approach aids in the removal of contaminants even at ppm or ppb levels. The solid matrix is generated during the adsorption process utilizing a range of materials such as ion-exchange resins, calcium alginate, activated charcoal, and others. The matrix and enzymes are held together by weak forces like hydrogen bonds, van der Waals forces, hydrophobic bonds, or ionic interactions. Desorption processes also allow for the regeneration of adsorbent materials. Covalent bonding allows enzymes to be directly attached to matrices (such as porous silica, polyacrylamide, and porous glass) for increased stability and solid connections (Abdel-Shafy and Mansour 2016). The enzymes are confined within polymer membranes (natural or synthetic membranes) in the entrapment approach, enabling the product and substrate to flow through while inhibiting the enzyme inside the solid matrix. When compared to alternative immobilization procedures, this approach, which may be obtained by gel or fiber encapsulation, is rapid and easy. The primary disadvantages are enzyme deactivation and mass limitation.

Through a reversible ionic bonding process, the solid matrix and the enzyme establish a salt link. The two steps involved in affinity binding are the stimulation of the support material with the ligand for enzyme addition and the interaction of a modified enzyme with the matrix. Warming the metal ions during metal-linked immobilization causes metal salts to build on the matrix's surface (Zdarta et al. 2022). This approach has several advantages, including its simplicity, high enzyme activity, and reversibility. Adsorption appears to be a simple, inexpensive, and active immobilization approach for removing contaminants such as heavy metals from water sources when compared to other methods. Table 1 summarizes the advantages, disadvantages, and applications of various immobilization techniques.

7 Parameters Affecting the Activity of Immobilized Enzymes

Numerous factors, including pH, temperature, the method used to immobilize the enzymes, the choice of support material, the quantity of enzyme used in the procedure, and others, might have an impact on how well the immobilized enzymes work. pH and temperature are important because changes in these factors can impact total enzyme activity. Variations may result in enzyme deactivation or release from immobilized carriers. As a result, depending on the type of enzyme used, optimal pH and temperature must be maintained throughout the process. Methods for immobilizing enzymes have both advantages and disadvantages. If a proper approach is not employed, bonds may be broken, enzymes may be unbound from the substrate, recovery may be poor, or product yield may be low. Carrier materials are another factor that influences the activity of an immobilized enzyme. These

Table 1 Comparison of advantages, disadvantages, and applications of enzyme immobilization techniques (Adapted from Yaashikaa et al. 2022)

Immobilization method	Advantages	Disadvantages	Applications	References
Entrapment	<ul style="list-style-type: none"> • Operate in mild conditions. • Low cost and simple method. 	<ul style="list-style-type: none"> • Leakage of enzyme. • Low level of pore diffusion. 	<ul style="list-style-type: none"> • Food industry. 	Sharma and Singh (2020)
Adsorption	<ul style="list-style-type: none"> • Less conformational changes during reaction. • High catalytic process. • Expansive materials are reusable. 	<ul style="list-style-type: none"> • Low level of efficiency. • Stability can be low. • Desorption of enzyme. 	<ul style="list-style-type: none"> • Biotransformation occurs in the molecule. 	Vo et al. (2020), Zhang et al. (2021)
Encapsulation	<ul style="list-style-type: none"> • Cell density maintains constant. • Expensive materials are usable. • Low MW compounds are easily movable. 	<ul style="list-style-type: none"> • Small molecules can be easily cross from the membrane. • Limitation of pore size. • Mass transfer will be low. 	<ul style="list-style-type: none"> • Biomedical field. 	Li et al. (2020), Moreira et al. (2021)
Cross linking	<ul style="list-style-type: none"> • Strong binding of biocatalyst and leakages to be prevented. • Decrease in desorption. 	<ul style="list-style-type: none"> • Low enzyme activity. • Diffusion may be less. • Formation of unwanted product. 	<ul style="list-style-type: none"> • Production of secondary metabolite. 	Lim et al. (2020), Olejnik et al. (2020)
Covalent binding	<ul style="list-style-type: none"> • Simple method and wide applicability. • Prevent the elution of catalytic activity. • Flexible enzyme and substrate concentration. 	<ul style="list-style-type: none"> • Low effective process. • Low functional conformational. • Carrier molecules are not regenerated. 	<ul style="list-style-type: none"> • Textile industry. 	Sutanto et al. (2020), Gatou et al. (2021), Vasseghian et al. (2022)

compounds must be less toxic, more freely accessible, and enzyme-compatible. The immobilized enzymes may be affected by the characteristics and structure of the carrier materials. Enzyme inactivation occurs when there are too many enzymes present, which restricts the stretching of enzyme production. The performance of the immobilized enzyme is directly influenced by the quantity of enzymes immobilized

on the support materials. Therefore, caution must be used when creating immobilized enzymes.

8 Advantages and Disadvantages of Immobilized Enzymes Versus Free Enzymes

8.1 Stability of Immobilized Enzymes

The main issue when employing enzymes in labs and large-scale operations is maintaining stability in adverse circumstances such as high and low pH and temperature, as well as the presence of oxidizing chemicals, solvents, and ionic liquids. Therefore, the most effective methods for tackling these stability difficulties are immobilization techniques and enzyme engineering (Boonnorat et al. 2016). Enzymes that are immobilized are less stable than unbound enzymes. Immobilized enzymes are found to have a larger portrait with little improvement and to be unaffected by pH variations. Horseradish peroxidase was immobilized using a magnetic graphene oxide composite that was developed by Ji et al. (2017) and its stability was investigated. The thermal stability of this enzyme was shown to increase when it was immobilized. Another research demonstrated the covalent stability of immobilized amylase onto organic frameworks. Using a simple adsorption immobilization approach, the stability of the immobilized enzyme was found to be higher than that of free enzyme. Covalent binding and adsorption were used to immobilize the laccase enzyme on a magnetic metal-organic framework (Zdarta et al. 2022). The enzyme showed great activity, enhanced resistance to changes in physicochemical parameters, and stability during heating and storage. After being immobilized and stored in ethanol, acetonitrile, and methanol, laccase activity was discovered. Immobilized laccase is simply removed from the reaction solution since it was coupled to a magnetic organic framework. The stability of immobilized laccase was similarly increased at elevated levels of salt. The ability of the enzyme to breakdown was unaffected by increasing the salt content, although it did affect the magnetic framework's adsorption. It was shown that immobilization increased structural stability. Recent studies have demonstrated that ionic liquids have a number of advantages over dangerous, flammable organic solvents, including stability, solubility, and catalytic activity. The stability of ionic liquids is significantly impacted by immobilization techniques.

Ionic liquids have been shown in studies to be effective at removing pollutants from wastewater. The extraction technique has recently gained attention; it is dependent on the type of solvents employed in the remediation operation. The interaction of the solute and solvent determines the effectiveness of the process, which is facilitated by properties such as viscosity, vapor pressure, and so on. In wastewater treatment operations, tricaprylmethylammonium methylthiosalicylate, tricaprylmethylammonium thiocyanate, methyltrioctylammonium chloride,

trihexyltetradecylphosphonium methylthiosalicylate, and other ionic liquids are used. Ionic liquids have further advantages, but their high cost and laborious extraction prohibit them from being extensively employed. However, efficient optimization approaches for using ionic liquids as a medium for successfully removing pollutants from wastewater can be developed in the future.

8.2 Enzyme Evolution and Engineering

The creation of specific and advanced enzymes is now possible because of recent discoveries and breakthroughs in enzyme engineering. Enzyme physicochemical properties and catalytic activity are being improved by the introduction of mutations (Miri et al. 2021). These changes improved stability in adverse conditions, including low pH, high temperature, excessive amounts of salt, solvent content, and the amount of substrate. Direct evolution and rational design are the two basic strategies used in enzyme engineering. Changes in the direct evolution approach were caused by either random mutations or gene shuffles. This approach has the benefit of requiring no structural knowledge and allowing alterations to be made anywhere, whether near to or far from an enzyme's active site (Ameri et al. 2021). Apart from the advantages, the practical application of this technology is time utilization, the requirement for high-throughput testing, and dependability. In rational design, site-directed mutagenesis is employed to boost the probability of finding advantageous mutations. In these techniques, the structure of enzymes is used to identify the site of the mutation. De novo enzyme design is the result of this method, which creates novel enzymes with greater activity than native enzymes. To boost the activity, the active site of an enzyme can be altered or modified (Shchemelinina et al. 2021). Oxidoreductases are the enzyme that is most frequently employed to clean up filthy water. This enzyme can catalyze oxidation reactions in both organic and inorganic substrates due to its high redox potential. For instance, peroxidase uses hydrogen peroxide as an oxidizing agent to oxidize a variety of substrates.

8.3 Immobilized Enzyme Reusability and Recycling

The immobilization of enzymes onto the membranes as a foundation has been the subject of recent research. Benefits of membranes include their composition, permeability, large surface space for efficient enzyme enforceable, and pore size. These characteristics facilitate the accessibility of the enzyme's active regions to the components of the reaction solution. To suit the demands of the user, the setup and design may be altered. The reuse of immobilized enzymes through multiple reactions is made possible by membranes. Due to their inertness, affordability, nontoxicity, durability against microbial community and degradation, and environmental friendliness, hard support structures can also be employed for enzyme

immobilization (Chen et al. 2016). Throughout the operation, these tough materials support and preserve the enzyme immobilized on them from severe environmental influences. Immobilization can be achieved using minerals, carbon and metal oxides, aluminum oxide, quartz, and other inorganic elements. Because of its features, including its large surface area, the presence of surface hydroxyl groups, and chemical and heat tolerance, silica is the most often utilized inorganic material for immobilization. Enzymes can be immobilized on silica gel, solgel silica, and fumed silica. Pollutant breakdown was considerably increased when the soybean peroxidase enzyme was immobilized on titanium inorganic oxide (Sohrabi et al. 2016). Another work exhibited manganese peroxidase immobilization onto ferric oxide composite for dye degradation, including reactive orange and methylene blue. This backing material was recycled around five times before a magnet was used to pull it out. Another study found that the immobilized peroxidase enzyme's first cycle of reusability for removing pollutants with nanomaterials achieved 93%. No enzyme activity was seen during the sixth or seventh reusability cycles. The second elimination step with a 50% reduction in reuse material (Torres et al. 2018).

As a result, when the accumulation response serves as a support, the enzyme activity denied the enzymatic reaction's product. As a result, in the subsequent cycle phase, the immobilized enzyme peroxidase has less ability. It may result in higher ability in recycling, according to several research on the reusability of the immobilized laccase enzyme (Xu et al. 2017). 95% of items are reusable the first time, whereas 66% are used more than seven times. According to the investigation, the more efficiently polluted effluent was removed utilizing nano-copper (Adamian et al. 2021).

8.4 Cost Comparison

Enzymes are valuable biocatalysts used in a variety of industrial operations. They are a superior option to chemical catalysts because of features such as resource availability, substrate selectivity, and low waste creation. At mild temperature and pH conditions, industrial enzymes outperformed standard catalysts (Vareda et al. 2016). The cost-effectiveness of enzyme-linked biological catalysts in industrial applications is still a subject that has to be explored. Enhancing stability is crucial to boost cost-effectiveness since adverse harsh conditions like high temperature and pressure as well as changing pH can cause enzymes to become inactive. Indirect measures of overall product yield such as enzyme specificity, reaction kinetics, and the number of cycles the enzyme has been utilized determine the cost of an immobilized enzyme. The main problem with using immobilized enzymes at the industrial level is the difficulty of calculating the entire economics of the process, including all expenses like liberated enzyme, ingredients for immobilization, recuperation, bioreactors, and carriage regeneration. As a result, both technical and economic aspects must be improved in order to use immobilized enzymes as biocatalysts for waste removal. The lifecycle assessment (LCA) is used to analyze the sustainability and overall cost.

LCA may also be used to assess the environmental effect by accounting for energy use, harmful product discharge, and chemical compound addition (Richardson et al. 2016). Techno-economic analysis can be used to look into the use of enzymes in large-scale companies. Utilizing enzymes that have been immobilized can improve cost-effectiveness. Despite being costly, the immobilization approach yields enzymes with higher stability, recyclability, and recovery.

8.5 Scaling-up of Bioreactors

Environmental toxins are being removed using bioreactors. The biological system being researched should be the major emphasis of the bioreactor design, along with determining the elements that need to be handled, such as service and expenditures on capital, scaling-up, security, and other factors (Jeon and Cha 2015). A few prerequisites must be satisfied before constructing an immobilized enzyme bioreactor. Maximum catalytic activity of the enzyme is required, and other requirements include resistance to force, recuperation and reuse ability, expense for manufacturing and construction, temperature of the reaction, and simplicity and ease of operation of the process. Mixed tanks bioreactors, static beds or stacked row bioreactors, and fluidized bed bioreactors are the most common bioreactor forms for constructing an immobilized enzyme bioreactor.

8.6 Current Advances in Designed Enzymes

The enzyme immobilization process could be applied with nanospace material to enhance the capability, security, and efficacy of industrial wastewater treatment. Recent studies have shown that the organic system may operate in a variety of ways, including covalent organic systems, metal-organic systems, and hydrogen-bonded organic systems (Wilson et al. 2022). In the meantime, immobilization based on the food business was introduced employing cutting-edge and various technology. To migrate with great effectiveness and performance, they use a carrier such as nanomaterials and agricultural waste products. Due to its effectiveness, large surface area, security, active site, and permeability, which would enable the transporter of an immobilized enzyme to pass through, the metal-organic system has drawn a lot of interest (Chauhan and Saxena 2016; Chauhan and Gupta 2017a; Chauhan et al. 2017b; Chauhan 2020; Xie et al. 2022).

9 Role of Immobilized Enzymes in Metal Removal

9.1 Lipases

The bulk of fats are digested by hydrolase enzyme-like lipases, with the largest source of lipase enzyme being the human pancreas. Lipase is found in a wide range of industries, including cosmetics, medicines, organic synthesis, detergents, and food (Niu et al. 2016). Many studies on immobilized lipases enzyme heavy metal removal have been carried out. Nickel ions were entangled by the nanoparticle chitosan after nickel was removed from the effluent throughout the experiment (Yang et al. 2016). Ion precipitation was achieved using entrapment, and the ceramic matrix was appropriately mixed. Lipase enzymes are immobilized using a ceramic doped with nickel ions (Ni-CP). The study discovered that 99.4% of the enzymes could be extracted with maximal efficiency, whereas 65% of the activity of the immobilized enzyme could be seen under optimal conditions. In the aforementioned doped ceramic nickel lipase, the enzyme responsible for recycling the doped nickel more than 20 times has great temperature stability and may produce an adsorbent with a 98% reusability (Kureel et al. 2016). The entire inquiry was improved, and it was discovered that the lipase enzyme is engaged in nickel ion elimination.

9.2 Ureases

Urease, a separate enzyme, has catalyzed the hydrolysis of urea, resulting in CO_2 and NH_3 . It is a metalloenzyme that is nickel-dependent. Plant seeds, soybeans, and jack beans are the primary suppliers of the enzyme, in addition to animal tissues and gut microorganisms (Gupta et al. 2021). The urease enzyme's primary role is assumed to be therapeutic. There has been little study on the immobilized urease enzyme in metal removal, and few studies have evaluated the fluctuations in metal-binding capacity and enzyme activity during the inhibitory period (Yan et al. 2013). Several studies have demonstrated that immobilized urease enzyme may remove heavy metals. *Bacillus badius* enzyme was isolated and immobilized utilizing hydrosol gel technology and a nylon membrane. Lead ions are present in the milk sample, and the absorbent can persist up to 2 months (Jegannathan and Nielsen 2013). In another research, the stability of the immobilized urease enzyme is investigated when elements such as copper ions and mercury are removed. It was proved that it was employed with the magnetic nanomaterial that was treated with the thiol and amino group under the name of siloxane layers employing solid matrix and the surface grafting technique of immobilization. The experiment improved the enzyme's stability following immobilization (Li et al. 2013). After immobilization, 65% of the predicted enzymatic activity remained, whereas trace amounts of copper and mercury ions remained. The activity of the natural enzyme is lowered in the presence of copper ions and mercury. Cadmium, copper, silver, mercury, and zinc ions are

hazardous to the extremely stable immobilized urease enzyme (Morshed et al. 2021). Glutaraldehyde-pretreated urease is kept in place by membrane chitosan. The findings demonstrate that urease is stable enough to remove heavy metals as the immobilization process progresses. Some enzymes are limited, whereas unrestricted enzymes are fully inert, such as ions of zinc, copper, cadmium, mercury, and silver. The concentration of immobilized urease in the metal solution that has not been activated is the same in both cases. In the water purification experiment, solgel adsorbents were utilized to extract cadmium and copper (Gosset et al. 2016).

The urease enzyme was immobilized as the porous material in the presence of magnetic nanoparticles, and DTPA, or diethylene triamino pent acetic acid, was utilized to prevent the enzyme from remaining dormant in a heavy-metal contamination mixture. Every physiochemical property characterization was researched and recorded. The absorbent can detect the DTPA group as well as cadmium and copper, according to the study. Furthermore, the Langmuir adsorption model performed admirably (Deng et al. 2016). The urease enzyme's activity remained stable throughout and while it was present in the metal solutions due to the DTPA group, indicating that it will continue to function during the restoration process.

9.3 *Laccases*

Copper is used to treat another oxidase enzyme, laccase. The major source is enzymes found in fungi, microbes, and plants and this enzyme work only in the presence of oxygen (Sirisha et al. 2016; Chauhan et al. 2017b). Phenolic molecules, like lignin, can oxidize by laccase enzyme. This enzyme's major applications include food businesses, wine production, etc. It have been less investigations on immobilized laccases in the bioremediation of toxic ions and metals. The study used the catechol adsorption technique on immobilized laccases (Girelli et al. 2021). Laccases were immobilized using oxide materials such as GO, MMT, and PAN. In order to extract catechol from various aqueous solutions, an adsorbent substance is used. The solution contains immobilized enzyme laccases, according to the scanning electron microscope examination (Chatterjee et al. 2016). However, a lot of assimilation took place in the oxides, affecting things like the pH and ideal temperature. The catechol-containing solution had a 40% COD level of removal. The immobilized laccases enzyme allows for the extraction of catechol from the alloy liquid.

9.4 *Papain*

It is also known as papaya proteinase and is classified as a proteolytic enzyme. It aids in the fragmentation of protein particles (Petronijević et al. 2021). It has commercial applications in areas such as food, cosmetics, and textiles. Research suggests that

after the immobilization procedure is finished, mercury may be removed from an aqueous solution. Under optimum experimental conditions, it focused on the removal of heavy metals including Hg and Pb from a stirred fluid comprising calcium alginate bead-immobilized papain (Hu et al. 2017). This study's adsorbent was immobilized papain based on alginate, which was well-optimized and capable of removing Hg and Pb from the stimulated aqueous solution. It was found that Pb and Hg had an impact on the enzyme activity of immobilized enzymes, and that the outcome was effective because a specific amount of papain was immobilized (Ariaenejad et al. 2021). As a result, the kinetic investigation was also completed in part and resulted in a model. They were modeled using several sorts of kinetic models. The immobilized papain enzyme had a bond with mercury and lead, according to desorption and X-ray spectrometry analyses, which allowed the adsorbent to reuse it. Response surface technique studies were used to confirm adsorbent reuse.

9.5 *Bromelain*

Bromelain, a protein-digesting enzyme, was discovered in pineapple stems (Pandey et al. 2021). The enzyme is categorized as a cysteine or sulfhydryl enzyme. Its primary application is in medicine, where it is used to treat blood clotting, burns, and cancer formation. It also has anti-inflammatory, anticancer, and antibacterial properties. Arthritic patients can utilize this enzyme as tablets because it has no side effects and can be taken orally. Because it has the potential to reduce natural inflammation, it lowers joint and knee discomfort (Jiang et al. 2022). Because bromelain serves as a digestive enzyme, it is employed in the beer and bread sectors. In its active site, bromelain has one free sulfhydryl group and two disulfide linkages. Due to its affinity for heavy metals, it can be used in bioremediation. It will get rid of heavy metal pollution and work as an enzyme-based test technique and a protease inhibitive assay approach. On charcoal, the bromelain immobilization method was used to remove metal. According to the study, activated charcoal and bromelain are used with tannery effluent and stimulating solution, which contain chromium and lead to process immobilization. The response surface approach was employed to achieve the appropriate conditions for the immobilization procedure (Chen et al. 2022). All parameters, including concentration, pH, temperature, and weight of the charcoal, were first set up in accordance with the experimental chart. The author claims that the current circumstance, sometimes referred to as CIB (charcoal immobilized bromelain), has reached the immobilization rate. Both before and after treatment, all physiochemical tests for both heavy metals were run. Heavy metal binding in the adsorbent was identified by energy-dispersive X-ray spectroscopy (EDS) (Swain et al. 2021). The experiment was conducted using bromelain that had been immobilized in charcoal under the same conditions. The findings show that compared to free enzyme substrate, the immobilized enzyme bromelain has a high specific affinity. As a result, immobilized bromelain and activated charcoal work

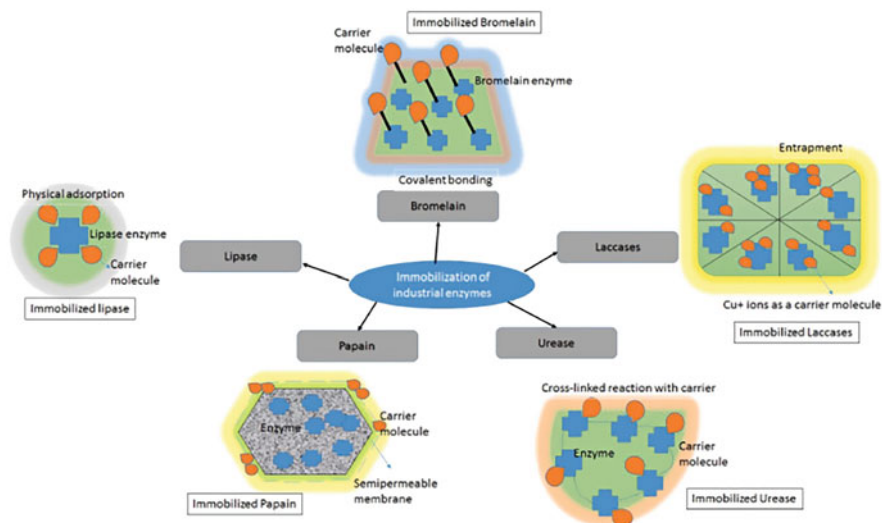


Fig. 2 Removal mechanism of immobilized industrial enzymes (Adapted from Yaashikaa et al. 2022)

well together in this condition's research. In 5 min or fewer, the responses reach the point of nearly full exclusion. In the ensuing 10 min, the separation process attained equilibrium (Aggarwal et al. 2021). Figure 2 shows how the main industrial enzymes are eliminated.

10 Conclusion and Perspectives for the Future

Enzyme immobilization is a technique used in a variety of industrial industries, including textiles, bioremediation, food, and pharmaceuticals. The immobilization of enzymes with distinct characteristics in support materials and their use in large-scale processes have been reported (Zhang et al. 2021). Since immobilization lends stability to enzymes, this approach reduces the cost required. Nevertheless, there are a number of difficulties with enzyme immobilization approaches that must be addressed before these processes may be scaled up from lab to pilot scale. The cost of enzyme production and its immobilization can be lowered through the invention of novel procedure and the optimization of existing technologies. (Zhang et al. 2020). Enzyme nature and its characteristics must be improved in an unfavorable hostile environment. Novel techniques for enhancing enzyme reusability must be established. An enzyme reactor and membrane bioreactor with enzyme beads immobilized at the surface for the treatment of aqueous and industrial wastewater (Pekgenc et al. 2022). To improve the effectiveness of pollution degradation and removal, unique and notable approaches will be evaluated. Implementing

immobilized enzymes in real-world industrial wastewater treatment processes by designing and developing novel ways to scale up small-scale processes. It is also known that enzyme activity is decreased when enzymes are immobilized. Material and method costs for immobilization were lower. In addition to preventing enzyme deactivation, this method also makes enzymes more reusable (Zhou et al. 2021). For the industrial treatment of wastewater, immobilized enzymes have evolved into a practical, cost-effective, and efficient solution.

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Graphene-Based Nanocomposites for Emerging Pollutants



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Abstract Graphene, graphene oxide (GO), and their nanocomposites have been prominently utilized for water and/or wastewater purification due to abilities of superior oxidation, adsorption, and catalytic properties. Graphene and GO-based nanocomposites certainly have considerably high conductivity, pore volume, vast surface chemistry, and an outstandingly large aspect ratio that allows them a favorable and effective material for catalysis and adsorption of various organic pollutants and other inorganic toxic wastes from wastewater. Comparatively, GO-based nanocomposites have been demonstrated as a potential adsorbent for eradicating organic contaminants, heavy metals, dyes, and industrial contaminants and other hazardous pollutants from water and environment. Fabrication and surface functionalization of graphene and GO-based nanocomposites have demonstrated that they can be efficiently applied in enzyme immobilization. In addition, doping and co-doping of GO with wide range of heterogeneous semiconductor-mediated metal oxides have been introduced and investigated for enhancing its efficiency. Researchers have showed more interest in the exploration of various potential applications of graphene and GO-based nanocomposites in removal of emerging pollutants with more efficiency and reduced synthesis concerns. Thus, in this chapter we have summarized the facts involved with the significance, synthesis process, and wide range application of graphene and GO-based nanocomposites in removal of emerging pollutants.

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1 Introduction

In order to address this urgent problem, it is necessary to investigate cutting-edge materials and technologies. The creation of new and persistent pollutants in our environment has become a major worry. Due to its distinct structural and functional characteristics, graphene, a two-dimensional carbon material with extraordinary capabilities, has emerged as a possible candidate for pollution remediation (Hwang et al. 2020). Graphene is a remarkable two-dimensional carbon substance that has piqued the scientific community's interest due to its outstanding features and prospective applications. It is made up of a single layer of carbon atoms organized in a honeycomb-like hexagonal lattice structure. The amazing capabilities of graphene are due to its unique structure, which makes it one of the most promising materials for different technological breakthroughs (Kumar et al. 2021). Graphene is extremely strong, with tensile strength 100 times that of steel. It is able to sustain tremendous mechanical stress without breaking, making it a suitable material for applications that require strength and endurance (Wu et al. 2022). Graphene has a high electrical conductivity, allowing electrons to pass across it at rapid speeds. It is regarded as one of the best electrical conductors, even outperforming traditional materials such as copper. This feature qualifies graphene for use in electronics, energy storage, and high-speed electrical devices (Liu et al. 2017). Graphene has a high thermal conductivity, allowing it to transport and dissipate heat efficiently. Its two-dimensional structure allows it to swiftly transfer heat, making it useful for thermal management applications such as electrical devices and heat sinks (Yang et al. 2020). Graphene, although being a single layer of atoms, is almost transparent, allowing more than 97% of light to flow through. Because of this feature, it is suitable for optoelectronic devices, touchscreens, and flexible displays (Morales-Masis et al. 2017).

Graphene is a very flexible substance that can bend and stretch without losing its extraordinary features. Because of its flexibility, it is perfect for applications requiring flexible and wearable electronics, as well as in the aerospace and automotive industries (Fan et al. 2016). Because of its closely packed carbon atoms, graphene is impenetrable to most gases and liquids. It operates as a strong barrier against water vapor, gases, and even some corrosive compounds, making it potentially useful for applications such as water purification, desalination, and protective coatings (Liu et al. 2015). However, graphene oxide exhibits varying functional groups (Fig. 1), including carboxylic and hydroxyl groups (present in the edges) and epoxy groups (present in the basal surfaces), and phenol and lactone groups. This structural configuration of graphene oxide allows it for possessing better amphiphilic features than the pristine graphene (Ricci et al. 2022). Graphene is an extremely light

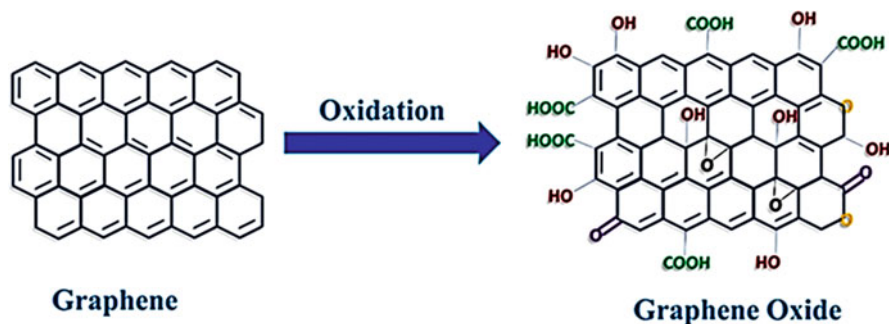


Fig. 1 Chemical structure of graphene and graphene oxide, formed through oxidation process. [Adapted from Ricci et al. (2022)]

substance, weighing approximately 0.77 mg/m^2 . This feature, paired with its strength, makes it excellent for lightweight structural applications like as aerospace and composite materials (Bera 2017).

Although graphene-based composites have multiple benefits, they also have some drawbacks that limit their efficient usage. The large-scale manufacture of high-quality graphene remains a hurdle. Current techniques for synthesis frequently produce small amounts of graphene, making manufacturing on an industrial-scale challenging. Furthermore, the manufacturing process can be costly, restricting its wider acceptance in industries (Zhang et al. 2020). It is difficult to achieve homogeneous dispersion of graphene within a composite matrix. Graphene sheets have a significant tendency to aggregate, reducing the desired qualities of the composites. Maintaining a consistent and homogeneous graphene dispersion throughout the material is critical for optimal performance (Gudarzi and Sharif 2012).

Graphene- and GO-based nanocomposites may have manufacturing compliance concerns, especially when graphene is included into current manufacturing processes. The inclusion of graphene may change the rheological behavior of the nanocomposite matrix, impacting its processing ability and possibly necessitating changes to production procedures (Ponnamma et al. 2021). For efficient transfer of load and structural reinforcement, the interaction between graphene and the matrix material is crucial. However, due to the inert nature of graphene and its limited compatibility with certain matrix materials, achieving a robust interfacial contact can be difficult (Xie et al. 2022). Because of their unique characteristics and functionalization possibilities, graphene-based nanocomposites have showed promise against variety of contaminants. Heavy metals such as lead (Pb), cadmium (Cd), mercury (Hg), and chromium (Cr) have been removed from contaminated water sources using graphene-based nanocomposites. Graphene's high surface area and adsorption capacity, along with integration with particular groups or nanoparticles, allow for effective elimination of heavy metallic ions via adsorption or ion-exchange processes (Velusamy et al. 2021).

Graphene- and graphene oxide-based nanocomposites have been used to treat organic pollutants in water systems such as pesticides, medicines, and dyes.

Graphene's vast surface area allows organic compound adsorption, whereas functionalization with molecules or nanoparticles improves removal effectiveness. Graphene- and graphene oxide-based nanocomposites can also be used to achieve the photocatalytic breakdown of organic contaminants by adding photocatalytic nanoparticles onto the graphene surface (Priyadharshini et al. 2022). Emerging pollutants such as per- and polyfluoroalkyl substances (PFAS), bisphenol A (BPA), and pharmaceutical compounds have showed promise in the removal of graphene-based nanocomposites. Graphene's adsorption characteristics, along with variable surface chemistry via functionalization, enable efficient absorption and removal of these developing contaminants from water sources (Gander 2022).

The synthesis, characterization, and application of graphene- and graphene oxide-based nanocomposites in the field of developing pollution treatment has been reported earlier (Fig. 2). Aloe vera extract was employed as a green synthesis technique to create composites based on graphene. In addition, natural antioxidants have also been used for the production graphene- and GO-based nanocomposites applicable for various therapeutic applications (Barkat et al. 2020b; Das et al. 2020a; b). In addition, various advantages and disadvantages of the various synthetic strategies have been reported earlier that are used to create these nanocomposites,

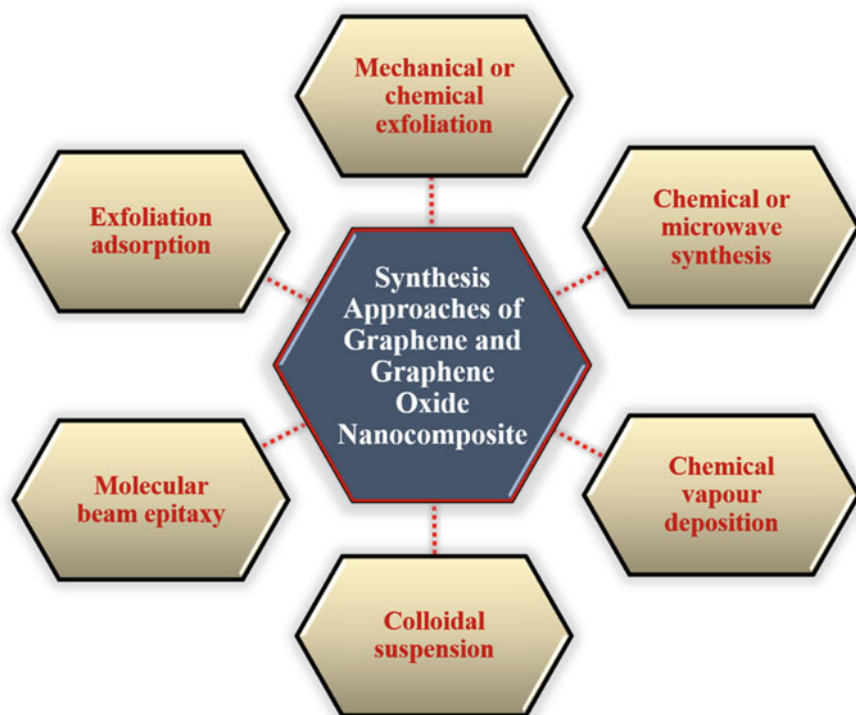


Fig. 2 Various synthesis approaches of graphene and graphene oxide nanocomposites

including chemical vapor deposition and solution-based methods (Xu et al. 2014). It shall also include exploration of the critical function of nanoscale modifiers and how they affect the performance and enhancement of graphene-based nanocomposites. Furthermore, graphene- and graphene oxide-based nanocomposites large surface area, strong mechanical strength, and excellent electrical conductivity all contribute to improved adsorption capacities, efficient catalytic degradation, and robust photocatalytic activity (Xu et al. 2014).

The investigation of the different applications of graphene-based nanocomposites in tackling emerging contaminants in various environmental matrices such as air, water, and soil. While graphene-based nanocomposites show great potential, practical application and scalability remain major hurdles. The barriers and limits that must be overcome before widespread adoption, such as cost, stability, and recyclability. The content of this chapter seeks to provide a thorough examination of graphene- and graphene oxide-based nanocomposites as a game-changing approach for dealing with emerging contaminants. Researchers, engineers, and policymakers can obtain important insights into the possible capacity of these materials to revolutionize pollutant remediation systems by knowing their synthesis procedures, qualities, and applications. Lastly, it is important to understand and work on a cleaner and more sustainable future by using the unique features of graphene-based nanocomposites, reducing the impact of new contaminants on the environment and the well-being of humans.

2 Applications of Graphene-Based Nanocomposites Against Pollutants

2.1 Bioorganic or Industrial Pollutants

The use of nanomaterials, particularly graphene (GR), in numerous domains is examined (Fig. 3). The three different kinds of graphene—pristine graphene, graphene oxide (GO), and reduced graphene oxide (rGO)—were studied followed by the examination of nanocomposites made of graphene and other inorganic and polymeric components. Examples include composites made of carbon fiber and graphene, activated carbon, metal oxide, and polymer and GR. The commercial usage of graphene nanocomposites, particularly in the fields of supercapacitors, biosensors, solar cells, and corrosion protection research is also explored (Lawal 2019).

Numerous studies have been done on their mechanical, electrical, thermal, optical, and chemical characteristics, as well as their suitability for diverse applications including solar cells, biomedical systems, sensors, and transistors (Ibrahim et al. 2021). The synthesis techniques, characterizations, mechanical characteristics, and thermal properties are the main topics of modern research in this field. For researching graphene flakes and their composites, it is important to use

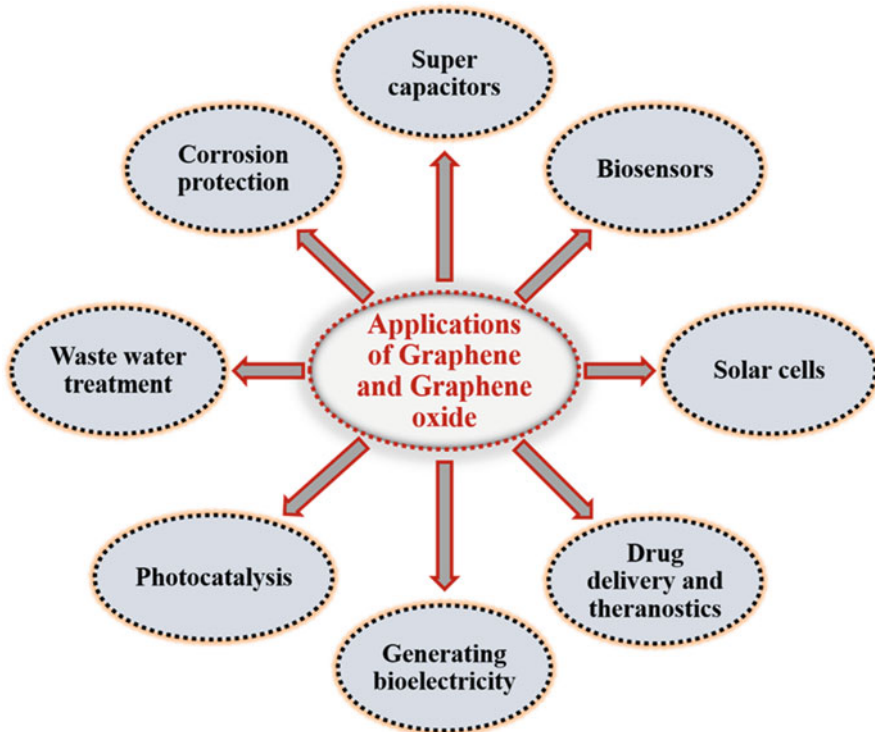


Fig. 3 Various applications of graphene and graphene oxide nanocomposites

characterization techniques as Raman spectroscopy, X-ray diffraction (XRD), atomic force microscopy (AFM), scanning electron microscopy (SEM), and high-resolution transmission electron microscopy (HRTEM). Furthermore, it has been demonstrated that even small concentrations of graphene have a significant impact on the mechanical properties of the composite matrix (Ibrahim et al. 2021).

The numerous uses for graphene and GO-based nanocomposites in industry, agriculture, and medicine have been reported (Azizi-Lalabadi and Jafari 2021). Polymer matrices' thermal, mechanical, electrical, and barrier characteristics are improved by adding graphene or GO. For graphene/GO-based bio-nanocomposites, various manufacturing techniques have been investigated, such as chemical vapor deposition, chemical synthesis, microwave synthesis, the solvothermal approach, molecular beam epitaxy, and colloidal suspension. However, each approach has disadvantages, especially when it comes to mass production. Finding a high-quality, efficient approach for large-scale production is therefore essential. Applications for graphene-based bio-nanocomposites include energy storage systems, biosensors, drug delivery systems, antimicrobials, and modified electrodes. Further research is required to determine the best biopolymers and carbon nanomaterial combinations for industrial usage (Azizi-Lalabadi and Jafari 2021).

The substantial influence of two-dimensional nanomaterial graphene in the area of biomedical applications. Graphene is a versatile material in drug delivery and theranostics due to its remarkable biocompatibility, physicochemical characteristics, and mechanical strength. It is investigated how various inorganic and organic compounds can be mixed with graphene nanoparticles to provide a variety of uses (Madni et al. 2018). The potential of graphene to combine with metallic nanoparticles to generate hybrids opens a wide range of possibilities for use. First off, nanoparticles can be attached to graphene to increase their mechanical strength. Second, graphene improves the performance of metallic nanoparticles in therapy, medication transport, biosensing, and diagnostics. Additionally, polymeric nanocomposites based on graphene are frequently used in drug delivery systems because they enable the integration of hydrophilic, hydrophobic, sensitive, and macromolecular molecules. Quantum dots made of graphene as well as hybrids made of carbon nanotubes and inorganic nanocrystals showed promise as diagnostic and therapeutic tools (Madni et al. 2018).

The potential of graphene-based nanocomposites for purposes in biotechnology and drinking water purification. The development of these materials has advanced dramatically, with a special emphasis on nanohybrid architectures of graphene-ceramic systems (Jakubczak and Jastrzebska 2021). Covalent graphene surface modification with ceramic nanoparticles and co-deposition of metals with properties are two methods used to create these structures. Innovative tools and methodologies for modifying the functionalities of these materials in drinking water decontamination and biocidal composites have also been investigated (Jakubczak and Jastrzebska 2021). The improvements in metal oxide/sulphide composites paired with analogs of graphene as electrode materials for the following-generation supercapacitors (SCs). Scientific accomplishments related to SCs have increased significantly, including papers, patents, and device creation (Tiwari et al. 2020). The goal has been to create electrode materials that are durable, economical, and high performing. Metal oxides and sulfoxides combined with carbon-based electrode materials have shown good energy density, cyclic stability, and durability. The review discusses several methods of making SCs based on graphene, such as intercalation, coating, wrapping, and covalent interactions. Current developments in graphene-based electrodes, electrolytes, and all solid-state SCs, as well as the influence of graphene-based nanostructures on the core concepts of SCs. Nickel oxide, nickel sulphide, molybdenum oxide, ruthenium oxides, stannous oxide, nickel-cobalt sulphide, manganese oxides, and multiferroic materials are only a few examples of the metal oxides/sulfides that have been described for their surface features (Tiwari et al. 2020).

The domains of biology and health care have paid a lot of interest to nanocomposites made of graphene. They offer special benefits such as large surface area, elasticity, biocompatibility, and mechanical strength and have been effectively coupled with medicines, nucleic acids, antibodies, and other compounds (Han et al. 2019). Additionally, these nanocomposites have a potent near-infrared absorbance, which enables them to function as photothermal agents to kill cells. Graphene-based matrices or scaffolds with special mechanical and electrical properties have been investigated extensively for use in bone, neuron, heart, and muscle tissue

engineering, where they encourage cell growth and differentiation (Han et al. 2019). Due to their remarkable qualities and biocompatibility, graphene-based nanocomposites are becoming more popular in the field of biomedicine as a result of the rising need for multifunctional and integrated composites. Researchers developed a novel technique for mechanically exfoliating graphene in this paper, which produced a high yield of graphene nanoflakes with a significant amount of single-layer graphenes. In a poly (vinyl alcohol) (PVA) matrix, these mechanically exfoliated graphene (MEG) flakes were successfully distributed. Nanocomposite PVA/MEG fibers were created by stretching and spinning gel, and they have a much higher ultimate tensile strength than neat PVA fibers (2.1 GPa). The PVA/MEG nanocomposite fibers additionally showed antimicrobial reduced cytotoxicity as well as other positive traits. The findings showed that, 5 days after surgery, wounds treated with PVA/MEG nanocomposite fibers healed more effectively. The positive characteristics of this surgical suture made of nonoxidized graphene, as well as its low-cost manufacturing technology and straightforward manufacturing procedure, point to possible commercial availability (Ma et al. 2018).

Graphene and biomacromolecules together offers a viable strategy for creating new nanocomposites. Due to its increased biocompatibility, specific surface area, electrical conductivity, and tensile qualities, graphene-based composites have attracted more scientific attention. Graphene-biomacromolecule nanocomposites outperform conventional graphene-based materials in biological and biomedical applications due to their superior biocompatibility, biofunctionality, and reduced cytotoxicity. Discovering new uses for the material is made possible by recent research on the interactions of graphene with biomacromolecules (peptides, DNA/RNA, proteins, and enzymes), as well as the methods for making functionalized graphene-biomacromolecule composites (Wang et al. 2023).

Reduced graphene oxide/bismuth vanadate/titanium oxide (RGO/BiVO₄/TiO₂) ternary nanocomposites were produced using a simple, ultrasonic wave-assisted one-pot hydrothermal process. A multifunctional structure called graphene oxide (GO) was used to create RGO/BiVO₄/TiO₂ (GBT) nanocomposites with different band gap energies. The band gap energies of both BiVO₄ and TiO₂ could be controlled simultaneously by varying the amounts of GO and TiO₂ during synthesis. Under visible light irradiation, the GBT nanocomposites demonstrated increased photocatalytic degradation of methylene blue (MB). The photoluminescence data and the photocatalytic activity rates of the GBT series composites were connected, indicating revealed TiO₂ served as a powerful mediating co-catalyst while GO served as an electron trap. The time needed for full MB deterioration to occur decreased from 40 min with RGO/BiVO₄ to 10 min with the ternary composite GBT as a result of the band gap energy tuning. Research opens up the possibility of creating numerous graphene-based ternary composites with varying band gap tunings, which may find use in a variety of industries (Nanakkal and Alexander 2017). GO was created using a modified Hummers process at various levels of oxidation. The graphitic AB stacking order was disrupted, according to XRD investigations, with more oxidation. Epoxide groups were shown to be present at higher levels of oxidation than hydroxyl and carboxyl groups, according to XPS research. Increased

oxidation levels were associated linearly with increased zeta potential, according to zeta potential analyses. Raman spectroscopy showed that as oxidation increased, a crystalline structure changed to an amorphous one. The amount of oxidation was discovered to have a substantial impact on the GO's electrochemical characteristics. The results imply that modifying the degree of oxidation presents prospects for modifying GO characteristics and improving GO-based applications (Krishnamoorthy et al. 2013).

In another study, wet impregnation was used to create a composite material made of sheets of reduced graphene oxide (RGO) embellished with ZnO nanoparticles. Using X-ray diffraction (XRD), Williamson–Hall plot (W–H plot), and scanning electron microscope (SEM) investigation, the material was described. The ZnO nanoparticles ordered hexagonal (wurtzite) structure was evident in the XRD pattern. The homogeneous distribution of ZnO on the RGO surface was observed by SEM analysis. The degradation of methylene blue dye was used to quantify the nanocomposite's photocatalytic activity. The speedy recombination of photoinduced electrons contributed to the deterioration of the dye. Scavenger analysis helped to support a viable mechanism that was put forth. It was determined that the wet impregnation technique was effective for generating RGO with uniform ZnO loading. Under UV light, the produced RGO-ZnO composite showed effective dye degradation (Labhane et al. 2016).

2.2 *Dyes and Chemicals Pollutants*

Industrialization has caused water to become contaminated with many contaminants, such as dyes, solvents, heavy metals, and chemicals, which has had a negative impact on ecosystems and people's health. These issues are made worse by improper wastewater treatment, emphasizing the necessity of efficient water treatment techniques (Ramalingam et al. 2022). Due to their outstanding physical, chemical, and mechanical qualities, graphene-based photocatalysts have gained attention as prospective alternatives for wastewater treatment. When combined with metals, metal-containing nanocomposites, semiconductor nanocomposites, polymers, MXene, and other compounds, graphene can significantly increase the photocatalytic activity due to its excellent electron conductivity, wide light absorption range, large surface area, and high adsorption capacity (Ramalingam et al. 2022).

The use of very sensitive and picky sensors for detecting biomolecules at low concentrations that are made of graphene-based nanocomposites. High surface area, exceptional conductivity, and the ability to be chemically functionalized are just a few of the special qualities that graphene and its derivatives, including graphene oxide and reduced graphene oxide offer (Sainz-Urruela et al. 2021). Studies are focused on the creation, functionalization, and characteristics of graphene-based nanocomposites, particularly in the area of bioactive chemical detection. The importance of antioxidants for various health advantages is emphasized, and the sensitivity and selectivity of electrochemical and fluorescence sensors based on graphene have

also been extensively studied (Sainz-Urruela et al. 2021). Recent developments in the in situ synthesis of nanomaterials have generated a great deal of curiosity and found extensive use in various disciplines (Nishchitha et al. 2023). Photothermal reduction technique was used to study a novel method for the ultrafast in situ synthesis of a cobalt-cobalt oxide-reduced graphene oxide composite using laser ablation. The composite underwent structural and morphological changes as the cobalt ion concentration was changed. The detection of alkaline phosphatase, a crucial bioanalyte demonstrated great promise for electrochemical sensing applications. With a linear detection range of 10–800 mU l⁻¹ and a low detection limit of 10.13 mU l⁻¹, the sensor exhibited remarkable selectivity. Real human serum samples were used to validate the sensor's performance utilizing a recovery-based methodology. This in situ material synthesis process may one day be scaled up for quick composite material synthesis (Nishchitha et al. 2023).

Due to its negative impacts on the environment and public health, the significance of cleaning textile wastewater has been declined. In addition, several investigations have showed that the study and effect of oxidation and adsorption in textile wastewater treatment has significantly increased. Hot spots for current research in this area include graphene oxide and nanocomposite adsorbents (Liu et al. 2023). The application of hybrid nanomaterial technologies, particularly porous chitosan, and graphitic carbon nitride (g-C₃N₄), has been observed for resolving the problem of safe drinking water supply. A composite made of graphitic carbon nitride and biopolymer was developed and investigated its capabilities for treating wastewater. The process used to create the material, a microstructural study, and its stability at 500 °C are all discussed. The study revealed the potential of chitosan-doped g-C₃N₄ nanosheets for enhancing the quality of tainted water and provides new directions for photocatalytic nanomaterials based on nanocomposite (Praseetha et al. 2023).

In another study, use of membrane technology as a potent tool for wastewater treatment is investigated by the researchers. To improve the functionality of polymeric composite membranes, they combine pore-forming agents, solvent, and nanoparticles. Hummer's method is used to create graphene oxide (GO), which is then further functionalized using chloroacetic acid (c-GO). Phase inversion is used to create thermoplastic polyurethane (TPU) membranes with different c-GO contents. According to the research, raising the concentration of c-GO in polymeric membranes improves water permeability, making c-GO an excellent candidate for enhancing the physicochemical characteristics of membranes. Due to their enhanced dye rejection properties, the composite membranes have promise for use in wastewater treatment and environmental remediation (Zahid et al. 2023). Researchers have seen enhanced hydrophilicity and wettability as well as extremely effective photocatalytic disinfection and algicidal effects by adding fluorine-functionalized rGO (rFGO-TiO₂). In this study, rFGO-TiO₂ was hydrothermally synthesized by the authors to obtain antibacterial characteristics against *Escherichia coli*, a gram-negative bacterium. The best results were obtained with an rFGO concentration of 1 weight percent, a hydrothermal temperature of 200 °C, and a hydrothermal period of 1 h, according to their investigation into various synthetic settings to optimize the antibacterial activity. The antibacterial effectiveness was decreased as a result of too

much rFGO and disruption of the rFGO-TiO₂ binding when the ideal conditions were exceeded by raising the hydrothermal temperature and rFGO concentration. Stress brought on by hydroxyl radicals and superoxide ions damages cell membranes and ultimately results in cell death, according to electron spin resonance spectroscopy (Jeong et al. 2023).

Due to their detrimental impact on both human health and the environment, hazardous chemical substances like hydrazine (N₂H₄), 4-nitrophenol (4-NP), and Hg²⁺ must be found and monitored in natural water resources. To solve this problem, research has concentrated on electrochemical nanostructured platforms that mix graphene derivatives and inorganic nanoparticles. In this study, rGO was functionalized with 1-pyrene carboxylic acid and combined with colloidal gold nanoparticles to create a hybrid nanocomposite that was applied on screen-printed carbon electrodes. Using differential pulse voltammetry, these modified electrodes were evaluated for their ability to electrocatalytically detect N₂H₄ and 4-NP. For the electroanalytical detection of Hg²⁺ using DPV, they were additionally modified with an electropolymerized film of polycurcumin bearing an imprint of Hg²⁺. These platforms were found to have a lower limit of detection (LOD) than other cutting-edge electrochemical sensors using comparable gold-graphene nanocomposites (Mejri et al. 2022).

Interest in nanocomposites with potential resolved multicolor electrochemiluminescence (ECL) characteristics has increased recently. This study used a straightforward approach to create a nanocomposite of graphitic carbon nitride modified with TiO₂ nanoparticles (TiO₂-NPs/g-C₃N₄). The TiO₂-NPs/g-C₃N₄ nanocomposite's shape and chemical makeup were characterized. When the synthesized nanocomposite was exposed to cyclic voltammetry scanning using K₂S₂O₈ as the co-reagent, it displayed dual-peak multicolor ECL emission. Turquoise blue emission (471 nm) at -1.3 V and olive-green emission (490 nm) extending from -1.4 to -2.0 V made up the first ECL peak (ECL-1). Navy blue emission (458 nm) at -3.0 V made up the second ECL peak (ECL-2). In order to explain the potential resolved multicolor ECL emission, the study put up an ECL mechanism. Additionally, rutin's effect on the quenching of the ECL of TiO₂-NPs/g-C₃N₄ led to the development of a sensing technique using the first ECL peak for the quantitative detection of rutin. It was discovered that the linear response range was 0.005–400 M, with a 2 nM low detection limit. This study provided a simple method for producing g-C₃N₄-based nanocomposites with potential-resolved multicolor ECL, opening new opportunities for their use in light-emitting and imaging systems (Lu et al. 2023).

The problem of wastewater pollution removal using materials based on graphene. Due to its hydrophilicity, large surface area, and functional groups, GO is an efficient adsorbent for dyes and heavy metals. It goes through the GO reduction mechanism, pollutant adsorption capabilities, toxicity of heavy metals, and interactions with dyes applications like antimicrobial (Barkat et al. 2020a; Bhattacharjee et al. 2022), anticancer (Bharadwaj et al. 2021; Jha et al. 2022), drug delivery (Bharadwaj et al. 2021; Sivasankarapillai et al. 2020), and photocatalytic dye removal as well as doing a market analysis and comparing green and chemical reduction techniques is vastly

studied recently (Shaheen et al. 2023). The process of cleaning contaminants out of wastewater using compounds based on graphene. Due to its hydrophilicity, large surface area, and oxygenated functional groups, GO is emphasized as an efficient adsorbent that makes it possible to remove dyes and heavy metals from water. Along with talking about the elimination of dyes and heavy metals and their related toxicity, the method of GO reduction utilizing plant extract is also emphasized. The polyaromatic resonating system, pi-pi interactions, various production methods, and the biotoxicity of graphene-based composites are used to explain how GO and dyes interact (Cosma et al. 2022).

A bipolar electrode (BPE)-based ECL-photoacoustic (PA) dual-signal output biosensor with wireless capabilities. The anode ECL collecting, cathode catalytic amplification, and intermediate functional sensing units were the three distinct components of the BPE construction. A laser-induced polyoxometalate-graphene electrode was included in the cathode unit to improve the ECL signal, and eosin yellow, and effective ECL reagent, was used in the anode unit. In addition, the use of a carbon nano-onion nanocomposite as a signal tag led to modifications in the electrical conductivity of the film due to heat transfer, which in turn affected the ECL signal and produced a potent PA response. This approach made it possible to output PA and ECL signals simultaneously. The study contributed to improvements in ECL detection technology and other cutting-edge detection techniques by achieving modularization in sensor design as well as signal output mode diversity (Huang et al. 2022).

Concerns concerning the widespread use of azo dyes as food colorants, notably in beverages like soft drinks, have been highlighted by recent studies. An azo dye called amaranth is thought to be mutagenic and carcinogenic. A SnO_2/rGO nanocomposite was developed as a chemically modified sensor for detecting low concentrations of amaranth in water and soft beverages in order to satisfy the need for quantification. Through characterization methods, the nanocomposite demonstrated positive traits, and Tafel plot analysis and EIS were used to assess its electrocatalytic capabilities. The ideal settings for sensitive amaranth detection were found, and the sensor showed outstanding anti-interference skills and stability. In two calibration ranges, the $\text{SnO}_2/\text{rGO}/\text{Nafion}/\text{GCE}$ composite shown promising performance for amaranth detection with low limits of detection (Buledi et al. 2022). The creation and use of $\text{MnFe}_2\text{O}_4/\text{G}$, a hybrid nanocomposite based on graphene, for the elimination of synthetic dyes from aqueous solutions. The results showed that it had a high BET surface area of $382.98 \text{ m}^2/\text{g}$, indicating improved adsorption capability compared to pure MnFe_2O_4 . With the presence of functional groups such as carboxylic acid, phenolic, lactone, and basic groups, $\text{MnFe}_2\text{O}_4/\text{G}$ displayed a variety of surface chemistry. In addition, the nanocomposite successfully removed mixed colors and mixed dyes when antibiotics were present, with overall efficiencies ranging from 65.8% to 87.9% after 120 min. The work emphasizes the importance of the π - π stacking interaction between ions and molecules in the adsorption process. Additionally, $\text{MnFe}_2\text{O}_4/\text{G}$ demonstrated cyclability for up to four cycles, highlighting the possibility of using it in useful water treatment applications (Tran et al. 2022).

The creation of environmentally acceptable adsorbents based on poly (glycerol sebacate) (PGS) for the efficient removal of water-soluble colors during the treatment of wastewater. The study examines different nanocomposites as possible dye adsorbents, including PGS-graphene oxide nanoparticles (GO), PGS-graft-chitosan (CS), and PGS-CS-GO. While the inclusion of CS in PGS/GO nanocomposites improved the exfoliation of GO, the use of CS in PGS produced a smooth and uniform structure. PGS's glass transition temperature was similarly lowered by the addition of CS and GO, possibly leading to an increase in chain regularity and crystal size. The created PGS-CS-GO nanocomposites have a great deal of potential as effective adsorbents for cleaning up dye-tainted water solutions (Rostamian et al. 2022). The fabrication and evaluation of a photocatalyst is based on metal nanoparticle-encrusted graphene oxide (GO) and zinc oxide (ZnO) nanocomposites. The degradation of model water contaminants, methylene blue (MB) dyes, was used to gauge the photocatalytic activity of the nanocomposites. 90 min of exposure to sunshine resulted in an 84% catalytic activity for the nanocomposite containing 3.125% GO. Additionally, copper and silver nanoparticles were added as dopants to examine how they affected the performance of the photocatalyst. In comparison to the GO-ZnO-Ag nanocomposite, the GO-ZnO-Cu nanocomposite showed a 50% reduction in MB degrading activity (Al-Rawashdeh et al. 2020).

Due to the enormous number of harmful chemicals that are emitted into water bodies by various sectors, the remediation of organic dyes from wastewater is essential in water treatment technology. Solar-powered photocatalysis is one wastewater treatment method that holds promise for removing new toxins and persistent organic pollutants. However, the practical use of efficient photocatalysts is complicated by the integration of reactors. Zinc oxide (ZnO) nanocomposites based on graphene oxide (GO) have shown promise in addressing ZnO photocatalyst shortcomings. Improved light absorption, charge separation, charge transportation, and dye photooxidation have all been seen in these nanocomposites. However, it is still difficult to create practical, affordable GO-based ZnO nanocomposite photocatalysts with adequate efficiency, stability, and photostability, especially for incorporation into photocatalytic reactors (Yaqoob et al. 2020).

2.3 Agriculture Pollutants

Heavy metals, biomedical waste, personal care products, endocrine disruptors, pharmaceutically active substances, and colorants are just a few of the dangerous contaminants that have been released into the environment as a result of population growth and industrialization (Qamar et al. 2022). To solve this problem, researchers have concentrated on creating new adsorbents that combine various polymers and nanostructured materials to improve their efficiency and physicochemical characteristics. Due to their special electrical and chemical properties, quantum size effects, adjustable functionalization, scalability, and high surface-to-volume ratio, nanomaterials have drawn a lot of attention in the field of environmental cleanup.

For the elimination of various inorganic and organic contaminants, sodium alginate has become increasingly popular for use in the production of bio adsorbent materials because it is biocompatible and biodegradable (Qamar et al. 2022). Recent research has focused on using agricultural waste to produce bacterial cellulose. To bacterial cellulose acetate-based nanocomposite membranes for water filtering, TiO_2 nanoparticles and graphene were added. The efficacy of the membranes' bacterial filtration was improved, and they displayed higher crystallinity. The membrane's structure and functional groups were also changed by the addition of TiO_2 and graphene, resulting in a rougher surface with mesoporous properties (Suryanto et al. 2023).

For use in electrical and electroanalytical applications, sustainable nanocomposites were developed. Transition metal dichalcogenides (TMDs) and nanofibrillar biochar (BH), produced from paper industry waste, were used to make 1D/2D nanocomposites. Sodium cholate was used as a surfactant during the liquid-phase exfoliation process to create the NCs. For their electrochemical and morphological characteristics, four distinct BH-TMD NCs were thoroughly characterized and investigated. The NCs showed promise in identifying a range of biological and agro-food-related analytes. The most efficient NCs, with good linearity and low detection limits, were employed for simultaneous measurement of neurotransmitters and flavonoids. The suggested BH-TMD NCs provide an eco-friendly, reasonably priced, and viable answer for electrochemical and biosensor applications (Fiori et al. 2023). Endocrine-disrupting chemicals (EDCs) are widely present in the environment due to their ubiquitous manufacture and use. Exposure to EDCs can cause a variety of problems in aquatic animals and people, disrupting the metabolism, sexual development, and reproduction, even at low levels. For the elimination of EDC from wastewater, the use of adsorption treatment, specifically utilizing nanocomposites, appears to be a promising and sustainable method (Liao et al. 2022). EDCs have been successfully removed from wastewater using a variety of carbon-based nanomaterials, including carbon nanofiber, carbon nanotubes, graphene, magnetic carbon nanomaterials, carbon membranes, carbon dots, and carbon sponges. Further investigation is required into the use of carbon nanocomposites for the removal of different types of EDCs, adsorption theories, current developments in synthesis and characterization technology, as well as factors influencing their use (Liao et al. 2022).

Rapid development has resulted in water contamination, which calls for efficient removal methods for dangerous chemicals. Graphene oxide-based composite materials, which have qualities like mechanical strength, hydrophilicity, flexibility, and ease of synthesis, are gaining popularity as effective adsorbents for water treatment. Targeting different pollutants, graphene oxide-modified nanocomposites perform optimally in water purification. It is investigated how to make and characterize graphene-based nanocomposites (GO, rGO, and MGO), as well as their potential for long-term water filtration and resolving problems with water remediation (Asghar et al. 2022). In another study, citrus-pectin-based Ag@AgCl (CP-Ag@AgCl) was assembled onto a graphite carbon nitride (g-C₃N₄) surface using daylight-driven reduction to create unique citrus-pectin-based Ag@AgCl/

graphite carbon nitride nanocomposites (CACNs). The increased photoelectrochemical characteristics of the CACNs resulted in high photocatalytic activity for the degradation of the food colorant new coccine (NC) when exposed to visible light. Within 60 min of exposure to visible light, the suggested photocatalyst degraded NC with an estimated 95.7% efficiency, exhibiting better photostability and reusability. A model of pseudo-first-order kinetics described how the NC degraded. The created nanocomposites provide a useful means of eliminating dangerous food colorings and making use of peel waste resources (Gong et al. 2022). In order to make graphene oxide nanosheets from sugarcane bagasse, which are then utilized to make epoxy nanocomposite coatings with photoluminescent, hydrophobic, and anticorrosive qualities, a green technique was created. Sugarcane bagasse nanostructures are subjected to oxidation before being added to epoxy coatings. The resultant paints have strong corrosion resistance, long-lasting luminescence, and high durability (Al-Nami et al. 2022).

The microbial fuel cell (MFC) has attracted a lot of interest as a green technology for producing bioenergy and treating wastewater. Its real-time applications are hampered by issues like limited power output, high ohmic resistance, and expensive electrode and membrane production. Research has concentrated on improving energy production and lowering losses related to MFC electrodes to overcome these problems. Carbon and graphite electrodes are frequently employed because of their large surface area, biocompatibility, affordability, and mechanical strength. Nanocomposites made of graphene or graphene oxide have become possible substitutes for expensive catalysts and electrode modifications in MFC. Cost-effective electrode production is another benefit of producing graphene oxide from trash. However, the creation of bioelectricity using graphene requires expensive and uneconomical graphene synthesis (Aiswaria et al. 2022). As a sustainable supply of silica, rice husk ash (RHA) was used to create mesostructural graphene oxide (GO)/SBA-15, a hybrid material based on graphene. The substance displayed a variety of oxygen functional groups as well as favorable dye adsorption properties, such as a high pore volume, wide pore width, and big surface area. The gelation pH, GO content, adsorbent dosage, and initial MB concentration were revealed to be influences on the adsorption capacity of GO/SBA-15 for methylene blue (MB). The adsorption capacity that was highest was 632.9 mg/g. The study further investigated the GO/SBA-15 adsorption isotherms and kinetics, emphasizing the material's potential for organic dye adsorption and the worth of treated RHA (Liou and Liou 2021).

The creation of antimicrobial materials, particularly active antibacterial packaging technologies, is essential for use in food applications. Recent innovations seek to satisfy consumer demand for environmentally friendly packaging materials while minimizing plastic waste-related environmental problems. Recent developments include research on antimicrobial composite materials for active food packaging that combine effective antibacterial nanoparticles (like metal, metal oxide, mesoporous silica, and graphene-based nanomaterials) with biodegradable and green polymers (like gelatin, alginate, cellulose, and chitosan) derived from natural sources (Omerovic et al. 2021). nZVI/GO-AC is a brand-new nanoadsorbent with

potential uses in separation and removal procedures. It combines zero-valent iron (nZVI), graphene oxide (GO), and active carbon (AC). For better physical qualities, ultrasonication was also used during the sodium borohydride reduction of ferrous sulphate, active carbon, and graphene oxide during the synthesis of the nanocomposites (Bagheri et al. 2021). Characterization techniques showed that the addition of GO, especially when paired with ultrasonication, reduced the particle size to less than 10 nm. At room temperature, the nanocomposites displayed superparamagnetic behavior and could be separated using an external magnetic field. Higher adsorption rates were achieved by accommodating nZVI more fully at lower GO concentrations. Its stability was increased by immobilizing nZVI on the composite platform, and graphene's capacity to allow electron transport while preventing surface passivation enhanced the adsorption of target chemicals (Bagheri et al. 2021). Moreover, the overall applications of graphene and graphene oxide nanocomposites or conjugated systems have been described in Table 1.

3 Conclusion and Future Perspectives

Water is one of the most vital matters on the earth, crucial for the endurance of the living beings and the endurance of daily life. In recent era, water preservation is very critical and has become a global concern, thus wastewater treatment systems play a crucial role in water sustainability. Wastewater treatment confirms the absence of any harmful and hazardous pollutants in the sewage systems. Thus, it becomes necessary for the researchers to develop effective nanomaterials leading to establish water reservoir systems with high purity. Graphene and graphene-based nanocomposites have established their proficiency as novel materials for the elimination of various pollutant types in water sources, including organic, inorganic, dyes, industrial and agricultural wastes, and others. The oxidation of graphene leads to the formation of graphene oxide and reduced graphene oxide that significantly improves the characteristics and enhances its hydrophilic nature thus enhances its capability to interact with the organic pollutants. They have also showed wide scope for remediation of environmental pollutants deprived of interfering with the processes of nature. GO-based nanocomposites are categorized by the ease of fabrication, reusability, high adsorption capacity, biocompatibility, and liveness to structural alterations for extended applications. Thus, GO-based nanocomposites have been one of the most investigated and used topic in the water or wastewater treatment for the elimination of a wide range of hazardous or unsafe pollutants. In modern era, researchers have amalgamated graphene with other stable nanomaterials which leads to several synergistic effects in the elimination of organic pollutants.

Table 1 Applications of graphene or graphene oxide-based nanocomposite systems in eradication of various pollutants

Types of nanocomposites	Major compounds	Method of preparation	Outcome	References
Magnetic	Carbon and iron	The 3D graphene and graphene oxide-based nanostructures	Inactivation of gram-positive and gram-negative bacterial species (e.g., <i>Escherichia coli</i> and <i>Staphylococcus aureus</i>)	Asghar et al. (2022)
Magnetic	Fe ₃ O ₄ /RGO nanocomposites	Solvent-thermal reduction	Cr (VI) adsorption and removing heavy metal ions from wastewater	Zhang et al. (2021)
Magnetic	Fe ₃ O ₄ @G-TEOS-MTMS)	Solgel hybrid magnetic nanocomposite	Analysis of polar and nonpolar organophosphorus pesticides	Rashidi Nodeh et al. (2017)
Polymeric	Gum tragacanth, carbohydrate and graphene oxide, Ag	Graft polymerization to form hydrogel	Removal of heavy metal ions such as Pb (II), Cd(II), and Ag(I)	Sahraei and Ghaemy (2017)
Synthetic	Hg polyethyleneimine	–	Adsorb mercury (Hg) from contaminated seawater	Coppola et al. (2021)
Metallic	Metal and hazardous contaminants, graphene oxide, modified nanocomposites	Magnetic separation method	Detection and elimination of contaminants using graphene oxide, reduced graphene, and reduced graphene oxide	Asghar et al. (2022)
Bioorganic	Microbial fuel cell	Biomass technique	Sludge carbon	Li et al. (2020)
Polymeric	Antimicrobial nanoparticles, polymeric aromatic hydrocarbon	Synthesis and process technique, electrokinetic remediation technique	Reduce the risk of pathogen growth and food safety Nano oxidants and phytoremediation	Omerovic et al. (2021)
Adsorbents	Graphene oxides, reduced graphene oxides, and their nanocomposites	Nanoadsorbents	Adsorption capacities of various graphene-based nanoadsorbents for the removal of different inorganic and organic contaminants Evaluated the effects of key water-quality parameters such as pH, temperature, ions/ ionic strength, and natural organic matter on adsorption The potential regeneration and reusability of nanoadsorbents	Kim et al. (2018)

(continued)

Table 1 (continued)

Types of nanocomposites	Major compounds	Method of preparation	Outcome	References
Functionalized	GO	Surface modification of GO	Determined different surface functional groups, such as oxygen-containing, nitrogen-containing, and sulfur-containing functionalized GO composites in the adsorption of cationic and oxyanionic heavy metals	Ahmad et al. (2020)
Polymeric	GO, chitosan	Green nanocomposite based on the self-assembly of GO with chitosan CH	Removal of Hg(II) at equilibrium in river and seawater Removal of mercury is not affected by the presence of NO_3^- and Na^+	Bessa et al. (2020)
Metallic	ZnCr-layered double hydroxide (ZnCr LDH) GO and rGO	Co-precipitation method	Maximum sonophotocatalytic degradation efficiency was achieved in the presence of ZnCr LDH/rGO nanocomposite Higher antibacterial activity of ZnCr LDH/GO compared with ZnCr LDH and ZnCr LDH/rGO against <i>Staphylococcus aureus</i>	Sadeghi Rad et al. (2022)
Metallic	TiO ₂ , diclofenac	Advanced oxidation processes	Heterogeneous photocatalysis involving TiO ₂ -reduced graphene oxide (T-RGO) nanocomposite and activated persulfate-based oxidation was attempted to remove diclofenac	John et al. (2021)

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Bio-Based Porous Materials for Remediation of Pollutants



Shruti Awasthi, Preethi Rajesh, and Naveen Dwivedi

Abstract Globalization and industrialization have increased environmental pollution in soil, air, and water, which has posed a threat globally in recent years; because of this there is a change in climate that has impacted the entire world, and therefore, it is high time that we act proactively to take measures that will help to decrease the level of pollution. Porous materials are in huge demand because they have a lot of potential applications in safeguarding the environment and conservation of energy as they have unique properties: absorption, light, large surface area, low thermal conductivity, and interconnected pores, e.g., graphene. Bio-based porous materials are in huge demand as they have the great potential to impact the development of technology in the near future, e.g., nanotechnology which could be used in various fields for the benefit of society. Bio-based porous materials have a lot of applications in different areas like electrochemistry, catalyst, separation of gas, adsorption, and membranes. Bio-based porous materials have a lot of challenges, especially in the design of the porous material, size, stability, activity, and selectivity of porous material. This chapter discusses the comprehensive overview of bio-based porous materials, their synthesis, and applications in various fields with advantages and disadvantages.

Keywords Globalization · Industrialization · Pollution · Porous material · Environment

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1 Introduction

1.1 Pollution

Pollution is the presence of substances or agents in the environment that have harmful or deleterious effects on living organisms and the natural world (Manisalidis et al. 2020). It is a major problem that affects every aspect of our lives, including the air we breathe, the water we drink, and the food we eat. Pollution is caused by various human activities such as industrialization, transportation, energy production, and agriculture. Pollution is a widespread problem that affects the health of both people and the environment. The adverse effects of pollution can be felt across the globe, and they can have severe and long-lasting impacts on our physical, mental, and social well-being. The consequences of pollution are severe and can range from minor irritation to life-threatening diseases, environmental degradation, and biodiversity loss (Ghorani-Azam et al. 2016).

There are several types of pollution, including air pollution, water pollution, soil pollution, noise pollution, and light pollution. Air pollution is the most common form of pollution and is caused by the release of harmful gases, particulate matter, and other pollutants into the atmosphere. It can cause respiratory problems, heart disease, and other health problems (Lee et al. 2014). Water pollution is caused by the discharge of industrial waste, sewage, and other pollutants into water bodies; it can lead to the contamination of drinking water and harm aquatic life (Chowdhary et al. 2020). Soil pollution is caused by the release of industrial waste, pesticides, and other pollutants into the soil, which can lead to soil degradation and decreased crop yields (Maximillian et al. 2019). Soil pollution can lead to reduced crop yields, soil degradation, and contamination of food sources. It can also harm the natural balance of the earth, leading to decreased soil biodiversity and reduced soil fertility. Noise pollution is caused by excessive noise from sources such as traffic, construction, and loud music, which can cause hearing loss, stress, and other health problems. Noise pollution can disrupt the biosphere and negatively affect wildlife populations (Parris et al. 2009). It can also disrupt communication, interfering with the ability to learn, work, and socialize effectively. Light pollution is caused by the excessive use of artificial light. Light pollution can disrupt sleep patterns and interfere with the natural behavior of animals (Burt et al. 2023). It can also affect the quality of life in urban areas, leading to decreased health and well-being (Chepesiuk 2009). The effects of pollution are widespread and can have severe consequences. In addition to health problems, pollution can also cause environmental degradation, such as deforestation, loss of biodiversity, and climate change (Wigand et al. 2022). Air pollution can cause a range of adverse health effects, including respiratory problems like asthma, bronchitis, and lung cancer. It can also worsen existing heart and lung conditions, leading to increased hospitalizations and premature deaths. Additionally, air pollution can harm the environment by causing acid rain, smog, and ozone depletion. Acid rain can affect agricultural crops, forests, and even bodies of water (Villanyi 2010). Water pollution can lead to the death of aquatic life and make water bodies

unusable for cooking cleaning, bathing, and other activities (Weiner and Matthews 2003). Contaminated water sources can spread diseases, causing illness and death. Harmful chemicals and pollutants can also enter the food chain, disrupting the oceanic environment. Water pollution can also have long-term effects on the quality of water resources, making them unsafe to consume. Soil pollution can lead to decreased crop yields and the loss of valuable agricultural land (Maximillian et al. 2019). Pollution, particularly the release of greenhouse gases into the atmosphere, contributes to climate change, leading to global warming, rising sea levels, and extreme weather events. These changes have significant impacts on living ecosystems and human populations, leading to food and water scarcity and displacement of people, culminating in increased mortality and health risks.

To reduce pollution, various measures can be taken, including the use of cleaner technologies, better waste management practices, and the promotion of sustainable lifestyles. Governments can enact regulations and policies to control pollution, and individuals can take steps to reduce their own environmental footprint, such as reducing their energy consumption, using public transportation, and recycling.

1.2 *Pollutants*

Pollutants are substances that are harmful to the environment and living organisms. These can be natural or human-made, and they can come from a variety of sources, including industry, transportation, agriculture, and household waste (Yadav 2018). Understanding the types and sources of pollutants is essential for developing effective strategies to reduce and prevent pollution. Here are some examples of common pollutants:

1.2.1 **Particulate Matter**

Particulate matter is a type of air pollutant that can come from both natural and human-made sources, such as dust, pollen, and smoke from fires and burning fossil fuels. These tiny particles can cause respiratory problems, heart disease, and cancer (Hamanaka and Mutlu 2018). Particle pollution can come from two different kinds of sources such as primary or secondary. Primary sources cause particle pollution on their own. For example, wood stoves and forest fires are primary sources.

Secondary sources let off gases that can form particles. Power plants and coal fires are examples of secondary sources (Oberschelp et al. 2019). Some other common sources of particle pollution can be either primary or secondary; for example, factories, cars and trucks, and construction sites.

Particle pollution includes:

- PM_{10} : inhalable particles, with diameters that are generally 10 micrometers and smaller

- $PM_{2.5}$: fine inhalable particles, with diameters that are generally 2.5 micrometers and smaller (Goossens and Buck 2012)

1.2.2 Nitrogen Oxides

Nitrogen oxides are a type of air pollutant that comes from the burning of fossil fuels, such as coal and oil, in cars, trucks, and power plants. These emissions contribute to smog and acid rain and can cause respiratory problems (Sharma et al. 2013).

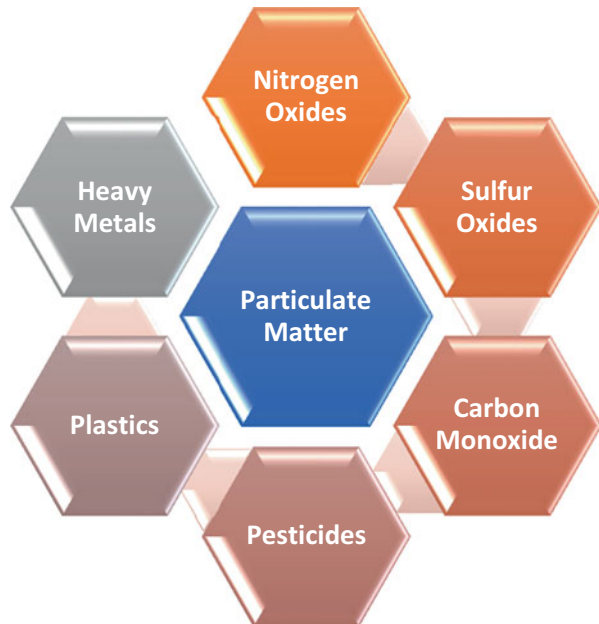
1.2.3 Sulfur Oxides

Sulfur oxides are a type of air pollutant that comes from the burning of fossil fuels, such as coal and oil, in power plants and industrial processes. These emissions contribute to acid rain and can cause respiratory problems (Aydin and İlkiliç 2017) (Fig. 1).

1.2.4 Carbon Monoxide

Carbon monoxide is a type of air pollutant that comes from the incomplete combustion of fossil fuels in cars, trucks, and other transportation vehicles. This gas can

Fig. 1 Particulate matter



be lethal in high concentrations and can cause headaches, nausea, and fatigue (Mohammed et al. 2019).

1.2.5 Pesticides

Pesticides are chemicals that are used to kill pests, such as insects, rodents, and weeds. These substances can contaminate soil, water, and air and can harm human health and the environment (Ozkara et al. 2016).

1.2.6 Plastics

Plastics are human-made materials that are commonly used in packaging and products. These materials can take hundreds of years to break down and can accumulate in the environment, harming wildlife and polluting water sources (Kik et al. 2020).

1.2.7 Heavy Metals

Heavy metals are naturally occurring elements, such as lead, mercury, and cadmium that can be toxic to humans and animals in high concentrations. These metals can come from industrial processes, mining, and waste disposal (Rahman and Singh 2019).

1.2.8 E-Waste

Electronic waste, or e-waste, is a growing problem that can cause environmental and health hazards. E-waste includes discarded electronics, such as computers, cell phones, and televisions, which contain hazardous materials like lead and mercury (Kiddee et al. 2013).

1.2.9 Pharmaceutical Waste

Pharmaceutical waste is a type of pollution that can come from unused or expired medications that are improperly disposed of. These substances can contaminate water sources and harm aquatic life (Ahammad et al. 2022).

1.2.10 Organic Compounds

Organic compounds include chlorofluorocarbon (CFCs), methylene chloride (CH_2Cl_2), trichloro ethylene (C_2HCl_3), vinyl chloride ($\text{C}_2\text{H}_3\text{Cl}$), formaldehyde (CH_2O), carbon tetrachloride (CCl_4), and ethylene oxide ($\text{C}_2\text{H}_4\text{O}$). These are commonly present in refrigerators, aerosol sprays, plastics, and foams. The CFCs interfere with stratospheric ozone layer of the atmosphere allowing UV radiations to penetrate into earth's atmosphere (Lickley et al. 2020). UV radiations can cause skin cancer as well as lethal effects on various life forms on the surface of the water. (Vollmer et al. 2018).

2 Bio-Based Porous Materials

Bio-based porous materials are a group of materials that are derived from natural sources such as plants, animals, and microorganisms. Many common materials, such as wood, paper, and leather, can be referred to as bio-based materials (Udeni Gunathilake et al. 2017). Bio-based materials are recognized as a potentially greener alternative to plastics and petroleum-based products (Vafai 2010). Approaches toward the synthesis of newer bio-based materials to weed out hazardous conventional materials are emerging continuously, and the synthesis of bio-based novel products will scale the world in the years to come (Naser et al. 2021).

2.1 Classification of Bio-Based Materials

Bio-based porous materials can be classified based on their origin, chemical composition, pore size, and morphology. The following are some common classifications of bio-based porous materials:

2.1.1 Origin

Bio-based porous materials can be derived from a variety of natural sources such as wood, plant fibers, agricultural waste, and animal products (Iannace and Park 2015). Depending on the source, the properties of the material can vary widely, including porosity, surface area, and chemical composition.

2.1.2 Chemical Composition

Bio-based porous materials can be classified based on their chemical composition, such as cellulose, lignin, chitin, and protein-based materials (Stevens 2013). These materials have unique properties that make them suitable for different applications. For example, cellulose-based materials (Hossen et al. 2020) have high porosity and surface area, making them useful for water filtration and adsorption applications.

2.1.3 Pore Size

Bio-based porous materials can also be classified based on their pore size, such as mesoporous, microporous, and macroporous materials. These classifications are based on the diameter of the pores, with mesoporous materials having pore sizes between 2 and 50 nm, microporous materials (Keplinger et al. 2016) having pore sizes below 2 nm, and macroporous (Valencia et al. 2019) materials having pore sizes above 50 nm. These materials can be used for different applications depending on the size of the pollutant to be removed.

2.1.4 Morphology

Bio-based porous materials can be classified based on their morphology, such as fibrous, granular, and monolithic materials (Prithivirajan et al. 2015). Fibrous materials are made up of individual fibers, while granular materials are made up of small particles, and monolithic materials are continuous structures. Each morphology has its unique advantages and disadvantages for different applications.

2.2 Classification of Biomaterial Depending on Source and Application

Bio-based materials are materials that are derived from renewable resources such as plants, animals, and microorganisms (Raquez et al. 2010). These materials have been gaining popularity in recent years due to their sustainability and low carbon footprint. They have a wide range of applications including packaging, construction, textiles, and electronics (Zia et al. 2016).

2.2.1 Plant-Based Materials

Plant-based materials are the most commonly used bio-based materials. These materials are derived from various parts of plants such as leaves, stems, roots, and

fruits (Wool and Sun 2011). Examples of plant-based materials include wood, bamboo, cotton, jute, sisal, flax, hemp, and kenaf. Plant-based materials are renewable, biodegradable, and have a low carbon footprint. They are commonly used in the construction industry for insulation, flooring, and roofing. They are also used in the textile industry for making clothing and accessories.

Plant-based materials are derived from plant sources such as wood, bamboo, cotton, and flax. These materials have been used for centuries for various purposes such as building materials, clothing, and paper (Cywar et al. 2022). Today, plant-based materials are being used in the production of bioplastics, biofuels, and other sustainable products. Some of the commonly used plant-based materials are discussed as follows:

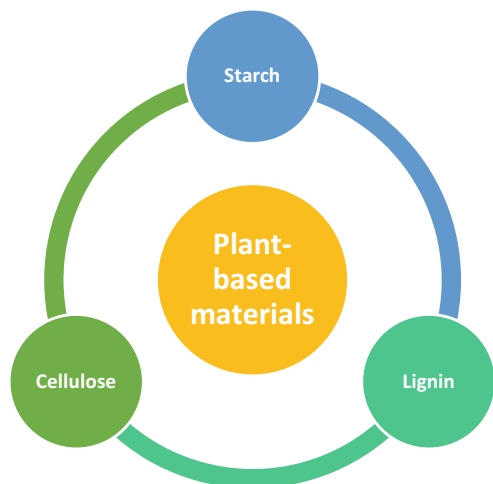
Cellulose

Cellulose is the most abundant biopolymer on earth and is found in the cell walls of plants. It is commonly used in the production of paper and textiles (Collinson and Thielemans 2010) (Fig. 2).

Starch

Starch is a carbohydrate found in plants, and it can be extracted from sources such as corn, wheat, and potatoes. Starch is used in the production of bioplastics and biofuels (Shafqat et al. 2021).

Fig. 2 Plant-based materials



Lignin

Lignin is a complex polymer found in the cell walls of plants, and it is the second most abundant biopolymer on earth after cellulose. Lignin is used in the production of biofuels and as a reinforcing agent in bioplastics (Mariana et al. 2021).

2.2.2 Animal-Based Materials

Animal-based materials are derived from animal sources such as skin, hair, wool, and silk. These materials have been used for centuries for clothing, accessories, and upholstery. Animal-based materials are not renewable and have a high carbon footprint (Lutz et al. 2022). However, some animal-based materials such as wool and silk are biodegradable. Animal-based materials are commonly used in the fashion and luxury industries.

Animal-based materials are derived from animal sources such as wool, silk, leather, and bone (Tyagi et al. 2023). These materials have been used for centuries for clothing, shelter, and tools. Today, animal-based materials are being used in the production of biomedical implants, bioplastics, and other sustainable products. Some of the commonly used animal-based materials are discussed as follows:

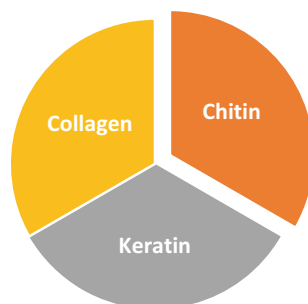
Collagen

Collagen is a protein found in animal tissues such as skin, bone, and cartilage. It is used in the production of biomedical implants, wound dressings, and cosmetics (Onwubu et al. 2023) (Fig. 3).

Chitin

Chitin is a polysaccharide found in the exoskeletons of arthropods such as insects and crustaceans. It is used in the production of bioplastics and wound dressings (Kadam and Barbhai 2022).

Fig. 3 Animal-based materials



Keratin

Keratin is a protein found in animal hair, nails, and feathers. It is used in the production of bioplastics, textiles, and cosmetics (Kadam and Barbhai 2022).

2.2.3 Microbial-Based Materials

Microbial-based materials are derived from microorganisms such as bacteria, fungi, and algae. These materials have unique properties such as high strength, flexibility, and biodegradability. Microbial-based materials have a low carbon footprint and can be grown using renewable resources. They are commonly used in the packaging industry for making biodegradable packaging materials. Microbial-based materials are derived from microorganisms such as bacteria, fungi, and algae (Cerimi et al. 2019). These materials have gained significant attention in recent years due to their potential to produce sustainable products such as bioplastics, biofuels, and biodegradable packaging. Some of the commonly used microbial-based materials are discussed as follows:

Polyhydroxyalkanoates (PHAs)

PHAs are biopolymers produced by many gram-positive and gram-negative bacteria and are used in the production of bioplastics (Philip et al. 2007).

Mycelium

Mycelium is the vegetative part of a fungus and can be used to produce sustainable materials such as bioplastics and building materials (Grasso et al. 2019).

Algae

Algae are photosynthetic microorganisms that can be used to produce biofuels and bioplastics (Grasso et al. 2019) (Fig. 4).

2.2.4 Synthetic Biology-Based Materials

Synthetic biology-based materials are materials produced through genetic engineering and synthetic biology techniques (Burgos-Morales et al. 2021). These materials have the potential to revolutionize the production of sustainable materials by enabling the production of new materials with specific properties. Some of the commonly used synthetic biology-based materials are:

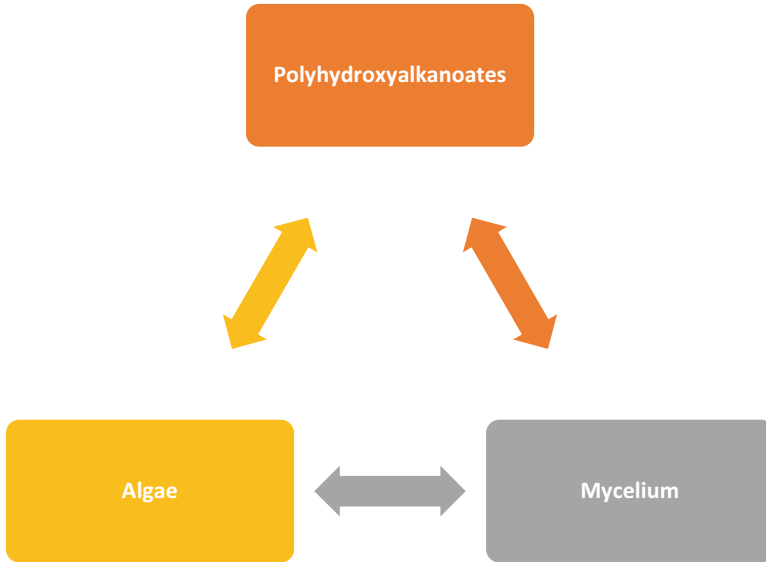


Fig. 4 Microbial-based materials

Spider Silk

Spider silk is a strong and lightweight protein fiber produced by spiders. Synthetic biology techniques have been used to produce spider silk in bacteria and other organisms (Kluge et al. 2008).

Bioluminescent Materials

Bioluminescent materials are those that can emit light through biological processes. These materials have potential applications in lighting and biomedical imaging (Burgos-Morales et al. 2021).

Bio-Based Sensors

Bio-based sensors are sensors that use biological components such as enzymes or cells to detect specific substances. These sensors have potential applications in medical diagnostics and environmental monitoring (Burgos-Morales et al. 2021) (Fig. 5).

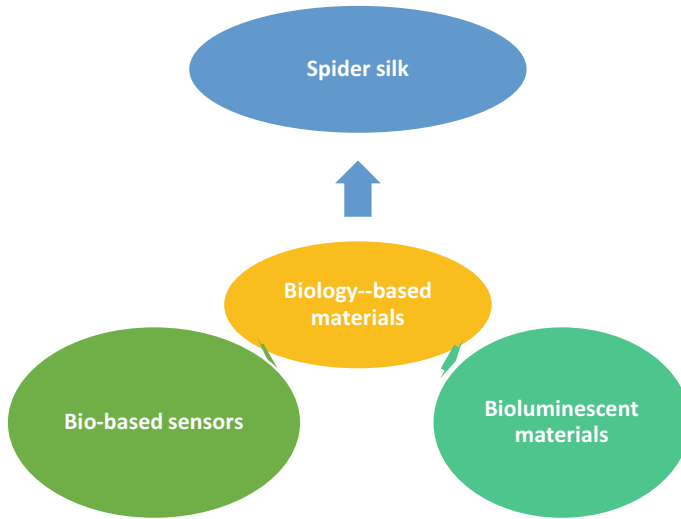


Fig. 5 Bio-based materials

2.2.5 Hybrid Bio-Based Materials

Hybrid bio-based materials are materials that combine two or more bio-based materials or bio-based and non-bio-based materials to create new materials with unique properties (Cai et al. 2022). Some of the commonly used hybrid bio-based materials are:

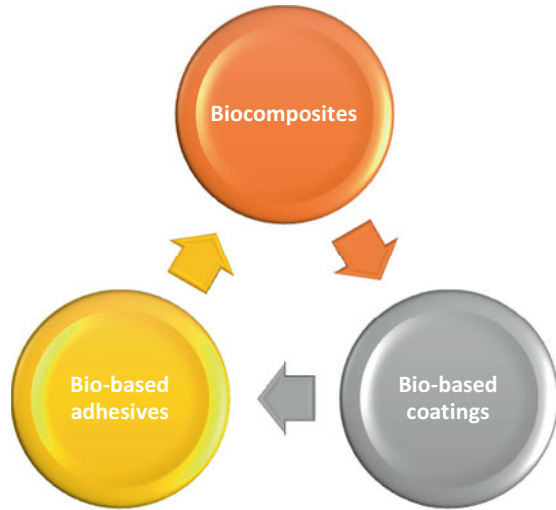
Biocomposites

Biocomposites are materials that combine a natural fiber such as flax or hemp with a biopolymer such as PLA to create a strong and lightweight material. Biocomposites have unique properties such as high strength, flexibility, and low weight. Examples of biocomposites include wood-plastic composites, natural fiber-reinforced composites, and biodegradable polymer composites (Nagalakshmaiah et al. 2019). Biocomposites are commonly used in the construction industry for making structural components. Biocomposites have potential applications in the automotive and construction industries (Fig. 6).

Bio-Based Coatings

Bio-based coatings are coatings that use bio-based materials such as oils, resins, and waxes as the main components. These coatings have potential applications in the wood and furniture industries (Lutz et al. 2022).

Fig. 6 Hybrid bio-based materials



Bio-Based Adhesives

Bio-based adhesives are adhesives that use bio-based materials such as starch, cellulose, and lignin as the main components. These adhesives have potential applications in the wood and packaging industries (Lutz et al. 2022).

2.3 Features of Biomaterials

Bio-based porous materials have a wide range of physical properties depending on their chemical composition, morphology, and processing techniques. Here are some common physical properties of bio-based porous materials:

2.3.1 Porosity

The porosity of a biomaterial refers to the extent to which it contains voids or empty spaces. Porosity can influence the material’s ability to support cell growth and tissue regeneration by providing space for cells to proliferate and form new tissue (Hernandez and Woodrow 2022). Porosity can also affect the material’s mechanical properties, such as its stiffness and strength. Bio-based porous materials have high porosity due to the presence of voids or pores within their structure. The porosity of these materials can range from a few percent to over 90%, depending on the type of material and the processing technique used.

2.3.2 Surface Area and Topography

The surface topography of a biomaterial refers to the texture and roughness of its surface. Surface topography can influence cell adhesion, proliferation, and differentiation, as well as the immune response to the material. Certain surface topographies, such as micro- and nano-topographies, have been shown to promote cell growth and tissue regeneration (Murthy 2011). Bio-based porous materials have a large surface area due to the presence of pores within their structure. The surface area of these materials can range from a few square meters per gram to over 1000 square meters per gram, depending on the type of material and the processing technique used. The surface area of a biomaterial can influence its interactions with cells and tissues, as well as its ability to absorb and release drugs or other molecules (Murthy 2011). Materials with higher surface areas may be more effective for drug delivery applications.

2.3.3 Pore Size and Shape

Bio-based porous materials can have different pore sizes and pore size distributions depending on their chemical composition and processing technique. The pore sizes can range from a few nanometers to several hundred micrometers. The size and shape of a biomaterial can influence its interactions with cells and tissues. For example, smaller particles may be more effective for drug delivery applications, while larger particles may be more effective for tissue engineering applications (Lemons and Lucas 1986).

2.3.4 Mechanical Properties

Bio-based porous materials can have a range of mechanical properties, including stiffness, strength, and elasticity. The mechanical properties of these materials can be tailored by adjusting the chemical composition and processing techniques (Meyers et al. 2008).

Elasticity

The elasticity of a biomaterial refers to its ability to deform and return to its original shape in response to external forces. Elasticity can influence the material's ability to support tissue growth and regeneration, as well as its interactions with cells and tissues (Shymanskyi and Sokolovskyy 2021).

Density

The density of a biomaterial can influence its mechanical properties, such as its stiffness and strength. Materials with higher densities may be more suitable for load-bearing applications, while materials with lower densities may be more suitable for tissue engineering applications (Fig. 7).

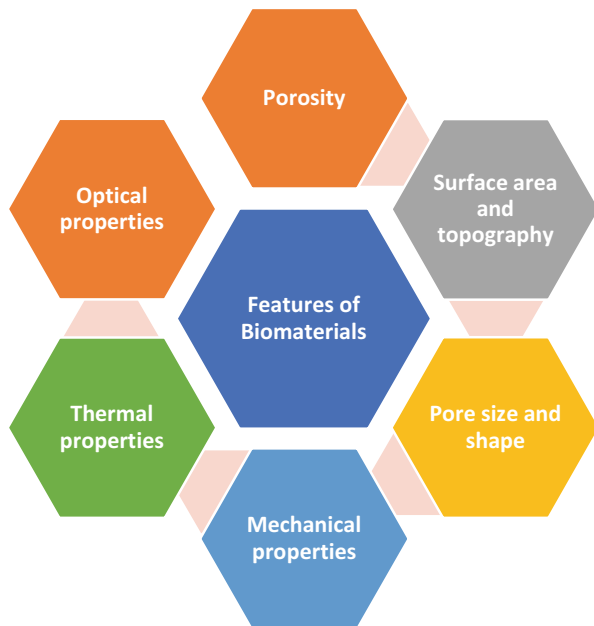
2.3.5 Thermal Properties

Bio-based porous materials can have different thermal properties depending on their chemical composition and processing technique. These materials can be thermally stable, and some of them can withstand high temperatures. Some biomaterials possess electrical conductivity, which can be useful for applications such as neural implants or cardiac tissue engineering. Electrical conductivity can influence cellular behavior and promote tissue regeneration (Abraham et al. 2008).

2.3.6 Optical Properties

Bio-based porous materials can have different optical properties, such as color and transparency, depending on their chemical composition and processing technique. The optical properties of biomaterials can influence their interactions with light and

Fig. 7 Features of biomaterials



their suitability for certain biomedical applications (Lu et al. 2020). These optical properties include:

Transparency

Biomaterials can be transparent, allowing light to pass through with minimal scattering or absorption. This property is important for applications such as contact lenses or artificial corneas, where the biomaterial must be optically clear to function properly (Lu et al. 2020).

Opacity

Biomaterials can also be opaque, blocking, or scattering light. This property can be useful for applications such as dental restorations or bone replacements, where the biomaterial must be visible and match the color of surrounding tissues (Lu et al. 2020) (Fig. 8).

Refractive Index

The refractive index of a biomaterial is a measure of how much the material bends or refracts light as it passes through it. This property is important for applications such as intraocular lenses or contact lenses, where the refractive index of the biomaterial must match that of the surrounding tissues to avoid optical distortion (Tadepalli et al. 2017).

Fluorescence

Some biomaterials exhibit fluorescence, meaning they emit light when excited by an external light source (Tadepalli et al. 2017). This property can be useful for applications such as imaging or biosensing, where the biomaterial can be labeled with a fluorescent dye to visualize or detect specific cells or molecules.

Bioluminescence

Bioluminescence is a special case of fluorescence in which the biomaterial itself emits light due to a biochemical reaction (Tadepalli et al. 2017). This property is found in certain bioluminescent proteins and can be useful for applications such as in vivo imaging or monitoring of biological processes.

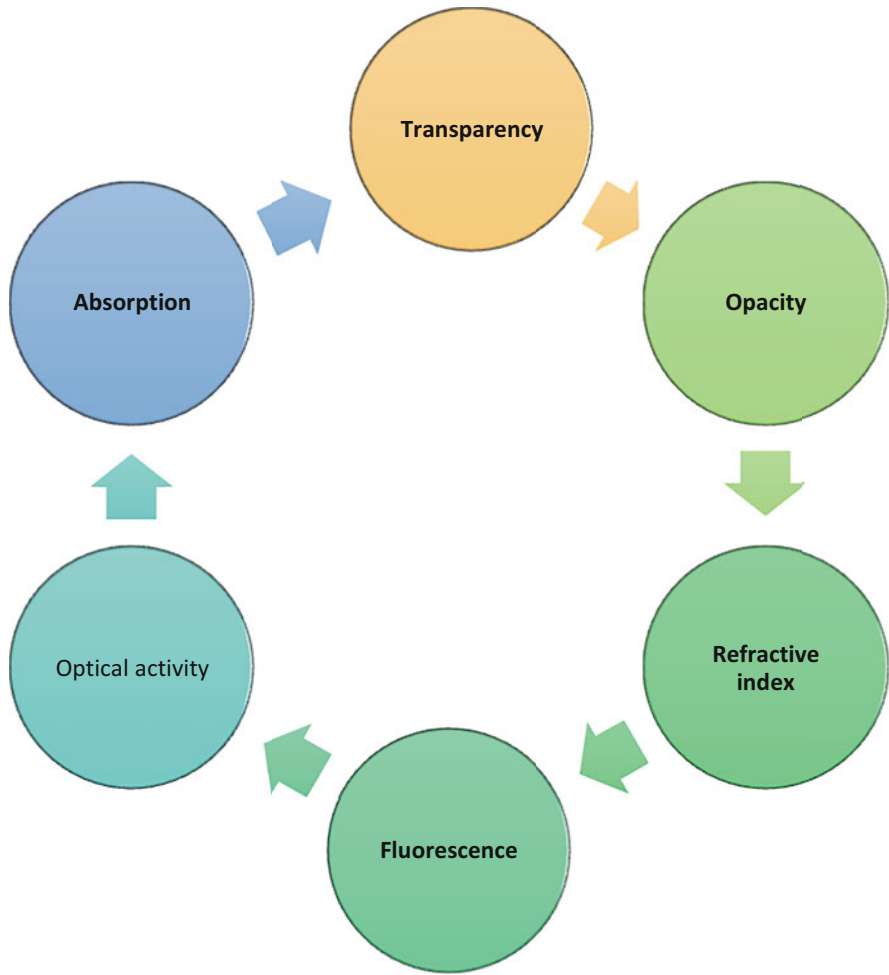


Fig. 8 Optical properties

Optical Activity

Some biomaterials exhibit optical activity, meaning they rotate the plane of polarization of light passing through them. This property is important for applications such as chiral separation or optical sensing (Lawrence et al. 2008).

Absorption

Biomaterials can absorb light, which can be used for applications such as photo-thermal therapy or photodynamic therapy, where the absorbed light is converted to

heat or reactive oxygen species to selectively kill cancer cells or pathogens (Lawrence et al. 2008).

2.4 Application of Biomaterial

Biomaterials have a wide range of applications in various fields, including medicine, dentistry, tissue engineering, and drug delivery (Bikramjit Basu et al. 2010). Here are some examples of how biomaterials are used in these fields:

2.4.1 Medical Implants

Biomaterials have been used extensively in the field of medical implants to replace or repair damaged tissues or organs. The biocompatibility and mechanical properties of biomaterials make them ideal for use as implants, as they can withstand the stresses and strains of the body and integrate with surrounding tissues (Abraham and Venkatesan 2023). Here are some examples of how biomaterials are used in medical implants:

Orthopedic Implants

Biomaterials such as titanium, cobalt-chromium alloys, and polyethylene are commonly used in orthopedic implants such as hip and knee replacements. These materials are strong, corrosion-resistant, and biocompatible, and can withstand the mechanical stresses of weight-bearing joints (Walker et al. 2014).

Cardiovascular Implants

Biomaterials are used in cardiovascular implants such as stents, heart valves, and pacemaker leads. Materials such as stainless steel, nitinol, and biocompatible polymers are used to make these devices. These materials have good mechanical properties, can be easily fabricated into complex shapes, and are compatible with the body's fluids and tissues (Patel and Gohil 2012).

Dental Implants

Biomaterials such as titanium and zirconia are commonly used in dental implants to replace missing teeth. These materials are biocompatible, have good mechanical properties, and can integrate with the surrounding bone tissue (Patel and Gohil 2012) (Fig. 9).

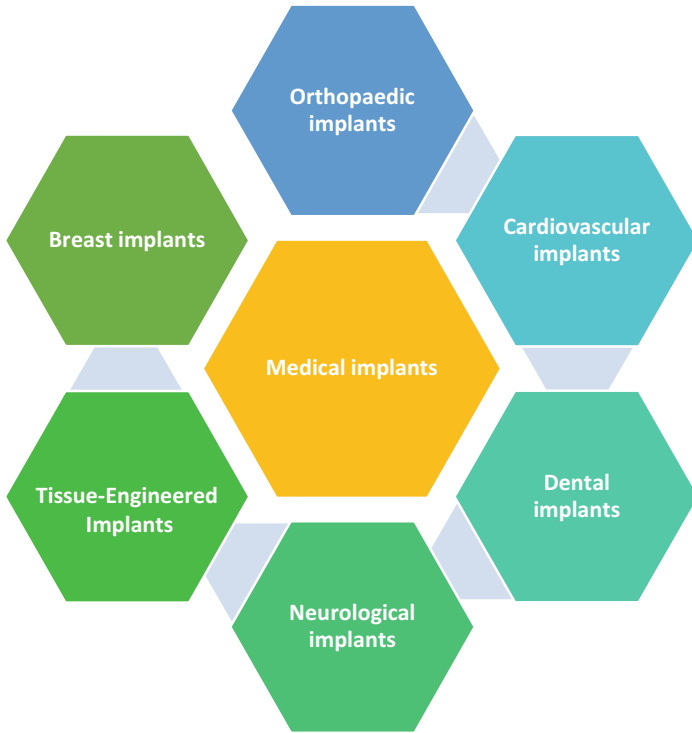


Fig. 9 Medical implants

Neurological Implants

Biomaterials such as platinum, iridium, and silicone are used in neurological implants such as cochlear implants and deep brain stimulators. These materials have good electrical properties and can interface with the body’s tissues without causing damage (Biswal et al. 2020).

Breast Implants

Biomaterials such as silicone and saline are used in breast implants for cosmetic and reconstructive purposes. These materials are biocompatible, have good mechanical properties, and can be easily shaped to the desired form (Biswal et al. 2020).

Tissue-Engineered Implants

Biomaterials are also used as scaffolds for growing new tissues or organs in vitro or in vivo. These scaffolds provide a framework for the cells to grow and differentiate

into functional tissues. Examples of tissue-engineered products include skin grafts, cartilage implants, and bone substitutes (Biswal et al. 2020).

2.4.2 Tissue Engineering

Biomaterials have revolutionized the field of tissue engineering by providing a platform for the growth and regeneration of functional tissues (Keane and Badylak 2014). Tissue engineering involves the use of cells, biomaterials, and biochemical signals to create functional tissues or organs *in vitro* or *in vivo*. Here are some examples of how biomaterials are used in tissue engineering:

Scaffold Materials

Biomaterials such as natural polymers (e.g., collagen, fibrin, and hyaluronic acid) and synthetic polymers (e.g., poly (lactic-co-glycolic acid) and polyethylene glycol) are commonly used as scaffold materials in tissue engineering. These materials provide a three-dimensional structure for the cells to grow and differentiate into functional tissues (Keane and Badylak 2014).

Growth Factor Delivery

Biomaterials can be used to deliver growth factors to the cells to promote tissue regeneration. For example, biodegradable polymers such as poly (lactic acid) and poly (glycolic acid) can be used to encapsulate growth factors and release them over time to promote tissue growth (Babensee et al. 2000) (Fig. 10).

Cell Encapsulation

Biomaterials can be used to encapsulate cells and protect them from the immune system while allowing for the exchange of nutrients and waste products. Hydrogels, which are cross-linked polymers that can absorb large amounts of water, are commonly used for cell encapsulation.

Tissue-Specific Biomaterials

Biomaterials can be designed to mimic the properties of specific tissues, such as the extracellular matrix (ECM). For example, decellularized ECM from tissues such as the heart, liver, and lung can be used as a scaffold material to promote tissue regeneration (Chan and Leong 2008).

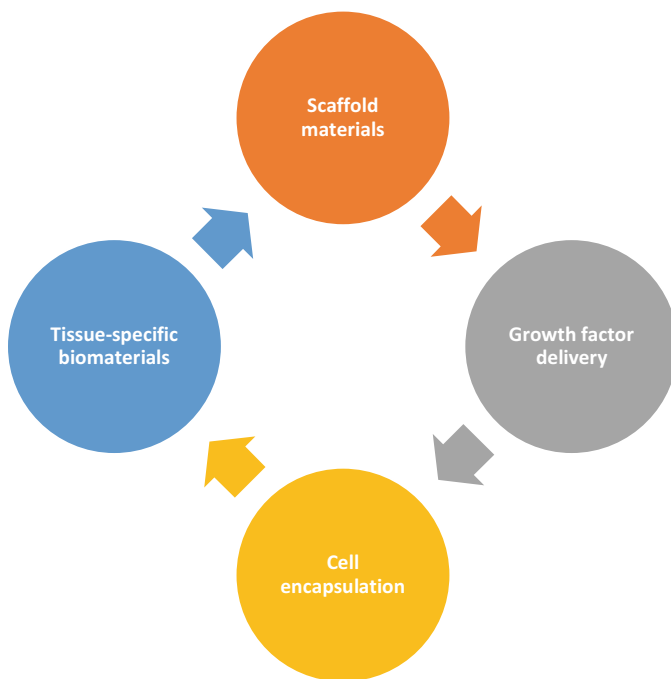


Fig. 10 Tissue engineering

Biomaterials can be used in 3D printing to create complex structures with precise control over shape, size, and mechanical properties. This technology allows for the creation of patient-specific implants and tissues. Biomaterials can be used in the development of organ-on-a-chip technology, which involves the use of microfabrication techniques to create microfluidic devices that mimic the structure and function of organs. These devices can be used for drug screening and disease modeling (Chan and Leong 2008).

2.4.3 Drug Delivery

Biomaterials have been widely used in the field of drug delivery to improve the efficacy and safety of drugs. Biomaterials are used as carriers for delivering drugs to specific sites in the body. The biocompatibility and biodegradability of biomaterials make them ideal for use in drug delivery systems, where they can protect drugs from degradation and deliver them to specific sites in the body (Prestwich and Luo 2001). The biomaterials can protect the drugs from degradation or elimination, control their release, and target specific tissues or cells. Examples of drug delivery systems include nanoparticles, microparticles, and hydrogels. Here are some examples of how biomaterials are used in drug delivery:

Polymeric Drug Delivery Systems

Biodegradable polymers such as poly (lactic-co-glycolic acid) (PLGA), poly (caprolactone) (PCL), and chitosan are commonly used in polymeric drug delivery systems. These polymers can be fabricated into various forms such as nanoparticles, microparticles, and hydrogels. They can encapsulate drugs and release them in a controlled manner, which improves drug efficacy and reduces toxicity (Prestwich and Luo 2001).

Lipid-Based Drug Delivery Systems

Lipid-based drug delivery systems such as liposomes, solid lipid nanoparticles (SLNs), and nanoemulsions are commonly used to deliver hydrophobic drugs. These systems can improve drug solubility and bioavailability, as well as protect the drugs from degradation and clearance by the body (Filipczak et al. 2021) (Fig. 11).

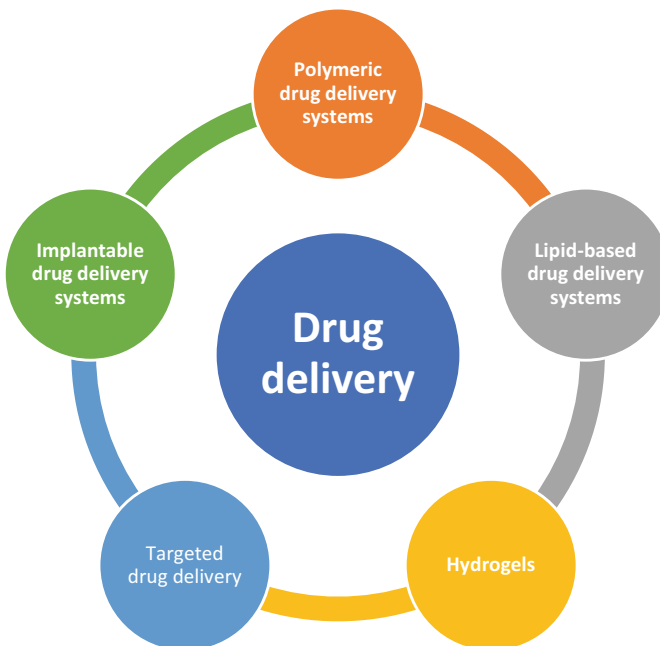


Fig. 11 Drug delivery

Hydrogels

Hydrogels are cross-linked polymer networks that can absorb large amounts of water. They can be used to deliver drugs to specific sites in the body, such as wounds or tumors. Hydrogels can also provide sustained drug release and improve drug efficacy.

Targeted Drug Delivery

Biomaterials can be functionalized by targeting moieties such as antibodies or peptides to deliver drugs to specific cells or tissues. This approach reduces off-target effects and improves drug efficacy (Prestwich and Luo 2001).

Implantable Drug Delivery Systems

Biomaterials can be used to create implantable drug delivery systems, such as drug-eluting stents or implants. These systems can provide sustained drug release and reduce the need for frequent dosing.

2.4.4 Wound Healing

Biomaterials are used as dressings or scaffolds to promote wound healing and tissue regeneration. The biomaterials can provide a moist and sterile environment for the wound, control the release of growth factors or cytokines, and promote angiogenesis or cell migration. Biomaterial-based dressings, such as hydrogels, films, and foams, are commonly used to cover wounds and promote healing. These dressings can protect the wound from infection, provide a moist environment for wound healing, and promote cell proliferation and migration. Biomaterials such as collagen, fibrin, and hyaluronic acid can be used as scaffold materials to support tissue regeneration and guide cell growth. These scaffolds can be designed to mimic the extracellular matrix (ECM) of different tissues, providing a platform for cells to grow and differentiate (Prestwich and Luo 2001). Biodegradable polymers such as PLGA and PCL can be used to encapsulate growth factors and release them over time to promote tissue growth. Mesenchymal stem cells (MSCs) can be encapsulated in hydrogels and applied to the wound site to promote wound healing. Chitosan and collagen can be applied to the wound site to promote clotting and prevent excessive bleeding.

2.4.5 Biosensors

Biosensors are analytical devices that combine a biological sensing element with a transducer to detect and measure specific analytes. Biomaterials are used as sensing elements for detecting biological molecules or events. Hence biomaterials have been widely used in biosensors as they can provide a biocompatible and stable matrix for the immobilization of biological sensing elements (Fenton et al. 2018). The biomaterials can interact with the target analyte or signal and generate a detectable response, such as fluorescence or electrochemical signal. Examples of biosensors include glucose sensors, DNA sensors, and immunoassays. Here are some examples of how biomaterials are used in biosensors:

Enzyme-Based Biosensors

Enzymes are commonly used as biological sensing elements in biosensors. Biomaterials such as chitosan, alginate, and polyvinyl alcohol (PVA) can be used as immobilization matrices for enzymes. These biomaterials can protect the enzymes from denaturation and improve their stability (Pérez et al. 2019).

Antibody-Based Biosensors

Antibodies can be used as biological sensing elements in biosensors for the detection of specific antigens. Biomaterials such as polymers and hydrogels can be used as matrices for antibody immobilization. These biomaterials can provide a stable and biocompatible environment for the antibodies, improving their sensitivity and specificity (Fig. 12).

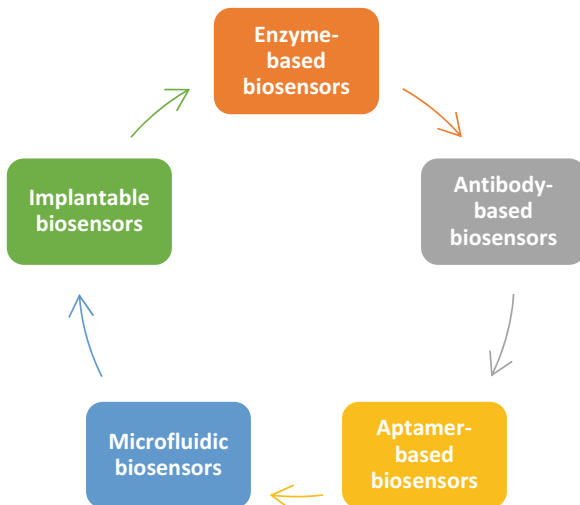
Aptamer-Based Biosensors

Aptamers are synthetic oligonucleotides that can bind to specific targets with high affinity and specificity. Biomaterials such as graphene oxide and gold nanoparticles can be used as immobilization matrices for aptamers. These biomaterials can improve the stability and sensitivity of aptamer-based biosensors (Shin et al. 2016).

Microfluidic Biosensors

Microfluidic biosensors use small channels and chambers to analyze small volumes of samples. Biomaterials such as PDMS (polydimethylsiloxane) and SU-8 can be used to fabricate microfluidic channels and chambers. These biomaterials can

Fig. 12 Biomaterials used in biosensors



provide a biocompatible and stable platform for the immobilization of biological sensing elements (Shin et al. 2016).

Implantable Biosensors

Biomaterials can be used to create implantable biosensors for continuous monitoring of analytes in the body. For example, glucose biosensors have been developed using biomaterials such as PLGA and PVA for the immobilization of glucose oxidase. These biosensors can be implanted in the body to monitor glucose levels in real time (Gray et al. 2018).

2.4.6 Medical Adhesives

Medical adhesives are materials used to seal or bond tissues during surgical procedures, in wound closure, or in the treatment of various medical conditions. Biomaterials are used as adhesives or sealants to close surgical incisions, repair tissues, or seal leaks. The biomaterials can adhere to the tissue surface, form a strong and flexible bond, and biodegrade or resorb over time. Examples of medical adhesives include fibrin glue, cyanoacrylates, and chitosan-based adhesives. Biomaterials have been widely used in the development of medical adhesives due to their biocompatibility and ability to adhere to biological tissues (Brown and Barker 2014). The following are some examples of how biomaterials are used in medical adhesives:

Fibrin-Based Adhesives

Fibrin is a natural protein found in the blood that plays a critical role in blood clotting. Fibrin-based adhesives use fibrinogen and thrombin to form a fibrin clot that can seal tissues and promote wound healing. These adhesives are biocompatible and biodegradable, making them an ideal choice for medical applications (Brown and Barker 2014).

Synthetic Polymer-Based Adhesives

Synthetic polymers such as cyanoacrylates and polyurethanes have been used to develop medical adhesives. These polymers can be formulated to have specific properties such as biocompatibility, biodegradability, and adhesive strength (Saha et al. 2020).

Protein-Based Adhesives

Proteins such as elastin, collagen, and gelatin have been used to develop medical adhesives. These proteins can be modified to improve their adhesive properties and biocompatibility. For example, elastin-based adhesives have been developed that can bond to tissues under wet conditions (Sun et al. 2020a, b) (Fig. 13).

Chitosan-Based Adhesives

Chitosan is a natural polymer derived from chitin, which is found in the exoskeletons of crustaceans. Chitosan-based adhesives have been developed that can adhere to biological tissues and promote wound healing. These adhesives are biocompatible and biodegradable, making them an ideal choice for medical applications (Petroni et al. 2023).

Hydrogel-Based Adhesives

Hydrogels are water-swollen polymer networks that can be used as adhesives. These adhesives can be formulated to have specific properties such as biocompatibility, adhesive strength, and biodegradability. For example, hydrogel-based adhesives have been developed that can bond to tissues under wet conditions (Zhang et al. 2021).

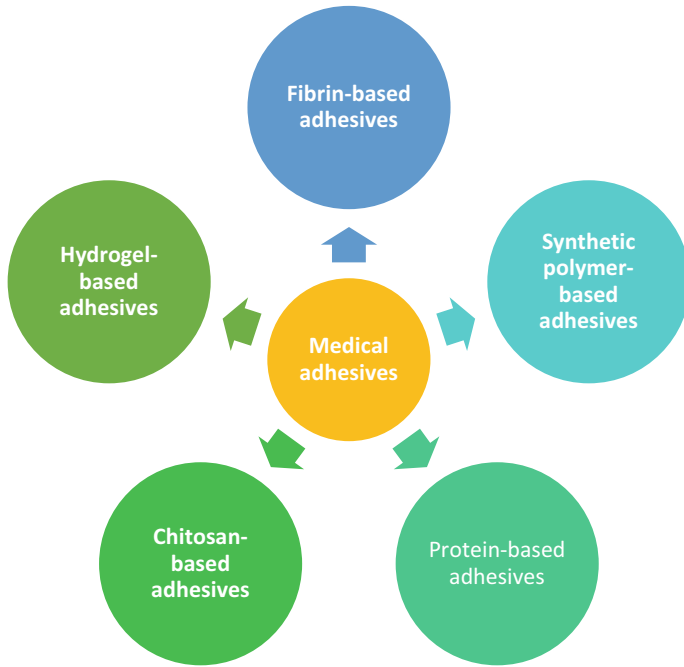


Fig. 13 Medical adhesives

2.4.7 Diagnostic Imaging

Biomaterials are used as contrast agents or imaging probes for various diagnostic imaging modalities, such as magnetic resonance imaging (MRI), computed tomography (CT), or ultrasound. The biomaterials can enhance the contrast between different tissues or cells, improve the sensitivity and specificity of the imaging, and target specific tissues or cells. Examples of imaging agents include gadolinium-based contrast agents, iron oxide nanoparticles, and micro-bubbles (Shi et al. 2020).

Contrast Agents

Biomaterials can be used as contrast agents to improve the visibility of tissues and organs in CT, MRI, and ultrasound imaging. Contrast agents are typically made of heavy metals or other materials that interact with the imaging equipment to produce a contrast effect (Karfeld Sulzer et al. 2011). For example, iodinated contrast agents are commonly used in CT imaging, while gadolinium-based contrast agents are used in MRI imaging.

Targeted Imaging Agents

Biomaterials can be used to develop targeted imaging agents that selectively bind to specific molecules or cells in the body. These agents can be used to detect specific diseases or monitor the effectiveness of therapies. For example, nanoparticles can be engineered to target cancer cells and provide information about the location and extent of the disease (Peng et al. 2017) (Fig. 14).

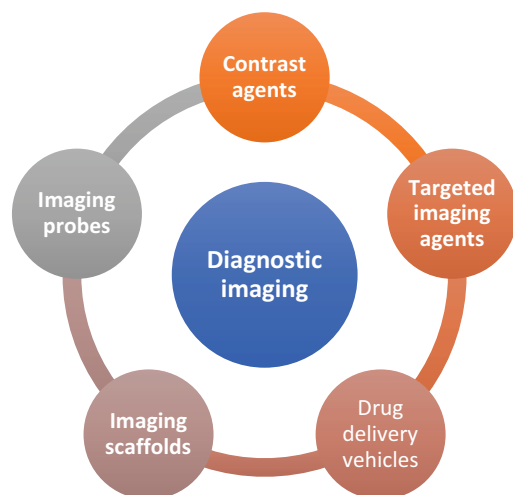
Drug Delivery Vehicles

Biomaterials can be used as drug delivery vehicles to target specific tissues or organs in the body. These vehicles can be designed to release drugs in response to specific stimuli, such as changes in pH or temperature. They can also be used to deliver contrast agents or other imaging agents directly to the site of interest. For example, liposomes are often used as drug delivery vehicles in cancer imaging and therapy (Felice et al. 2014).

Imaging Scaffolds

Biomaterials can be used to develop scaffolds that mimic the extracellular matrix of tissues or organs. These scaffolds can be used to support cell growth and development, and they can also be used as imaging targets in MRI and CT imaging. For example, magnetic nanoparticles can be incorporated into scaffolds to provide contrast in MRI imaging (Peng et al. 2017).

Fig. 14 Diagnostic imaging



Imaging Probes

Biomaterials can be used to develop imaging probes that can detect specific molecules or cells in the body. These probes can be used to diagnose diseases or monitor the effectiveness of therapies. For example, fluorescent probes can be used to detect cancer cells in vivo (Pinaud et al. 2006).

(a) Energy storage

Bio-based porous materials have been explored for energy storage applications such as supercapacitors and batteries. These materials can store and release energy efficiently due to their high surface area and porosity.

(b) Gas separation

Bio-based porous materials have been used for gas separation applications such as carbon dioxide capture and natural gas purification. These materials can selectively adsorb gases based on their molecular size and affinity (Pinaud et al. 2006) (Fig. 15).

(c) Food packaging

Bio-based porous materials have been used for food packaging applications as an alternative to synthetic materials. These materials can provide a barrier to oxygen and moisture, preventing spoilage and extending the shelf life of food.

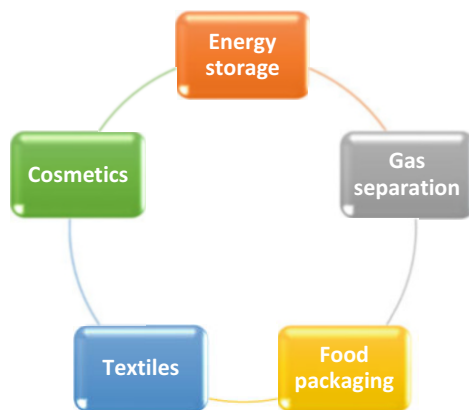
(d) Textiles

Bio-based porous materials have been used for textile applications such as clothing and filters. These materials can provide breathability and moisture-wicking properties in clothing and can remove pollutants and odors from the air in filters (Pinaud et al. 2006).

(e) Cosmetics

Bio-based porous materials have been used in cosmetics such as facial masks and exfoliators. These materials can provide gentle exfoliation and remove impurities from the skin.

Fig. 15 Energy storage



2.5 *Bio-Based Material for Bioremediation*

Bio-based porous materials have been gaining increasing attention as a potential solution for pollution control due to their eco-friendly and sustainable nature. These materials are made from renewable resources such as plant fibers, and they have unique characteristics that make them effective for removing pollutants from the environment. Biomaterials have proven to be effective in controlling pollution in different areas such as air, water, and soil (Tripathi et al. 2022).

2.5.1 Air Pollution Control

Bio-based porous materials, such as activated carbon, can be used to control air pollution by adsorbing and removing pollutants such as volatile organic compounds (VOCs), nitrogen oxides, and sulfur oxides from the air. These materials have a high surface area and a large number of pores, which makes them ideal for capturing and removing pollutants (Amulya et al. 2016).

2.5.2 Water Pollution Control

Bio-based porous materials, such as chitosan, have been found to be effective in controlling water pollution. Chitosan is derived from the shells of crustaceans, and it has been shown to be effective in removing heavy metals, dyes, and other pollutants from wastewater. It works by forming complexes with the pollutants, which can then be easily removed through filtration (Wu et al. 2022). Bio-based porous materials can be used in water treatment applications to remove pollutants such as heavy metals, organic compounds, and nutrients. The high surface area and porous structure of these materials provide a large number of active sites for adsorption and chemical reactions. For example, activated carbon made from coconut shells has been used to remove arsenic from contaminated water.

2.5.3 Soil Remediation

Bio-based porous materials can also be used for soil remediation applications to remove pollutants such as heavy metals, organic compounds, and pesticides. The high surface area and porous structure of these materials provide a large number of active sites for adsorption and chemical reactions. For example, biochar made from agricultural waste has been used to remediate contaminated soils and improve soil fertility (Tabasso et al. 2020).

2.5.4 Waste Management

Bio-based porous materials can also be used for waste management applications to remove pollutants from wastewater, landfill leachate, and other waste streams. The porous structure of these materials can provide a large surface area for adsorption, while the natural fibers can provide microbial activity and other chemical reactions. For example, biochar made from sewage sludge has been used to remove heavy metals from landfill leachate (Wojnowska-Baryła et al. 2020).

A few methods of utilization of biomaterial in the bioremediation process are as follows:

Bioreactors

Bioreactors are devices that use biological organisms to break down pollutants in the air. Biomaterials can be used as the support matrix providing a stable environment for microorganisms to grow and function. For example, bioreactors using algae and bacteria have been developed to remove pollutants such as carbon dioxide, nitrogen oxides, and sulfur dioxide from the air (Pachaiappan et al. 2022).

Bioreactors can also be used to remove pollutants from water. Biomaterials can be used as the support matrix for microorganisms, such as bacteria and algae, which can break down pollutants in the water. Bioreactors can be used to remove pollutants such as nitrogen and phosphorus from agricultural runoff, municipal wastewater, and industrial wastewater.

Biofilters

These are systems that use biological organisms to filter pollutants from water. Biomaterials can be used as the filter media in these systems, providing a large surface area for the organisms to attach and grow. Biofilters can be used to remove pollutants such as ammonia, nitrate, and organic matter from wastewater (Pachaiappan et al. 2022).

Biofilters use living organisms to filter pollutants from the air. Biomaterials can be used as the filter media in these systems, providing a large surface area for the organisms to attach and grow. Biofilters can be used to remove pollutants such as volatile organic compounds (VOCs), ammonia, and hydrogen sulfide from the air (Fig. 16).

Adsorbents

Biomaterials can also be used as adsorbents to remove pollutants from the air. Adsorbents are materials that attract and hold onto pollutants on their surface. For

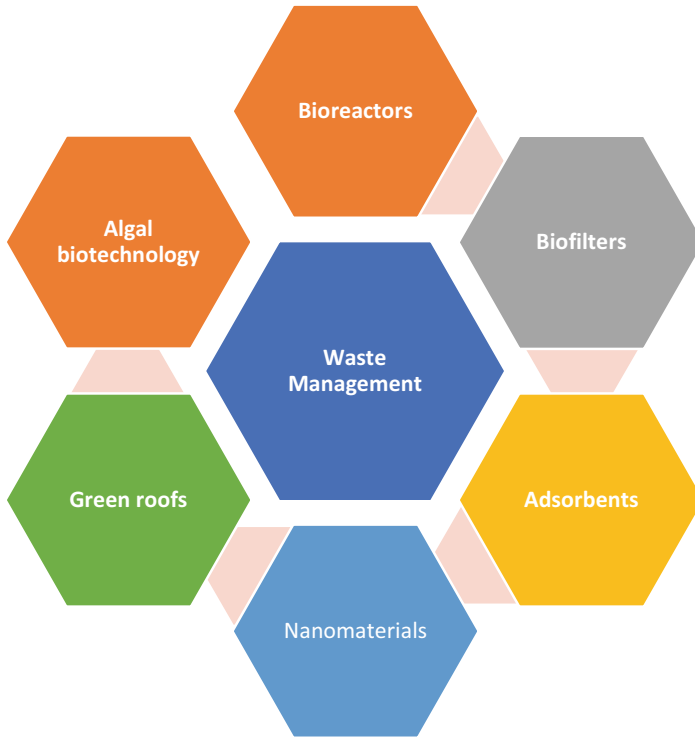


Fig. 16 Waste management

example, activated carbon made from biomass such as coconut shells or wood can be used to remove pollutants such as VOCs, mercury, and lead from the air (Breijaert et al. 2022).

Biomaterials can be used as biosorbents to remove pollutants from water. Biosorbents are materials that can attract and bind to pollutants on their surface. For example, chitosan, a biopolymer derived from shrimp and crab shells, has been used as a biosorbent to remove heavy metals, dyes, and other pollutants from water.

Nanomaterials

Biomaterials can be used to develop nanomaterials that have the ability to remove pollutants from the air. For example, nanoparticles made from chitosan, a biopolymer derived from shrimp and crab shells, have been shown to remove pollutants such as nitrogen oxides and sulfur dioxide from the air (Li et al. 2021).

Green Roofs

Biomaterials can be used to create green roofs, which are roofs that are covered with vegetation. Green roofs can help to absorb pollutants and reduce the heat island effect in urban areas. Biomaterials such as compost, soil, and plant roots are used to create the green roof structure (Breijaert et al. 2022).

Algal Biotechnology

Biomaterials can also be used in algal biotechnology to remove pollutants from water. Algae can be grown in a controlled environment using a variety of biomaterials as the support matrix. The algae can then be harvested and used to remove pollutants from water sources. Algal biotechnology has been used to remove nutrients, metals, and organic compounds from wastewater and other water sources (Syrpas and Venskutonis 2020).

Constructed Wetlands

Biomaterials can be used to create constructed wetlands, which are systems that use natural processes to remove pollutants from water. Constructed wetlands can be used to remove pollutants such as nitrogen, phosphorus, and organic matter from wastewater and agricultural runoff. Biomaterials such as gravel, sand, and soil are used to create the wetland structure (Patyal et al. 2021).

Biochar

Bio-based porous materials, such as biochar, have been found to be effective in controlling soil pollution. Biochar is produced from biomass through a process called pyrolysis, which involves heating the biomass in the absence of oxygen (Kumar et al. 2023). Biochar can be used to control soil pollution by adsorbing and removing pollutants such as heavy metals and organic compounds from the soil. The use of bio-based porous materials for pollution control has several advantages over traditional methods. They are renewable and sustainable, and they have a low environmental impact. They can also be produced locally, which can reduce transportation costs and greenhouse gas emissions. Additionally, bio-based porous materials are cost-effective, and they can be used in a variety of applications.

2.6 Advantages of Bio-Based Porous Material for Bioremediation

Bio-based porous materials have several advantages when used for bioremediation:

2.6.1 Sustainable

Bio-based materials are renewable and can be produced using sustainable methods. This makes them an environmentally friendly alternative to traditional materials, which may be produced using fossil fuels or other non-renewable resources (Udenni Gunathilake et al. [2017](#)).

2.6.2 Biodegradable

Bio-based materials are biodegradable, which means they can be broken down by microorganisms in the environment. This property is particularly useful in bioremediation, where the goal is to break down pollutants in the environment (Sun et al. [2020a, b](#)).

2.6.3 High Surface Area

Bio-based materials have a high surface area, which allows them to absorb pollutants effectively. This property is important in bioremediation, as it allows the materials to capture pollutants and facilitate their breakdown.

2.6.4 Versatile

Bio-based materials can be produced in a wide range of forms, including fibers, particles, and membranes. This versatility makes them suitable for a range of bioremediation applications, such as water and soil treatment (Sun et al. [2020a, b](#)).

2.6.5 Low Cost

Bio-based materials are often cheaper than traditional materials, making them an affordable option for bioremediation applications. They can also be produced using low-cost and low-energy methods (Gandavadi et al. [2019](#)).

2.6.6 Safe

Bio-based materials are generally safe for the environment and for human health. They do not contain harmful chemicals or pollutants, and their biodegradability means that they will not accumulate in the environment (Gandavadi et al. [2019](#)).

2.6.7 Specificity

Bio-based porous materials can be engineered to have specific properties, such as surface chemistry and pore size distribution. This allows them to selectively remove certain pollutants while leaving others untouched.

2.6.8 Scalability

Bio-based porous materials can be produced at a range of scales, from lab-scale experiments to large-scale industrial applications. This scalability allows for flexibility in bioremediation applications and can meet the needs of various projects (Fan et al. [2022](#)).

2.6.9 Compatibility

Bio-based porous materials are compatible with a range of bioremediation techniques, such as biodegradation, biosorption, and biofiltration. This compatibility makes them a versatile option for remediation in a variety of settings (Fan et al. [2022](#)).

2.6.10 Support for Microbial Growth

Bio-based porous materials can provide a substrate for microbial growth, which can enhance the effectiveness of bioremediation. This support for microbial growth can increase the rate and efficiency of pollutant removal (Ramdas et al. [2021](#)).

2.6.11 Minimal Waste

Bio-based materials can be produced with minimal waste, as they can often be made from by-products of other processes. This reduces the environmental impact of production and contributes to a circular economy.

2.6.12 Reduction in Greenhouse Gas Emissions

The use of bio-based materials for bioremediation can contribute to a reduction in greenhouse gas emissions, as they are often produced using renewable resources and can facilitate the breakdown of pollutants that contribute to climate change (Ramdas et al. [2021](#)).

2.6.13 Cost-Effectiveness

Bio-based porous materials can be cost-effective, as they can be produced using renewable resources and can often be produced from waste materials. In addition, they can be reused for multiple cycles of pollutant removal, which can further reduce the cost of bioremediation (Gandavadi et al. [2019](#)).

2.6.14 Low Energy Requirements

Bio-based porous materials require low-energy inputs compared to other methods of pollutant removal. This can be beneficial in reducing the overall carbon footprint of bioremediation processes and can contribute to the adoption of sustainable practices.

2.6.15 Non-toxic

Bio-based porous materials are often non-toxic and safe to handle, reducing potential health risks for those involved in the bioremediation process (Udenni Gunathilake et al. [2017](#)).

2.6.16 Adaptability to Different Environments

Bio-based porous materials can be adapted to different environmental conditions, such as temperature and pH, making them suitable for a variety of settings.

2.6.17 Durability

Bio-based porous materials can be durable, with some materials being able to withstand harsh environmental conditions and maintain their properties over time (Fan et al. [2022](#)).

2.6.18 Can Target Emerging Pollutants

Bio-based porous materials can be designed to target emerging pollutants, such as microplastics and pharmaceuticals, which can be difficult to remove using traditional methods.

The use of bio-based porous materials for bioremediation offers numerous advantages over traditional methods of pollutant removal. These advantages include cost-effectiveness, low-energy requirements, non-toxicity, adaptability to different environments, durability, and the ability to target emerging pollutants (Bilal et al. 2017). These factors make bio-based porous materials a promising solution for addressing environmental pollution and promoting sustainable practices.

2.7 Disadvantages of Bio-Based Porous Material

While the use of bio-based porous materials for bioremediation offers many advantages, there are also some potential disadvantages to consider as follows:

2.7.1 Limited Application Range

Bio-based porous materials may have limited applications in certain environments or for certain types of pollutants. For example, certain materials may not be effective for removing heavy metals or certain chemicals.

2.7.2 Long-Term Efficacy

The long-term efficacy of bio-based porous materials may be difficult to determine, as their properties may change over time due to exposure to environmental factors or the accumulation of pollutants (Neisiany et al. 2020).

2.7.3 Production and Sourcing

The production and sourcing of bio-based porous materials can be challenging, as they require specialized equipment and materials. Additionally, the production of some bio-based materials may compete with food or other resource production, which could lead to issues with resource allocation (Neisiany et al. 2020).

2.7.4 Scale-Up Challenges

Scaling up the production and use of bio-based porous materials for large-scale bioremediation projects may be challenging, as the materials may not be readily available in large quantities or may not be cost-effective at scale (Abbas et al. 2021).

2.7.5 Environmental Impact

While bio-based porous materials are generally considered environmentally friendly, their production and disposal can still have an impact on the environment. For example, the use of certain materials may require large amounts of water or energy or may produce waste products that need to be disposed of safely (Siracusa and Blanco 2020).

2.7.6 Lack of Standardization

The lack of standardization in the production and use of bio-based porous materials can make it difficult to compare their effectiveness or ensure consistent results across different applications.

2.7.7 Biological Variability

Bio-based porous materials rely on the activity of microorganisms to break down pollutants. However, the effectiveness of these microorganisms can vary depending on a range of environmental factors, such as temperature, pH, and nutrient availability. This can make it difficult to predict the efficacy of bio-based porous materials in different environments or under different conditions (Siracusa and Blanco 2020).

2.7.8 Contamination Risk

The use of bio-based porous materials for bioremediation can introduce new microorganisms into the environment, which can potentially cause unintended consequences, such as the spread of invasive species or the introduction of harmful pathogens. Additionally, the use of contaminated or low-quality materials can potentially exacerbate pollution issues or introduce new pollutants into the environment.

2.7.9 Cost

The cost of producing and using bio-based porous materials for bioremediation can be higher than other methods of pollutant removal, such as chemical treatments or physical filtration. This can make it difficult to justify the use of these materials in certain applications or for smaller-scale projects (Lynch et al. 2017).

Time

The use of bio-based porous materials for bioremediation can be a time-intensive process, as it relies on the natural processes of microorganisms to break down pollutants. This can be a disadvantage in situations where rapid pollutant removal is needed.

Regulatory Challenges

The use of bio-based porous materials for bioremediation may be subject to regulatory scrutiny and oversight, particularly if they are used in sensitive environments or for the removal of hazardous pollutants (Lynch et al. 2017). This can increase the complexity and cost of using these materials for pollution control.

3 Synthesis of Bio-Based Porous Materials

3.1 *Synthesis of Activated Carbon*

Due to globalization and industrialization, people started using biomass from waste as a precursor for synthesizing porous activated carbon and this is because of the biowaste availability in abundance as well as its low cost which proved to be the best alternative raw material rather than the one which is used as the conventional raw material like coal, petroleum, peat, and lignite which are very costly and non-renewable (Yu et al. 2021a, b). We can synthesize carbon through two very important processes: one is the carbonization of pyrolysis and the other one is hydrothermal (Bai et al. 2020).

In practice, we have to carbonize hard biological waste sources by using the method of pyrolysis carbonization, but when it is a soft biological waste material we need to carbonize it by using hydrothermal carbonization. The synthesized carbon needs to be activated later in two basic steps: i) carbonization and ii) activation.

3.1.1 Pyrolysis Carbonization

Biomass could be altered by a process of carbonization which is one of the oldest slow methods that need high temperatures, and it is a time-consuming process in which we convert it into carbon materials that could be used for the service of society. This process converts carbon or biochar residue through pyrolysis of raw material under an inert gas environment of a big furnace by removal of volatile and non-volatile carbon material such as hydrogen, oxygen, and nitrogen which will concentrate the carbon content (Radenahmad et al. 2020).

The degasification method will lead to narrow pore structures that will result in the removal of lingering material which is formed when the temperature is increased; sometimes the accumulation may result in the collision of lingering material causing hydrocracking and deposition of carbon (Lateef and Ogunsuyi 2021). Many factors which affect this process apart from temperature are heating rate, process duration, inert environment presence, and its rate. Normally, in this process temperature is very high near 600 °C resulting in a decreased yield and accelerates the liquid and gas release rate (Promraksa and Rakmak 2020). A higher temperature not only increases ash and fixed-carbon content but also reduces the amount of volatile matter. So, we know high temperatures decrease the yield but increase the quality of char; the decrease in char happens because of two reasons: primary decomposition and secondary decomposition (Reza et al. 2020; Negara et al. 2019).

3.1.2 Hydrothermal Carbonization

Hydrothermal carbonization is the most important alternative process that can convert biomass into activated carbon which is cheap and environmentally friendly. This process starts by heating the raw substances placed in an aqueous liquid and later autoclaving at saturated pressure, and temperatures should be maintained within the range of 150 and 350 °C for about 2 to 24 h; through these steps we get water-miscible substances as well as carbon saturated solid compound known as hydrochar (You et al. 2019; Usman et al. 2019). One of the advantages of using this method is no pre-drying is needed for wet waste and the product that is formed depends on different measures like time, pressure, and temperature (Putra et al. 2020).

Hydrothermal carbonization is an exothermic process followed by dehydration and decarboxylation reaction when the condition is subcritical; biomass will be first converted to a monomeric unit by the process of hydrolysis and later into soluble organics by dehydration and fragmentation (Maniscalco et al. 2020). Initial hydrolysis process is modified by reducing pH, and as a result, the concentration of the solution is increased due to polymerization and condensation process followed by nucleation and then finally growth takes place. This process is superior to other thermochemical technologies as in this process wet feedstock could be converted to a solid carbon product resulting in an increase in yield without undergoing dehydration and drying (Kumar et al. 2021) (Figs. 17 and 18).

This process is considered to be simple and efficient and can be used for doping on the surface of activated carbon by using metal and metal oxides (Figs. 19 and 20).



Fig. 17 Hydrothermal process for the preparation of ZnO/AC composite

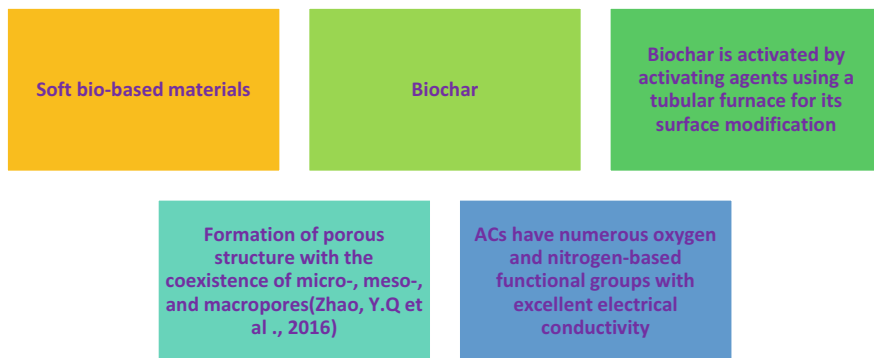


Fig. 18 Preparation of porous structure

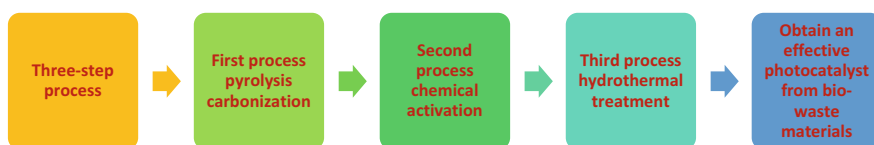


Fig. 19 A three-step process

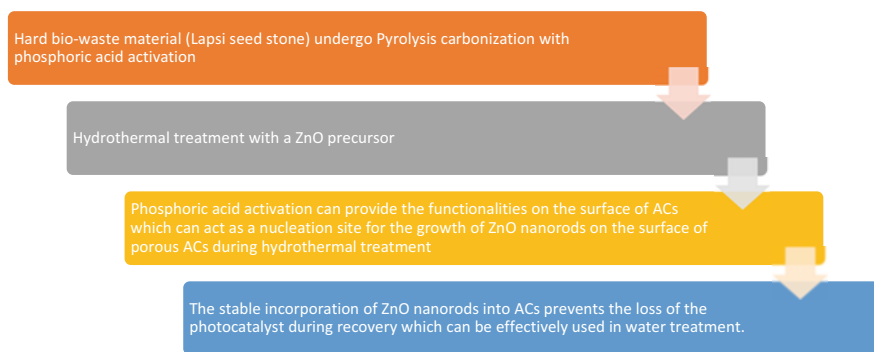


Fig. 20 Fabrication of ZnO-rod-decorated ACs using the hydrothermal process used in water treatment

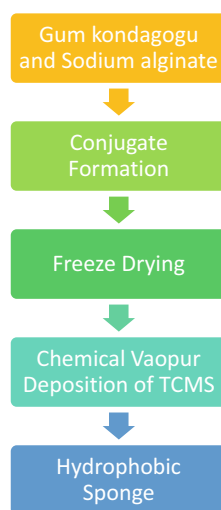
3.2 *Biopolymers Gum Kondagogu (GK) and Sodium Alginate (SA) Sponge Preparation*

Biopolymers formulated by gum kondagogu (GK) and sodium alginate (SA) for the fabrication of a sponge could be used for the separation of oil and organic solvents from an aqueous solution mixture (Fig. 21).

3.3 *Synthesis of Gum Hydrocolloids Reinforced Silver Nanoparticle Sponge*

We can make hydrophilic sponge by taking polymers of gum kondagogu and sodium alginate in 1:1 ratio (w/w) to different concentrations of silver nitrate solution: 4 mM, 6 mM, 8 mM, and 10 mM. Out of these different concentrations of polymers, the final concentration of the polymer which was selected resulted in a composite solution, and it is maintained at 1.5 wt.% (Ramakrishnan et al. 2021). The solution was then continuously stirred at 85 °C for 45 min using 0.1 N sodium hydroxide. By using the dialysis method, unreacted silver nitrate and excess sodium hydroxide were removed and solution obtained was poured into the mold and lyophilized for 24 h at −52 °C so that we get Ag.KS sponges, followed by crosslinking the synthesized Ag.KS sponges using 5% calcium chloride solution; later on excess of calcium chloride is removed by washing it with water. The pristine sample without silver nanoparticle is referred to as KS sponge (Ramakrishnan et al. 2021).

Fig. 21 The fabrication of conjugate GK/SA sponge and chemical vapor deposition of TCMS on its surface



4 Application of Bio-Based Porous Materials for Remediation of Pollutants

4.1 Application of Bio-Based Modified Activated Carbon in Adsorption

Bio-based ACs are considered important resource materials in a wide range of applications because of their large surface area, low cost of production, ease of handling, and modification (Li et al. 2020). The activated carbon can be used in the storage of energy, gas adsorption, and treatment of water. It also has the capability to adsorb CO₂ and NO_x, dyes and organic pollutants. ACs are increasingly used in water purification for the removal of pollutants and contaminants. The researcher has reported that 80% of the activated carbons globally is used in the liquid phase (Rivera-Utrilla et al. 2013). The pollutants which are present in the solution could be absorbed by the exchange process which depends on the porous structure and surface area of the activated carbon (Lewoyehu 2021; Ruiz-Rosas et al. 2019). The adsorption mechanism happens through two processes: electrostatic and non-electrostatic interaction between the solute and the carbon surface.

Electrostatic interactions will start with the ionization of electrolytes, whereas non-electrostatic interactions happen largely due to dissociation and aquaphobic interaction. If we compare pristine ACs to surface-modified activated carbon, the latter has the capability to increase adsorption as well as catalytic activity. Researchers have reported different types of surface-modified ACs (Joshi et al. 2019). Activated carbon has been explored to the core by various scientists; few of its applications are as a catalyst for toxic gases, altering the pore size and surface chemistry of activated carbons which will change the catalytic activity of toxic gases like NO. ACs have been studied by many researchers as promising catalysts for toxic gases. Altering the pore size and surface chemistry of ACs can effectively change the catalytic oxidation of some toxic gases such as NO.

4.2 Oil and Solvent Absorption

GK/SA sponge which is designed in such a manner gives a 3D interconnected open pore structure which is the bio-based porous system that has the capability to remove oils and organic solvents from water. Researchers carried out experiments and proved that when they take two solvents, chloroform having high density and diesel oil which is a low-density solvent, strong sorption of both the solvents was shown. When the GK/SA sponge came into contact with a diesel slick as well as which is stained with a dye named Oil Red EGN on the water surface, it absorbed the diesel entirely within seconds without losing its form. After sorption, the sponge floated on the surface, indicating its potential use for the easy removal of oil spillages and chemical leakages (Ramakrishnan et al. 2021). The silylated bio-based GK/SA

sponge shows a very high affinity for organic compounds with an absorption capacity of ≈ 43 times its initial weight. This high absorption capacity is comparable to carbon sponges and conjugate sponges made from the cellulose-based waste newspaper ($29\text{--}51\text{ g g}^{-1}$) (S Han et al. 2016) and cellulose nanocrystal/poly(vinyl alcohol) sponges (32.7 g g^{-1}) (Gong et al. 2019).

The removal of oil by the sponges is mainly governed by adsorption on the surface and absorption into the bulk by capillary diffusion (Ramakrishnan et al. 2021). The microchannels on the sponges formed during lyophilization greatly facilitate the transport of oils through the interior of the material, resulting in excellent oil absorption performance.

4.3 Crude Oil Absorption Study

One of the most common types of water pollutants is crude oil spillage. The absorption test was performed by mixing 2 mL of crude oil with 10 mL of distilled water; after 1 minute we can observe nearly 99.9% of the oil was absorbed by the GK/SA sponge (Ramakrishnan et al. 2021). In total, we can observe that 23.8, 27.8, and 28.5 g g^{-1} of crude oil was absorbed within 0.5, 1, and 2 min, respectively, which shows the high affinity of the sponges for the absorption of crude oil. The maximum absorption we can see in 28.5 g g^{-1} achieved at 3 min is nearly double that of polypropylene fibrous mats (Wei et al. 2003) and higher than that of cellulose sponges made from waste paper (20 g g^{-1}) (Nguyen et al. 2013) and superhydrophobic sawdust (17.5 g g^{-1}) (Zang et al. 2015) and is comparable with graphene-carbon nanotube sponges (30 g g^{-1}) (Kabiri et al. 2014).

4.4 Catalytic Degradation

The catalytic reduction was performed by slight modification in the procedure on MB dye (Liu et al. 2017). Different concentrations of Ag.KS sponge were made (1.5, 1.9, and 3.1 mg) and dipped separately in a mixture of NaBH_4 (1 mL, 50 mM) and MB dye (4 mL, 30 μM) which was continuously stirred for 1 hr. at room temperature and the process of discoloration of MB dye was recorded by using UV-vis absorption spectroscopy at 664 nm for time intervals 0, 0.5, 1, 2, 3, 4, 5, 10, 15, 20, 30, 40, and 60 min. Similarly, we can perform the catalytic reduction on 4-NP (Silvestri et al. 2018). Different concentrations of Ag.KS sponge were made (1.0, 1.8, and 3.6 mg) dipped separately in a mixture of NaBH_4 (0.3 M, 5 mL) and 4-NP (1 mM, 10 mL) which was continuously stirred for 1 hr. at room temperature, and the process of discoloration of 4-NP dye was recorded by using UV-vis absorption spectroscopy at 400 nm (Ramakrishnan et al. 2022).

4.5 Catalysis Mechanism of Ag.KS Sponge

Ag.KS sponge could be used for the removal of pollutants in a defined pathway; the sponge is hydrophobic and consists of many micropores and many open channels; later silver nanoparticles are immobilized on the surface walls of the sponge; presence of nanoparticles on a sponge will induce oxidation of BH_4 from NaBH_4 followed by release of electrons; as a result, it will make a negatively charged layer on the sponge surface (An et al. 2012). The moment pollutant molecules come in contact with the charged layer of the sponge surface silver nanoparticles will release electrons from BH_4 – to MB/4-NP which will damage the contaminant's structure as it will reduce 4-NP dye into 4-aminophenol and MB dye will be reduced to leucomethylene blue (Ramakrishnan et al. 2022).

5 Future Perspective

Biomaterials have great potential in bioremediation, the process of using living organisms or their by-products to remove or detoxify pollutants from the environment. The use of biomaterials in bioremediation can enhance the effectiveness of the process while minimizing its environmental impact. In the future, it is likely that biomaterials will be developed and optimized specifically for bioremediation applications. Researchers may develop biomaterials that are more effective in degrading specific types of pollutants, or those which have better durability to survive in harsh environmental conditions. Advances in nanotechnology may also play a role in the future of biomaterials in bioremediation.

Nanoparticles can be engineered to have specific properties, such as increased surface area or catalytic activity, which could make them more effective at breaking down pollutants. Another area of research that may contribute to the future of biomaterials in bioremediation is synthetic biology. By engineering microorganisms to produce specific enzymes or other biomaterials, researchers may be able to create highly targeted bioremediation solutions. Overall, the future of biomaterials in bioremediation is promising, and continued research and development in this area could lead to significant advancements in our ability to clean up contaminated environments.

6 Conclusion

Globalization and industrialization have increased environmental pollution, and its impact has become a global concern in the present scenario. Many types of pollution are known which are alarming in the present scenario; out of this water pollution has been considered one of the biggest threats in recent years; if we do not take steps

right now, this problem will aggravate, and in the near future, there would be a shortage of clean drinking water. Recycling of water in the twenty-first century became one of crucial issues as more regions in the globe started encountering water crises. Researchers started finding new technology for detoxifying wastewater; one of the methods was via adsorption removal and another method is the degradation of pollutants or the contaminant and converting wastewater into purified and drinkable water; these methods are organic, cost-effective, and economical.

One of the other methods which are of enormous importance in this context is a wonder porous material that has the ability to detect pollutants in the effluents which come from industries and followed by the treatment of wastewater. Later on, this porous substance was modified into nanosorbents which are having unique properties like high porosity, robustness, and tuneability in regard to structural configuration; this wonder material has turned out to be the best in the remediation of the environment. Material that needs to be selected can be organic frameworks made of metals or porous organic solid covalent organic frameworks made of porous material that has been used extensively in cleaning of the environment to achieve the sustainable goal.

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Role of Biosurfactants in the Remediation of Emerging Pollutants



Subhasree Ray, Shivangi Sankhyan, Madan Sonkar, and Prasun Kumar

Abstract Biosurfactants are produced by numerous microorganisms. Such amphiphilic compounds are either extracellular or a part of the cell membrane. Biosurfactants were found to enhance pesticide bioavailability and accelerate their bioremediation. In addition, due to their amphiphilic character, they alleviate the interfacial tension of immiscible liquid as well as the surface area and increase the sorption and solubility of hydrophobic pollutants. Being of biological origin, biosurfactants are highly selective, less toxic, and biodegradable in nature. They possess a wide range of action spectra under extreme physical conditions (variable pH, temperature, salinity, and low critical micelle concentration). These properties of biosurfactants enable their usage as a potent alternative agent for the remediation of emerging pollutants. Among the various pollutants released into the environment, petroleum hydrocarbons and pesticides are the major contributors, damaging the environment as well as human health. Therefore, controlling these pollutants and other recalcitrant organic compounds and remediating the contaminated area through the development of sustainable alternative technologies is desirable. The application of biosurfactants is suitable to circumvent the pollutants issue without causing auxiliary harm to the environment. With the advances in metagenomic and in silico tools, the characterization of pollutant-degrading microbes at taxonomic and functional levels has become feasible. This chapter presents a comprehensive outlook of the kind of microbial biosurfactants, their properties, and their utility in the remediation of emerging pollutants.

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1 Introduction

The rapid expansion of industries and agriculture in global urbanization and industrialization has led to the emergence of many chemicals in the environment. These pernicious compounds, known as emerging pollutants are a diverse group of chemicals that are not commonly monitored and are not currently regulated by environmental agencies. These chemicals can be found in many environmental compartments, including soil, water, and air. The sources of emerging pollutants are diverse, including industrial and agricultural activities as well as domestic use of personal care products, microplastics, nanomaterials, and pharmaceuticals. Industrial effluents comprise waste material that is largely a mix of hazardous inorganic and organic chemicals, including heavy metals (Unal et al. 2020; Parhi et al. 2021). The presence of these metals beyond a certain level results in severe trouble for the ecosystem and causes various ailments in humans such as cerebral and bodily retention, skin lesions, cancer, birth defects, and malfunction of vital organs. Pharmaceuticals are also the most significant category of emerging pollutants. These are substances that are used in human and veterinary medicine, and they can be released into the environment through wastewater. Some of the commonly detected pharmaceuticals in the environment include antibiotics, hormones, and painkillers. Personal care products are another category of emerging pollutants. These are substances that are used for personal hygiene and cosmetic purposes. Some of the commonly detected personal care products in the environment include fragrances, UV filters, and preservatives. Similarly, microplastics are small particles that are less than 5 mm. These particles can be found in various sources, including wastewater, stormwater, and marine environments. Microplastics can have a significant impact on human health and the environment. Therefore, the presence of these compounds in the environment is a growing concern. For example, the use of antibiotics in agriculture and aquaculture has led to the evolution of antibiotic-tolerant microbes posing a major threat to human health. Emerging pollutants have also been linked to the decline of aquatic biodiversity, including fish populations, due to their toxic effects. On the other hand, nanomaterials are materials that have at least one dimension less than 100 nm. These materials can have unique properties that make them useful in various applications. However, their impact on human health and the environment is not fully understood.

In order to tackle the troublesome situation appearing across the globe due to these emerging pollutants, several approaches have been proposed. A direct approach could be to utilize or manage the emerging pollutants in such a way that their release into the environment becomes negligible. Transforming emerging

pollutants into value-added products is another strategy that can be used to mitigate pollution. This approach has several advantages including

- (a) Reducing pollution: By converting pollutants into useful products, the amount of pollutants released into the environment can be reduced.
- (b) Resource conservation: The transformation of pollutants into value-added products can conserve resources by providing an alternative source of raw materials.
- (c) Economic benefits: The transformation of pollutants into value-added products can provide economic benefits by creating new products and industries.
- (d) Sustainable development: Transforming pollutants into value-added products can promote sustainable development by reducing waste and pollution.

There have been significant developments in transforming emerging pollutants into value-added products. The types of value-added products depend on the nature of the emerging recalcitrant and the transformation process used. Some of the common value-added products from emerging pollutants include

1. Biofuels: Pharmaceutical residues may be converted into biofuels using various processes, including pyrolysis, gasification, and fermentation. Biofuels are a renewable source of energy that can decrease dependence on fossil fuels and aid in reducing greenhouse gas emissions.
2. Fertilizers: Personal care products can be converted into fertilizers using various processes, including composting and anaerobic digestion. Fertilizers are essential for agriculture, and the conversion of personal care products into fertilizers can provide an alternative source of nutrients.
3. Construction materials: Emerging pollutants, such as microplastics, can be converted into building materials, such as bricks and tiles. These building materials can replace traditional building materials and reduce the environmental impact of construction.
4. Chemicals: Emerging pollutants, such as pharmaceuticals, can be converted into chemicals through various chemical processes. These chemicals can be used in various applications, such as the production of plastics, cosmetics, and pharmaceuticals.
5. Biodegradable plastics: Emerging pollutants, such as microplastics, can be converted into biodegradable plastics. Biodegradable plastics can decompose naturally and reduce the environmental impact of traditional plastics.
6. Nutraceuticals: Emerging pollutants, such as algae and seaweed, can be converted into nutraceuticals through various processes, such as extraction and purification. Nutraceuticals are functional foods that provide health benefits and can be used in various food and beverage products.
7. Animal feed: Emerging pollutants, such as food waste, can be converted into animal feed through various processes, such as fermentation and drying. Animal feed is essential for livestock production and can reduce the environmental impact of traditional animal feed production.
8. Water treatment products: Emerging pollutants, such as microplastics, can be converted into water treatment products, such as filtration membranes. These

water treatment products can improve the quality of water and reduce the environmental impact of traditional water treatment processes.

Overall, the transformation of emerging pollutants into value-added products can provide several economic and environmental benefits. The production of these value-added products can create new industries, reduce waste, and promote sustainable development.

Remediation of emerging pollutants is challenging due to their diversity and complex chemical structure. Traditional remediation technologies, viz., physical and chemical methods have limited effectiveness in removing emerging environmental pollutants. Bioremediation, the use of microorganisms to degrade or transform pollutants, has emerged as a promising substitute to traditional remediation technologies due to its potential to be cost-effective and environmental friendly features. In this regard, microbially produced extracellular polymeric substances (EPS) and biosurfactants have attracted increasing attention as potential tools for remediation of emerging pollutants (Mahto et al. 2022). There are methods to exploit biofilm-EPS forming bacteria for heavy metal detoxification. In a contaminated environment, biofilm bacteria increase dramatically. Heavy metal detoxification is greatly aided by EPSs, which act as a heavy metal resistance mechanism. Functional groups like amino acid and carboxylic acid groups are usually present in the polysaccharides, sugar, and uronic acid components of EPS. These functional groups bind or detoxify heavy metal ions. In the complexation of metal ions, the proteinaceous portion of EPS is crucial. Several investigations showed that bacteria isolated from water sources acquire antibiotic resistance genes (ARGs) and metal resistance genes (MRGs).

The coexistence of MRG and ARG enhances microbial co-selection and survival, particularly since they are situated on the same mobile genetic element (Chen et al. 2019; Yu et al. 2022). A greater number of undiscovered metabolic properties of the biofilm-forming microbial community toward the biofilm-based detoxification of heavy metals will be present due to the stable structure of the biofilm.

Recently, a nonvirulent isolate of *Bacillus* sp. GH-s29 was found to remediate arsenic—As(V), chromium—Cr(VI), and cadmium—Cd(II) from individual solutions as well as multimetal solutions. It was found that the EPS produced by this *Bacillus* strain is negatively charged due to carboxyl, hydroxyl, sulphate, and phosphate as functional groups that help in binding and removal (up to 73.65%) of the metal ions (Maity et al. 2022). In contrast, biosurfactants are microbially synthesized surface-active compound that have attracted increasing attention as a prospective tool for the bioremediation of emerging pollutants due to their unique characteristics. These amphiphilic molecules are produced by several microbes, including yeasts, fungi, and bacteria. They possess both hydrophilic and hydrophobic regions, which enable them reducing the surface and interfacial tensions amid two immiscible phases. Bio-based surfactants have several benefits over synthetic surfactants such as their low toxicity, biodegradability, biocompatibility, and potential for large-scale production. Biosurfactants have been classified into several categories on the basis of their chemical structure, including glycolipids,

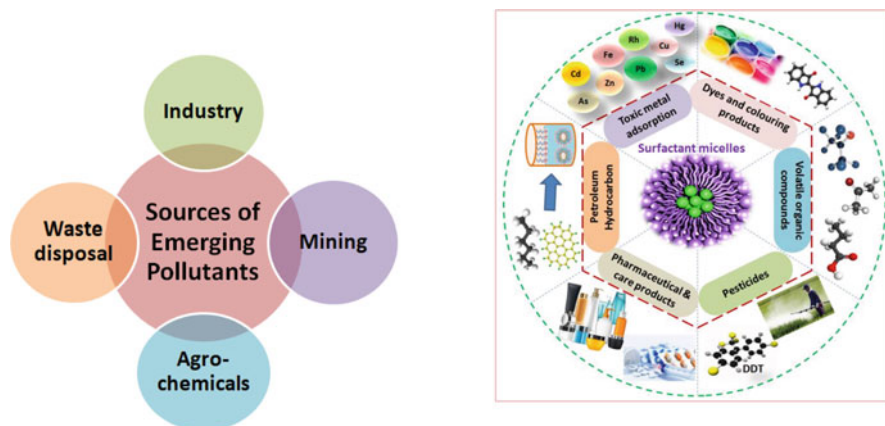


Fig. 1 Sources of emerging pollutants (left) impacting the environment and potential role of biosurfactants (right)

lipopeptides, sophorolipids, phospholipids, surfactin, rhamnolipid, lichenysin, and polymeric biosurfactants. The diversity of biosurfactants produced by microorganisms allows them to function in various environmental conditions, making them attractive for a varied range of applications, including bioremediation (Fig. 1). This chapter will encompass the role of biosurfactants in the remediation of emerging pollutants.

2 Structure and Role of Biosurfactant

A typical surfactant molecule comprises two ends (based on their affinity to water), that is, hydrophilic and hydrophobic ends (Fig. 2). The former includes carbohydrates, amino acids, peptides, alcohol, or a phosphate group (which can be nonionic, ionic, or amphoteric), while the latter is represented by long hydrocarbon chains such as hydroxyl fatty acids, α -alkyl- β -hydroxy fatty acids (common in C8 to C22 alkyl chains), or fatty acids. The amphiphilic nature of surfactants leads to an effective reduction of surface tension and interfacial tension among surfactant molecule at the surface as well as at the interface (Rahman and Gakpe 2008).

Thus, surfactants are useful as they raise the surface area along with the bioavailability of hydrophobic pollutants. Surfactant molecules within mixture of oil and water will place themselves at the oil-water interface, providing foaming, emulsification, and dispersal capacities that render the suitable for bioremediation purposes. Being an amphiphilic compound, biosurfactants preferentially partition among liquid surfaces of diverse polarities, such as oil/water or water/air interfaces (Fig. 2). It also controls the proliferation of bacterial biofilm formation on various surface (Vijayakumar and Saravanan 2015). Based on the microbial origin and their chemical composition biosurfactants can be classified. This classification primarily

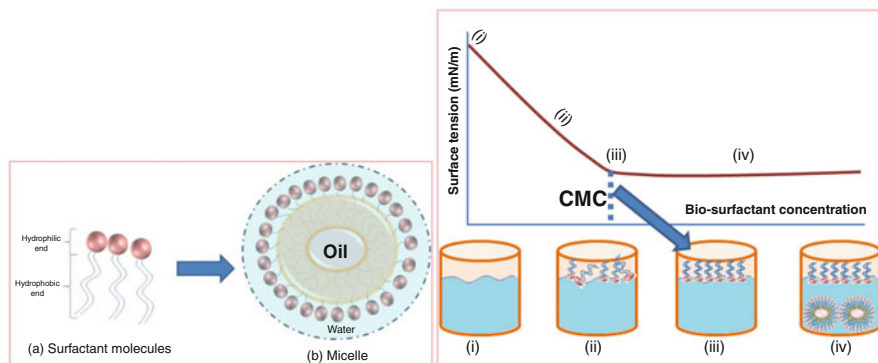


Fig. 2 Surfactant molecule and their behavior at the water-oil interface to form micelle structure (left). Mechanisms of solubilization and displacement (above or below the CMC; iii) of biosurfactant during the washing of hydrocarbon contaminated soils (right)

distinguishes between two types of biosurfactants according to their molecular weight. The first type comprises low-molecular-weight compounds that exhibit lower interfacial surface tension. Included in this category are lipopeptides, glycolipids, and phospholipids. The second type consists of high-molecular-weight biosurfactants, which serve as highly efficient stabilizing agents. Polymeric surfactants fall within the category of high-molecular-weight biosurfactants (Table 1). Glycolipids having carbohydrates as hydrophilic parts (namely, glucose, galactose, glucuronic acid, rhamnose, di-, tri-, or tetra-saccharides, etc.) are quite common. Trehalolipids, sophorolipids, rhamnolipids, and mannosylerythritol lipids are a few well-known biosurfactants having rhamnose, sophorose, trehalose, and mannose sugar attached to fatty acids, respectively. *Pseudomonas aeruginosa* is the representative organism well studied for rhamnolipid production. Similarly, *Starmerella bombicola* produces the highest amount of sophorolipids, to the tune of 300 g/L, and is well studied for its commercial usage. Trehalolipids, having both long- and short-chain fatty acids as hydrophobic moiety, are synthesized by bacterial strains belonging to the genus *Rhodococcus* and *Mycobacterium*. Furthermore, mannosylerythritol lipid was produced in large quantities when *Pseudozyma antarctica* was cultivated on vegetable oils.

3 Properties of Biosurfactants

There are several unique features of biosurfactants that make them a suitable alternative to their chemical-based counterparts: (i) surface and interface activity, (ii) anti-adhesive property, (iii) biodegradability, and (iv) emulsion forming and emulsion breaking. Surface tension is a systematic force that works among different liquid molecules; the same applies to the interface between two immiscible liquids.

Table 1 Types of biosurfactants produced by microbes and their characterization methods

Surfactant type	Production	Properties	Characterization	Surface tension (mN/m)	References
Glycolipid	<i>Pseudomonas aeruginosa</i> , <i>Rhodococcus erythropolis</i>	Long-chain aliphatic acids or hydroxyaliphatic acids linked through ester groups	TLC, FTIR, LC/MS	29	Abbasi et al. (2012)
	<i>Bacillus safensis</i> YKS2				
Lipopeptides	<i>Bacillus licheniformis</i> <i>Bacillus subtilis</i> ZNI5	Lipid attached to the polypeptide chain	TLC, FTR	27	Li et al. (2016)
	<i>Klebsiella pneumonia</i>	–	Biochemical tests	27.8	Mnif et al. (2021)
Phospholipids	<i>Klebsiella pneumonia</i>	Lipid coupled with phosphate group	Biochemical tests	–	Jamal et al. (2012)
	<i>Acinetobacter calcoaceticus</i> , <i>Candida lipolytica</i>	Polysaccharides linked with protein complex such as emulsan, lipomannan, and liposan	TLC, LC/(ESI) MS	29–32	Anaukwu et al. (2015); Santos et al. (2017)
Surfactant exopolysaccharide	<i>Ochrobactrum pseudintermedium</i> C1	–	FTIR, CHN analyzer, SEM	28.27	Sengupta et al. (2021)

The latter is known as interfacial tension. The surfactant efficiency depends on its ability to reduce the surface tension of the medium. For example, surfactin synthesized by *B. subtilis* has been found to be potent in reducing surface tension in stringent conditions. Similarly, *P. aeruginosa* produces rhamnolipid, while other microbes also produce surfactants that decrease the water surface tension from 72.0 mN/m to 35.0 mN/m reflecting their potential (Kim et al. 2015; Mulligan 2005).

Biodegradability is another unique property of biosurfactants. Besides being nontoxic or hazardous to the environment, biosurfactants are biodegradable in nature and thus suitable for application in the cosmetic and pharmaceutical industry (Gregorich et al. 2015). Sophorolipid biosurfactants derived from the nonpathogenic *Candida bombicola* were assessed for biodegradability as per the OECD chemical testing guidelines (301C Modified MITI test). After cultivation, it exhibited rapid biodegradation, where the degree of degradation was evaluated by the ratio of biochemical oxygen demand to theoretical oxygen demand. During sophorolipid degradation, it was observed that about 61% of the requisite oxygen gets consumed in an 8-day culture period. Such degradation was also found when surfactin and arsloractin were studied for degradation under similar conditions (Hirata et al. 2009).

Biosurfactants possess anti-adhesive properties that offer a novel and effective way to combat the colonization of harmful microorganisms. They prevent the attachment of these microorganisms to solid surface or infection site (Singh and Cameotra 2004). Biosurfactants may modify the hydrophobicity of surfaces, directly impacting the adherence of microbial populations and biofilm formation. For instance, biosurfactants derived from *Pseudomonas fluorescens* were found to hinder the attachment of *Listeria monocytogenes* to steel surfaces (Meylheuc et al. 2001). Literature reveals that crude biosurfactants exhibit anti-adhesive activity against various microbes, even at minimal concentrations as low as 0.75 mg/L. The extent of the anti-adhesive property correlates directly with the concentration of the biosurfactant. Specific anti-adhesive effects were observed against *Lactobacillus casei* with inhibition values of up to 99% at the minimal biosurfactant concentration. Comparatively lower inhibition was observed for *Staphylococcus epidermidis* (27%) and *Escherichia coli* (21%) at the maximum biosurfactant concentration (Rufino et al. 2011). Biosurfactants can work as emulsifier or de-emulsifier in heterogeneous systems, such as emulsions where one immiscible liquid is dispersed as droplets in another. These emulsions can be oil-in-water (o/w) or water/oil emulsions. Biosurfactants stabilize such emulsions, preventing their separation. For example, water-soluble liposan produced by *Candida lipolytica* was studied for emulsification of edible oils, coating the oil droplets and forming a stable emulsion (Vijayakumar and Saravanan 2015). In the case of biosurfactants derived from *P. aeruginosa* RB28, production commenced during the late logarithmic growth phase and reached its peak (2700 mg/L) during the stationary phase. The rhamnolipid biosurfactant produced showed effective emulsification of heptadecane, sunflower oil, and paraffin. With hydrocarbons, the rhamnolipid formed a stable emulsion (Sifour et al. 2007).

4 Microbial Biosurfactant Production

Biosurfactants are active on the surface of extracellular fluid and show biological activity against insecticides, viruses, chemicals, and even microorganisms (Fenibo et al. 2019). Several microbes are known to produce environmentally friendly surfactants from various different carbon and nitrogen sources that may be obtained from many renewable sources such as wastewater, potato waste, industrial residues, cassava flour, soyabean oil, palm oil, and glycerol. Unique substrates have also been discovered for the biosurfactant production; these include substrates coming from fruit processing plants, oil refineries, coffee roasting facilities, molasses, and agro industries such as used cooking oil and date flour (Md Badrul Hisham et al. 2019; Mnif et al. 2021; Nor et al. 2023). Several microorganisms are known to produce biosurfactant, such as *Acinetobacter*, *Arthrobacter*, *Candida*, *Bacillus*, *Enterobacter*, *Halomonas*, *Rhodococcus*, *Pseudomonas*, and a few yeast species (Bach et al. 2003; Nor et al. 2023; Rufino et al. 2014; Vijayakumar and Saravanan 2015). However, their individual capacities to produce this biomolecule and the type of biosurfactant vary significantly. In addition, several factors affect the production of biosurfactant. Its production is mainly regulated by the availability and type of carbon sources, nitrogen sources (e.g., urea, ammonium nitrate, and peptone), salt concentration, and environmental factors, namely, temperature, aeration, agitation speed, and pH. Nitrogen sources such as urea and ammonium salt are preferred by *Arthrobacter paraffineus* for biosurfactant production, while nitrate is essential for *P. aeruginosa* high surfactant production rates.

5 Genomic Tools in Aid of Microbial Surfactants

Untapped microbial diversity has been considered the most abundant biomass on the planet. Yet, they remain to be intellectually explored to develop biotechnological products due to a few limitations in their cultivation and genetic inaccessibility. For efficient pollutant degradation and/or removal through biological routes, a proper understanding of microbial resources and their underlying metabolic systems including genes, enzymes, and population dynamics/diversity is required. The culturable method of exploring biosurfactant-producing microbes has been in practice for a long time particularly those involved in plant growth or associated with agricultural applications. Such approaches are now augmented with advanced genetic and genomic tools to identify efficient degraders of contaminants. The communication ability and genetic information transfer among microbial communities allow them to evolve and adapt their metabolism according to the changing pollutants in any dynamic human-interfered environment. Metagenomic approaches enable us to understand complicated networking, adaptation, critical gene regulation, phylogeny, enzymes, and biosurfactant secretion. In addition, proteomics and interatomic approaches shed light on the expression profiles to figure out the genetic interplay

of microbes flourishing in contaminated environments. Furthermore, recent advances in synthetic biology, particularly gene editing methods, have enabled researchers to precisely modify the genetic makeup and reconstitute the metabolic networks for the removal of specific pollutants using improved microbial strains.

In this regard, several studies have been conducted in the past few years. Microbial communities (both bacteria and archaea) have a complex role in oil bioremediation as they can secrete biosurfactants and degradation enzymes. Such microbes are useful in autochthonous bioaugmentation, though a few nondirect degraders are also known. Using new-generation-sequencing and metagenomic approaches, 46 diverse metagenomes collected from 20 different geographical locations were studied. It was found that surfactant production and oil degradation are related events and thus must be studied together. Among the samples, terrestrial metagenomes showed more genes for degradation (particularly cyclic compounds) than metagenomes collected from the water biome. In addition, latitude also had an influence on biosurfactant production and degradation genes. Microbiomes collected near the equator showed more rich genes with potent biotechnological applications (Oliveira et al. 2017).

It is imperative from the above study that there exists an enormous diversity of microbes and that the search for unique biosurfactant molecules must be executed at pace. Only a handful of studies are available in the public domain regarding metagenomic studies for the selection of commercially important biosurfactant-producing microorganism. Although metagenomic studies bypass the conventional culture technique and reduce cumbersome screening for media requirements. However, the isolation of a metagenome and subsequent analysis require expertise. Isolated metagenomic DNA is analyzed by DNA sequencing, polymerase chain reaction, and functional activity. Screening is done on the basis of primers/probes designed for the genes responsible for encoding the target enzyme or compound. Databases such as NCBI, KEGG, clusters of orthologous groups of proteins, and alignment tools are used. Software such as antiSMASH allows the detection of gene clusters for target biosynthetic routes/genes involved (Islam and Sarma 2021). Once the search is narrowed down to a handful of final genes, they may be checked using *in silico* tools before heterologous expression and functional characterization through clone libraries or other related methods. The use of stable isotope probes can further enhance the efficacy of metagenomics. Thus, metagenomics is a potent tool to discover novel bacteria and/or gene(s) producing biosurfactants. For instance, drilling residues were enriched in the presence of culture media fortified with petroleum to select oil-degrading microbes. The DNA samples collected were sequenced and analyzed on the Ion Torrent platform indicating the rich diversity of Proteobacteria in the metagenome. Further functional roles in terms of biosurfactant production were checked using the BioSurfDB database. It was observed that biosurfactant production and hydrocarbon metabolic pathways exist in the metagenome. The consortium studied in this work was found to be positive for pathways for fatty acid and chloroalkane metabolism. It was also able to produce lichenysin, iturin, and surfactin with about 66% degradation of total alkanes. Such consortia may be explored further to develop autochthonous bioaugmentation

strategies for bioremediation of drilling residue (Guerra et al. 2018). In another study, through metagenomic study, a new gene termed metagenomic biosurfactant protein 1 (MBSP1) was identified. It was found to be related to the production of biosurfactant and the degradation of hydrocarbons. This gene coding for protein with tensoactive properties, when expressed in *E. coli* RosettaTM (DE3) as a host, showed degradation of hydrocarbons. MBSP1 is the first of its kind in the domain of archaea or bacteria (Araújo et al. 2020).

6 Biosurfactants and Bioremediation of Emerging Pollutants

Biosurfactants have several properties that make them attractive for the bioremediation of emerging pollutants. Biosurfactants can enhance the solubility and bioavailability of hydrophobic pollutants, allowing microorganisms to access and metabolize these compounds. Additionally, biosurfactants can increase the mobility of pollutants in the environment, allowing them to be transported to areas where they can be more easily degraded or removed (such as heavy metals) (Table 2).

Biosurfactants have been used in several bioremediation strategies for emerging pollutants, including the following:

1. Biodegradation of hydrophobic pollutants: Biosurfactants have been used to enhance the biodegradation of hydrophobic pollutants, such as polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls. Biosurfactants increase the solubility of these compounds, making them more accessible to microorganisms that can degrade them. For example, a study conducted by Saimmai et al. (2011) demonstrated that a biosurfactant produced by *Bacillus subtilis* enhanced the degradation of PAHs by a soil microbial community. During anaerobic digestion, biosurfactants work as solubilizing agents that help in separating sludge, release encapsulated hydrolase, and promote a change in microbial activity leading to enhanced methanogenesis (He et al. 2019).
2. Phytoremediation: Biosurfactants can be used to enhance the phytoremediation of emerging pollutants. Phytoremediation is a plant-based remediation technology that uses plants to remove pollutants from the environment. Biosurfactants can enhance the uptake and translocation of pollutants by plants, increasing their effectiveness in removing pollutants from the environment. For example, a study conducted by Becerra-Castro et al. (2011) demonstrated that a biosurfactant produced by isolates of plant rhizomes enhanced the removal of nickel through its solubilization.
3. Bioaugmentation: Biosurfactants can be used to enhance the effectiveness of bioaugmentation, a bioremediation strategy that involves the introduction of microorganisms that can degrade pollutants in contaminated environments. Biosurfactants can increase the mobility of microorganisms in the environment, allowing them to access and degrade pollutants more effectively (Sonkar et al.

Table 2 Microbial biosurfactants and their action on various heavy metals

Bio-surfactant	Heavy metal	Microorganism	Removal mechanism	References
Glycolipid				
Rhamnolipids	Ni(II), Cd(II), Cu(II)	<i>Marinobacter</i> sp., <i>Shewanella</i> sp. BS4, <i>Pseudomonas</i> sp.	Washing	Lee and Kim (2019); Shen et al. (2019)
Sophorolipids	Cu(II), Zn(II)	<i>Candida</i> sp. AH62, <i>C. bombicola</i> ATCC 22214	Washing	Da Rocha Junior et al. (2019)
Trehalolipids	Co(II)	<i>Rhodococcus</i> sp.	Washing	Narimannejad et al. (2019)
Mannosylerythritol lipids		<i>Ustilago</i> sp., <i>Moesziomyces antarcticus</i>	–	Bakur et al. (2019)
Lipopeptides				
Lichenysin	Cu(II), Pb(II)	<i>Bacillus</i> sp.	Washing	Saleem et al. (2019)
Surfactin	Pb(II), Cu(II), Zn(II), Fe(II), Ca(II), Ni(II), Cr(VI), Cd(II)	<i>Bacillus subtilis</i> , <i>Paenibacillus</i> sp. D9	Washing	Jimoh and Lin (2020); Md Badrul Hisham et al. (2019)
Carbohydrate/lipid /protein	Cr(VI)	<i>P. fluorescens</i>	Washing	Kalaimurugan et al. (2020)
Mannan-lipidprotein	Pb(II), Zn(II), Cd(II), Cu(II)	<i>C. tropicalis</i>	Biosorption	Mbachu et al. (2019)
Lipopeptide with a metal-complexing property	Pb(II), Cd (II) and Cr (VI)	<i>Bacillus cereus</i> NWUAB01	Biosorption	Ayangbenro and Babalola (2020)
Lipopeptide isoform	Cu(II), Co(II)	<i>B. subtilis</i> ZN15	Chelation and biosorption	Mnif et al. (2021)
Phospholipids				Jamal et al. (2012)
Polymeric biosurfactants	Cu(II), Pb(II)	<i>Candida lipolytica</i>	Chelation/ precipitation	Anaukwu et al. (2015); Santos et al. (2017)
Surfactant exopolysaccharide	Cd(II), Ni(II), Pb(II)	<i>Ochrobactrum pseudintermedium</i> C1	Biosorption	Sengupta et al. (2021)
Particulates				
Vesicles	Cd(II)	<i>Pseudomonas marginalis</i>	Plant-growth promotion and phytoremediation	Safronova et al. (2006)
Whole microbial cells	Cd(II), Cu (II), Pb(II)	Cyanobacteria	Biosorption	Delneuveille et al. (2019)

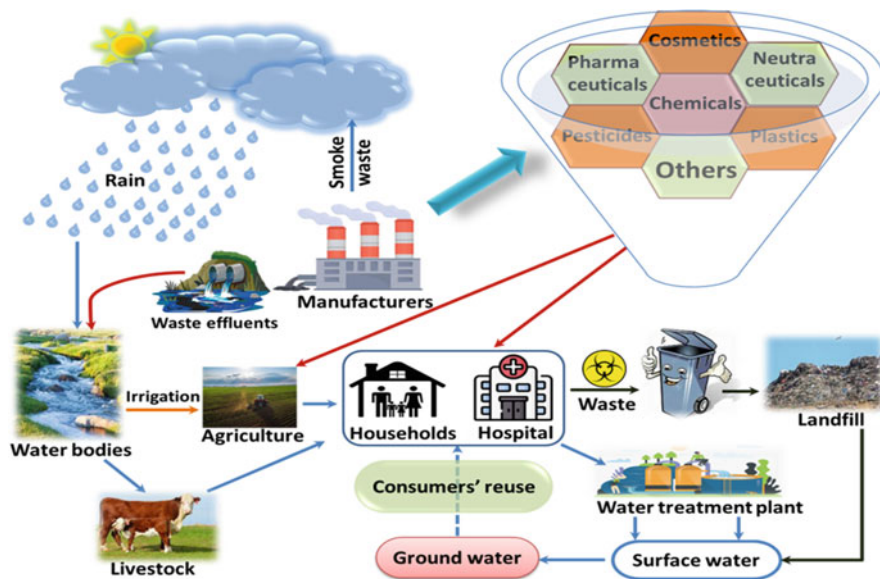


Fig. 3 Potential source of emerging pollutants, routes of groundwater pollution and life-cycle distribution of emerging pollutants

2021). For example, a study conducted by Zhang et al. (2021) demonstrated that a biosurfactant produced by *Serratia marcescens* improved the biodegradation of PAHs by a bacterial consortium.

Since the dawn of industrialization, a plethora of organic compounds have been put to use in industries and agricultural sectors (Bhatt et al. 2021). The rapid expansion and acceptability of this led to a gross mistreatment of ecological niches by contaminants such as benzene, chloroform, pesticides, plastic compounds, paints, and gasoline (Chen and Chang 2020). Now there is hardly any ecosystem untouched by the negative impact of these emerging pollutants.

For instance, petroleum hydrocarbons are valuable energy resources but also contribute significantly to environmental pollution, posing severe health risks. In order to address these contaminants, the exploration of sustainable alternative technologies that mitigate further harm to the environment is underway. One such alternative is biosurfactants, which are naturally produced by various microbial species. Biosurfactants exhibit low toxicity and are biodegradable, making them well suited for remediating organic pollutants. These compounds are amphiphilic in nature and can be categorized into two types based on their molecular mass. Microorganisms such as bacteria, fungi, and algae can produce biosurfactants either extracellularly or as integral components of their cell membranes.

There are hundreds of reports on the negative impacts of pollutants on humans and nature, indicating that the remediation of such pollutants is essential (Fig. 3). A few proposed remediation strategies include soil washing, oxidation, aeration,

pumping, and incineration (Yoshikawa et al. 2017). However, such methods have their own limitations and drawbacks, as they are quite cost-intensive and may lead to the generation of secondary pollutants. To circumvent such issues, natural routes of microbe-based bioremediation have been advocated as economical and sustainable. Microbial bioremediation of pollutants involves several different approaches that may or may not include enzymes based on the fate of the pollutants (Table 2). These include adsorption, assimilation, bioaccumulation, reduction, surface precipitation, complexation, emulsification, binding, and degradation (Mahto et al. 2022). The most common of these are uptake of pollutants by glycolipids present of microbial membranes. Glycolipids work as an emulsifying agent and are often referred to as “biosurfactants” (Liston et al. 2017). It must be recalled that for microbial growth, a wide variety of compounds may be used as carbon sources and to derive energy. But carbon present in pollutants such as hydrocarbons is insoluble in the aqueous phase and therefore needs the help of an emulsifying agent for their assimilation or degradation by microbes. Thus, biosurfactants play a critical role in solubilizing the hydrocarbons in the media. For instance, *Pseudomonas* produces rhamnolipids (surface tension: 29 mN/m) to consume complex hydrocarbons, while some other microbes alter their cell walls as they produce lipopolysaccharides (Leuchtle et al. 2015).

Oil spills significantly affect marine life and the ecosystem. In attempts to address oil spills, chemically synthesized surfactants have been utilized in the ocean. However, these artificial surfactants have a few shortcomings, including degradability and toxicity issues. A more promising approach involves exploring naturally occurring biomolecules with surface activity and emulsifying properties (Fig. 2). When biosurfactants are introduced into a water-oil mixture, their monomers rearrange into micelles, forming spherical structures. The hydrophobic portion of the biosurfactant is oriented toward the center of the micelle, forming the core, while the hydrophilic part faces the outer surface, creating an interface with the water. As a result, the biosurfactant molecules reduce the surface tension between the water and oil interfaces, facilitating the exposure of hydrocarbons to bacteria and oxygen, thereby promoting hydrocarbon degradation (Soberon-Chavez and Maier 2010). Biosurfactants induce changes in the cell membrane, such as modifications in protein composition or increased hydrophobicity of the cell wall. These alterations enhance the accessibility of hydrocarbons to microorganisms. The formation of aggregates occurs through weak chemical interactions, including van der Waals forces and hydrogen bonding. The formation of micelles decreases the repulsive forces between the immiscible liquid phases, aiding in the overall process (Aparna et al. 2012). A detailed mechanism by which microbial polymers can interact with pollutants is shown in Fig. 4.

Bacillus cereus KH1 picked from textile effluent produced 2.98 g/L of biosurfactant (lipopeptide) using molasses as feed. The lipopeptide was relatively stable in broad physical conditions of varying temperatures, salt concentrations, and pH. The microbial strain, along with the secreted biosurfactant, was capable of decolorizing up to 87% of the dye from textile effluent (Nor et al. 2023). Like hydrocarbons containing oil waste, benzo(a)pyrene—(BaP), a high-molecular-

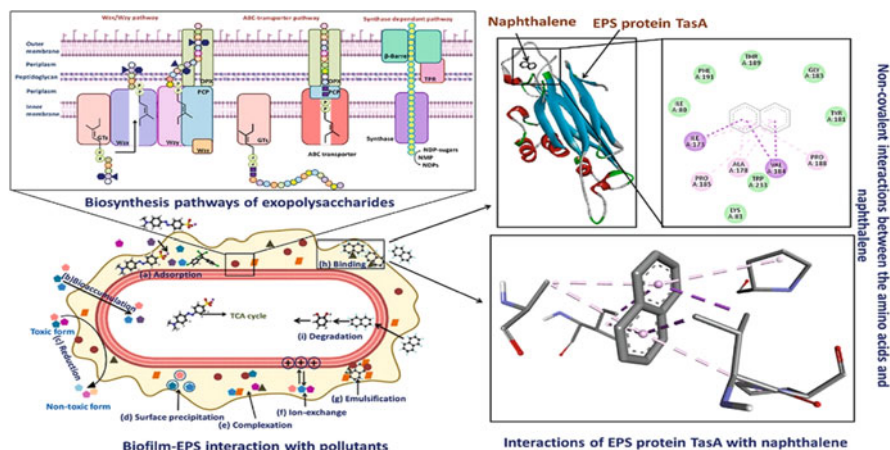


Fig. 4 Different ways microbial polymers interact with pollutants. [Reprinted with permission from Mahto et al. (2022). Copyright 2022 Elsevier]

weight PAH, is a biohazard and persists longer in the environment. *Bacillus flexus* S1126 and *Paenibacillus* sp. S118 were explored for the rhizodegradation of the benzo(a)pyrene plant *Melia azadirachta*. Both the isolates solubilize benzo(a)pyrene (up to 24.41%) by producing surfactin-type biosurfactants with a higher emulsification index. Its pollutant solubilization efficiency was better than that of synthetic surfactants but was not as effective as tween-80. In liquid medium, >70% of the benzo(a)pyrene gets degraded within 21 days. In contrast, pot experiments show that application of microbial biosurfactant degrades >86% of the benzo(a)pyrene after 2 months (Kotoky and Pandey 2020). It was demonstrated through pot trial experiments that efficient rhizodegradation of BaP within the soil occur in a span of about 2 months in the plant *Melia azadirachta* rhizosphere. After addition of microbial cultures—S118 (*Paenibacillus* sp.) and *B. flexus* S1126, the degradation rate was found to be significantly higher (up to 87.42) than in the bulk (68.22%). Thus, it was recommended to explore these biosurfactant producing bacteria as a promising bioremediation tool for BaP within the soil. These microbes may also be utilized for the bioremediation of hydrocarbon contaminated sites. A brief summary of microbial degradation of polyaromatic hydrocarbons is provided in Table 3.

Biosurfactants have the ability to emulsify hydrocarbons in water, creating different blends and rendering them soluble in water. Surfactants such as lichenysins, rhamnolipids, and surfactins have been recognized for their effectiveness in remediating oil contamination (Table 3). It has been suggested that biosurfactants produced by marine bacteria are capable of effectively treating oil spills that float on the water surface by forming stable emulsions, thereby enhancing the rate of biodegradation. These properties make biosurfactants promising for cleaning up oil spills in coastal areas and the open sea. Marine environments harbor a wide range of hydrocarbonoclastic microorganisms that degrade hydrocarbons present in polluted sites. Numerous studies have shown that the combination of

Table 3 Degradation of polyaromatic hydrocarbons using microbial biosurfactants

Type of polyaromatic hydrocarbons	Microorganism	Biosurfactant	Remarks
Fluorene, phenanthrene, naphthalene	<i>Pseudomonas</i> sp.	Surfactin, lichenysin, and fengycin	Enhanced degradation of PAHs and heavy oil
Naphthalene	<i>P. fluorescens</i>	Viscosin and amphisin	Enhanced solubility of low-molecular-weight aromatic hydrocarbons
Pyrene, phenanthrene, naphthalene, and related compounds	<i>Paenibacillus dendritiformis</i> , <i>P. aeruginosa</i> CB1, <i>Bacillus cereus</i> SPL-4	Lipopeptide	Increased bioavailability and enhanced recovery of oil
Anthracene, alkyl phenanthrene, fluorene, and pyrene	<i>Bacillus amyloliquefaciens</i> , <i>B. axarquiensis</i> , <i>Aeribacillus pallidus</i> , <i>B. siamensis</i> , and <i>B. subtilis</i> subsp. <i>inaquosorum</i>	Surfactin	Reduced surface tension of water (26.75 mN/m) with enhanced degradation of aromatic hydrocarbons
Naphthalene, pyrene, phenanthrene	<i>Aeribacillus pallidus</i> SL1	Glycoprotein	Better solubility as well as degradation
Phenanthrene	<i>P. aeruginosa</i> ATCC9027	Rhamnolipid	Effective degradation of phenanthrene
Anthracene, pyrene, and phenanthrene	<i>P. aeruginosa</i> PF2		Higher removal of soil hydrocarbons with increasing concentration of rhamnolipid
Naphthalene, indene, and related compounds	<i>P. aeruginosa</i> SR17		60–80% of degradation efficiency
Phenanthrene, naphthalene, and pyrene	<i>Bacillus</i> sp. Lz-2		Biosurfactant was stable and active at high pH with maximum solubility at pH 11
Fluorene	<i>Pseudoxanthomonas</i> sp. PNK04		Degradation efficiency of 96% obtained; equivalent to tween-80
Anthracene, pyrene, and phenanthrene	<i>Pseudomonas sihuiensis</i>	Mono- and di-rhamnolipid	This bacterium is capable of producing biosurfactant during the hydrocarbon degradation for enhanced removal

biosurfactants and microbial growth stimulates the degradation of hydrocarbons in marine environments. A consortium of hydrocarbonoclastic bacteria exhibits diverse degradation capabilities for both aliphatic and aromatic fractions of crude oil.

Generally, biosurfactants produced by oil-degrading microbes enhance the absorption of hydrocarbons and available nutrients in the environment (Peele et al. 2018).

Certain microbes produce emulsifying agents that aid in the degradation of hydrocarbons, and these emulsifiers have been used in oil spill cleanup efforts (Bach et al. 2003). Biosurfactant production can be scaled up to an industrial level through the fermentation. Lichenysins, derived from *Bacillus licheniformis* JF-2 isolated from well water, have shown significant surface tension reduction between interfacial surfaces even at lower concentrations (10–60 mg/L), reaching levels as low as 10–2 mN/m. Their activity remains unaffected by variations in temperature as high as 140 °C, pH range of 6–10, and salinity equivalent to 10% w/v NaCl (Bach et al. 2003). Knowledge regarding the use of biosurfactant systems for enhanced oil spill remediation is expanding and bio-based and biodegradable biosurfactants hold potential for addressing oil spill-related challenges. However, further research is needed to advance our understanding of the mechanisms underlying the interaction between oil spills and microbial surfactants. In conclusion, biosurfactants have shown great promise as a tool for the bioremediation of emerging pollutants. These microbial-produced surface-active molecules have unique properties that make them attractive for the remediation of a wide range of emerging pollutants. Biosurfactants enhances the solubility and bioavailability of hydrophobic pollutant and increase their mobility.

7 Commercial Demand of Biosurfactants

Besides bioremediation, there are several other usages of biosurfactants in petroleum, agriculture, pharmaceuticals, food, cosmetics, paper and pulp processing, etc. In the petroleum industry, there is a significant demand of surfactants for the extraction of oils from reservoirs. Manufacturing commercial biosurfactants for the application of microbial-enhanced oil recovery (MEOR) may be achieved using renewable resource and waste materials, resulting in an economical overall process (Rufino et al. 2014; Fenibo et al. 2019; Liu et al. 2023). In addition, for the transport of crude oil through pipelines, alasan, emulsan, and biodispersan biosurfactants are used, while rhamnolipids are used for oil storage tank cleaning. Similar to oil recovery, biosurfactants are used in mining technology for the extraction of precious metals such as gold and silver (e.g., biodispersan). Furthermore, biosurfactants find their role in agriculture, where glycolipids, rhamnolipids, and lipopeptides are used for soil quality improvement, plant-microbe interaction, and pathogen/pest control. On the other hand, MEL, surfactin isoform, sophorolipids, etc. are used in pharmaceuticals for antiviral, anticancer, and antimicrobial activities, as well as immunological adjuvants and anti-adhesive agents (Fenibo et al. 2019). Several global manufacturers, including AGAE Technologies, Soliance, Jeneil Biotech, MG Intobio, Saraya, and Ecover, dominate the biosurfactant markets in Europe, North America, and Asia-Pacific regions (Sajna et al. 2015; Nagtode et al. 2023). Notably, Jeneil Biosurfactant Co., based in Saukville, USA, has made significant strides in

scaling up biosurfactant development, successfully producing up to 20,000 gallons in batch mode (Rufino et al. 2014). As per research reports, global market of these environmental friendly biosurfactants, as opposed to synthetic alternatives, reached a value of US\$1735 million in 2011, with a total production of approximately 344 kt in 2013. The biosurfactants market is expected to reach US\$1.9 billion by 2027 demonstrating a compound annual growth rate of 11.2% from 2022 to 2027. Among the different types of biosurfactants, glycolipids are the most commonly utilized, characterized by the presence of mono- or disaccharides connected to hydroxyaliphatic or long-chain fatty acids. Sophorolipids, a type of glycolipid, are extensively employed in detergents, cosmetics, and agricultural applications due to their efficient performance and cost-effectiveness. Detergents, on a global scale, represent a significant application area for biosurfactants. The substantial demand for environmentally friendly solutions and the increasing awareness among consumers and manufacturers are the primary factors driving the high demand for biosurfactant-based detergents (web source: MarketsandMarkets 2022).

8 Conclusion

There is a growing interest in using alternative adsorbents and bacterial surfactants to eliminate heavy metals, as they are readily available, have low toxicity, and are biodegradable. Microbial biosurfactants have garnered significant attention for their potential in bioremediation, and numerous studies have demonstrated their specific role in facilitating degradation. These biosurfactants are instrumental in promoting cell adhesion within biofilms, which enhances the efficiency of organic pollutant degradation. Compared to synthetic surfactants, biosurfactants exhibit superior micelle formation capabilities, possessing diverse bioactivities and are biodegradable. Consequently, biosurfactants hold great promise for industrial applications such as food processing, pharmaceutical additives, and cosmetics production. Wastes from agro-industrial origin can be directly used or modified by treatment processes to serve as raw materials for producing biosurfactants, which makes the remediation process more cost-effective. Recent advancements in biosurfactants have further expanded their noteworthy functions across diverse industries. However, there remains a crucial need to delve into and comprehend the mechanisms involved in remediating organic pollutants. This chapter highlights the potential of this integrated approach to provide a fresh perspective on removing heavy metal ions from the environment. Several types of biosurfactants, their production, and their role in bioremediation were discussed in detail. In the mixed system, micellar solubilizations of pollutants are more useful than a single micellar system. Factors such as biosurfactant concentration, types, temperature, microbial culture used, and pollutant level at the site all play a critical part in the biosurfactant-assisted bioremediation of emerging pollutants. It must be noted that very limited fieldwork has been done so far, and additional research regarding the biosurfactant behavior in the movement and/or density of soil pollutants is required. Further research is required

to discover new materials and innovative biosurfactants to ensure a sustainable environment.

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Impacts of Emerging Pollutants on Environmental Microbial Communities and Their Consequent Public Health Concerns



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Abstract Emerging contaminants (ECs) are the mirror of society's behavior and lifestyle. Despite the emerging knowledge about the presence of ECs in ecosystems, their impact has mainly been explored in animals (including humans). On the other hand, the impact of ECs on microbial communities has been disregarded to some extent. Most of the available works focused on the impact of ECs in microbial cells are directed to fluvial biofilms or wastewater microbial communities. Only a few works are focused on the effects of ECs in animal and plant microbiota and even in drinking water microbial communities. This work summarizes the possible impact of ECs in microbial communities in general, emphasizing the need to further investigate the risk of exposure of microbial communities to ECs, especially in drinking water, to predict or even prevent consequent problems for public health. Despite the variability of procedure and experimental design among the published works, it is known that specific ECs may alter microbial tolerance to antimicrobials and change microbial diversity and function in different ecosystems. However, the variations in experimental design among different studies hinder their comparison and consequently, the general conclusions about the impact of specific molecules. Moreover, the presence of mixtures of ECs with alterations in microbial behavior and biofilm characteristics cannot be disregarded. Therefore, the presence of ECs in water sources and ecosystems worldwide should be evaluated considering a "One-Health" perspective.

Keywords Antimicrobial resistance · Bioaccumulation · Biofilms · Biomagnification · Micropollutants

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1 Introduction

The current lifestyle all over the world imposes a daily dependency on a wide variety of chemicals with a large variety of structures and properties. It is estimated that globally more than 350,000 different chemicals are being produced (González-Gaya et al. 2021). These chemicals will potentially contaminate the environment as a consequence of their daily and routine use in the most varied products (pharmaceuticals, personal-care products, house-care products, pesticides, preservatives, food additives, and materials such as nanomaterials, plasticizers, and paints). Emerging contaminants (ECs) are the mirror of societal needs and may change over the years attending to new requirements, such as the replacement of toxic substances, the improvement of the properties of the existing ones, or even the need to answer to global threats, such as the recent COVID-19 pandemic. For instance, this pandemic period changed our daily routines and several products become of mandatory use worldwide, not only to protect against the virus but also to test and identify new positive cases and also to treat the infected patients (Revilla Pacheco et al. 2021). A huge increase in the production and use of hand sanitizers, chemical biocides, test reagents, specific pharmaceuticals, and masks, among others, was observed. Therefore, it will possibly be translated into a significant change in the type and amounts of chemicals that reached the environment and water sources worldwide (Revilla Pacheco et al. 2021).

The presence of ECs in ecosystems means that plants, animals (including humans), and microorganisms are exposed to a huge variety of chemicals, even at very low concentrations (ng/L or µg/L), over their entire lifetime. This exposure may result in serious toxicological consequences for the ecosystem. However, the challenges to understanding the consequences of ECs are huge and start right away with the identification and quantification of the molecules that are contaminating the environment (Simonnet-Laprade et al. 2021). The high diversity of chemicals present in the environment as well as their low concentrations constitute the main problems that hinder the identification and quantification of environmental contaminants (Snow et al. 2019). Moreover, identification and quantification are also challenging due to their high dependency on target methods of analysis, which were developed to detect and quantify known compounds (González-Gaya et al. 2021). Beyond these difficulties found in analytical methods of contaminants in different environmental matrices, the characterization of mixtures and the understanding of their impact in the ecosystem become a major challenge for ecological and human health risk assessment (Simonnet-Laprade et al. 2021).

Despite all these barriers to the identification and quantification of ECs, the contamination of the environment is unquestionable. ECs have been detected all over the world in different matrices: soil, groundwater, surface water (i.e., sea, rivers, and lakes), and even in the polar regions (Arctic and Antarctica) where they are not extensively used and produced (Nejmal et al. 2018; Duarte et al. 2021). Some of these chemicals may persist and accumulate in the environment. These two phenomena are extremely concerning and are the main ones responsible for the

accumulation of contaminants in most remote locals, such as polar regions (Mangano et al. 2017). Also, the recalcitrancy to conventional water treatments has been translated into the unavoidable presence of ECs in surface waters and in treated drinking water (tap and bottled water) (Riva et al. 2018; Lee et al. 2021; Wei et al. 2021). The scientific community has been exploring the consequences of the presence of ECs on human and environmental health in general; however, their impact on microbial communities, specifically in drinking water has been disregarded, mainly for non-pharmaceutical ECs. Therefore, this work will review the consequences of exposure to ECs for the ecosystems and specifically for microorganisms. The implementation of the “One-Health” approach is required when environmental contamination is under discussion. The One-Health approach recognizes that the health of humans is connected to the health of animals and the environment. In this case, it is of utmost importance to evaluate the impact of ECs on the environmental microbiome and their possible consequences for public health.

2 Impact of ECs on Ecosystems and Living Organisms

The continuous exposure of living organisms to ECs may result in several behavioral and toxicological problems. The main concern regarding environmental pollution is the direct consequences to humanity. It is known that exposure to some environmental pollutants may be responsible for serious problems in human health, such as infertility, diabetes, cancer, or even cognitive disorders (Kahn et al. 2020; Lincho et al. 2021). However, there is much more interaction of ECs in the ecosystem that may result in indirect serious consequences for humans. Therefore, the presence of ECs in the environment should be followed through the “One-Health” approach, to understand the consequences of ECs for living organisms and consequently the impact on organisms’ interactions and public health—Fig. 1.

To better evaluate the impact of ECs in the ecosystems and trophic chains, sentinel species have been used to get information about the presence, amount, type, and effects of ECs (Stewart et al. 2008). Sentinel species may be related to wildlife that tends to concentrate on environmental contaminants and consequently provide biologically relevant information on possible exposure effects. In addition, these species may be associated with wildlife with diets and/or physiologies like those of humans and consequently may demonstrate early indications of potential health effects of exposure to environmental levels of contaminants, predicting their effect on humans (Stewart et al. 2008). For instance, aquatic living organisms (from invertebrates to large vertebrates) have been often used as sentinel species attending to the contamination of water sources and the high dependency of ecosystems on water quality. Therefore, fish have been used as “sensors” to monitor water contamination and to early indicate contamination of the food chain. Algae have also been affected by the presence of different ECs. For example, triclosan is accumulated in *Cymbella* sp., becoming toxic to this freshwater alga (Ding et al. 2018). Also, the green algae *Pseudokirchneriella subcapitata* are predictably sensitive to the

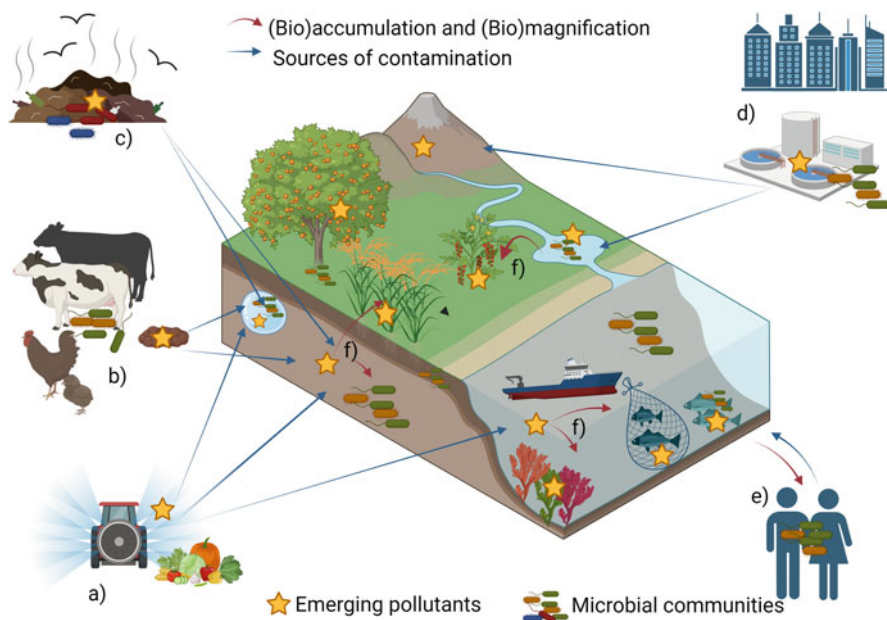


Fig. 1 The “cycle” of emerging contaminants (ECs) in the environment should be managed through a One-Health perspective. Intensive agriculture highly contributes to soil and groundwater contamination, not only due to the intensive use of pesticides and fertilizers (a) but also due to the use of veterinary pharmaceuticals in livestock activities (b). Cities with high-density populations are huge sources of ECs. ECs can reach soils and groundwater due to waste accumulation in landfills (c). Moreover, ECs and fecal microorganisms also enter WWTPs through sewage. ECs reach WWTPs and may interact with microbial communities used in activated sludge treatments (d). The removal of ECs in WWTPs is not complete, so they will reach the surface water or soil (d), when treated wastewater or biosolids are used for irrigation or fertilization of soils, respectively. Humans are the main actor in the ECs cycle; however, humans are also highly affected by ECs exposure, by eating contaminated food (crops and animals), being exposed to contaminated (recreational) water, drinking water, and using pharmaceuticals and personal-care products containing these pollutants (e). Therefore, ECs are present in surface water, which may also be used for crop irrigation (f). The presence of ECs in surface waters also results in the interaction of these contaminants with aquatic organisms (f), such as algae, microbial communities, and aquatic animals. ECs accumulation in water and also in organisms may contribute to their bioaccumulation and biomagnification (f). The presence of ECs in the soil will also affect soil microbial communities and groundwater as well as plants cultivated in contaminated soil. Therefore, ECs may also be found in plants and fruits used for human and animal consumption. (Created with [BioRender.com](https://www.biorender.com))

presence of ECs such as diclofenac, carbamazepine, atrazine, dibenzazepine, and their metabolites in freshwater (Zind et al. 2021). However, not only fishes and algae are exposed to environmental ECs, but all living organisms will contact with the widespread contaminants at some point. For instance, the presence of ECs in soil has been highly discussed mainly due to the reuse of treated wastewater for irrigation or even due to the reuse of treated biosolids/activated sludge as fertilizers (Buta et al. 2021; Singh 2021). The presence of these ECs on soil not only has a direct

interference with plants and microbial communities but may also affect groundwater quality. Several researchers have been studying the impact of the presence of ECs in soil on plants (Yang et al. 2021a, b; Wang et al. 2022). At first, pesticides were the most studied ECs under this context; however, more recently, interest in the evaluation of the effects of pharmaceuticals, nanomaterials, and metals on plants has emerged. For example, Leitão et al. (2021) demonstrated that the exposure of lettuce to three pharmaceuticals (acetaminophen, carbamazepine, and metformin) altered protein expression in lettuce roots and leaves. Carbamazepine exposure was more related to the expression of stress-related proteins in lettuce roots, such as catalase, superoxide dismutase, and peroxidase. Moreover, acetaminophen mainly altered leaves proteins related to the respiration pathways (Leitão et al. 2021). Several works have demonstrated that ECs can be translocated to different parts of plants, representing also significant alterations in plant growth and germination as well as cytotoxic and genotoxic effects (Ramos et al. 2021; Liu et al. 2022; Wang et al. 2022). This phenomenon seems to be interesting from the perspective of phytoremediation and reduction of ECs load in soil; however, it can become a public health issue when these plants are used for human and animal consumption (Buta et al. 2021). Several recent studies have demonstrated the presence of different ECs in vegetables for human consumption and related this phenomenon to their presence in soils (Bidar et al. 2020; Martínez Bueno et al. 2021; Ramos et al. 2021). For instance, recently, Liu et al. (2022) demonstrated the accumulation of nano- and microplastics in rice seedlings' roots and the consequent translocation for other plant parts, suggesting the impact of this phenomenon in the transfer of these ECs through the trophic chain. Also, Ramos et al. (2020, 2021) reported the accumulation of UV filters and synthetic musks in tomato fruits, but the hazardous quotients were determined to support the negligible risk by ingestion. Besides the impact of ECs on Animalia, Plantae, and Chromista kingdoms of life, there are other three (fungi, protozoa, and bacteria) that are also exposed to ECs in the environment and, as one can infer, the presence of ECs also affects the behavior of those organisms (Gao et al. 2015; Wang et al. 2020; Yang et al. 2021b).

3 Effect of ECs on Microbial Communities

Among the low information regarding the impact of ECs in environmental microbial communities, most of the works are focused on the effects of pharmaceutical ECs in the spread of antibiotic resistance genes (ARG) and bacteria (ARB). Fewer works are paying attention to non-pharmaceuticals ECs. Gomes et al. (2020) reviewed the effects of ECs in aquatic microbial communities, demonstrating that antibiotics, carbamazepine, and diclofenac are the most studied ECs in water microbial communities. The scientific community has been looking at the impact of some ECs in aquatic microbiomes, to understand their impact on microbial function in ecosystems. However, due to the high variability in the methodology used, it is difficult to conclude the impact of ECs on aquatic microbiota (Gomes et al. 2020). Nevertheless,

the impact of ECs on microbial function in ecosystems, as well as in their diversity has been reported. For example, Drury et al. (2013) found that triclosan reduced the microbial diversity in artificial streams biofilms. Also, caffeine and ciprofloxacin present in surface waters reduced the biofilm respiration rate by 53 and 91% (Rosi-Marshall et al. 2013). In its turn, diphenhydramine reduced the biofilm respiration rate by 63% and altered the bacterial community of biofilms (Rosi-Marshall et al. 2013). Moreover, Subirats et al. (2018) studied the impact of a mixture of pharmaceuticals in stream biofilms and observed that exposure resulted in a reduction of taxa richness of biofilms in combination with an increase of biofilm metabolic rate (Subirats et al. 2018). These studies demonstrated that, even at trace concentrations, ECs are responsible for significant alterations in microbial function in ecosystems.

The accumulation of ECs in vegetables was already discussed and presented as a low-risk phenomenon for consumers' health. However, it is mandatory to think about the impact of this exposure in microbial communities, not only in aquatic natural ecosystems but also in other contexts of exposure, such as in animals' gut (including humans) or in drinking water distribution systems (DWDS). For instance, the presence of ECs in vegetables, and possibly in DW, has been related to alterations (in microbial diversity and function) in animals' gut microbiome as demonstrated by Gálvez-Ontiveros et al. (2020), Claus et al. (2016), and by Adamovsky et al. (2018). Bioaccumulation and biomagnification are concerning phenomena that are responsible for ECs transfer across the food chain, increasing the number of organisms exposed to the same contaminant.

3.1 Impact of the Presence of ECs in Drinking Water on Microbial Communities

Regarding DWDS, it is important to have in mind the constant and unavoidable presence of biofilms in those systems. The presence of biofilms in DWDS constitutes a source of multiple problems (Simões and Simões 2013). Besides their impact on pipes corrosion and the organoleptic characteristics of delivered water, biofilms harbor microorganisms, including some pathogens. When they are detached from the pipe walls into bulk water, being transported to consumers' taps, they may be responsible for the spread of waterborne diseases (Simões and Simões 2013). Attending that DW biofilms are continuously exposed to ECs that enter DWDS, it is important to understand how this exposure affects microbial behavior and diversity, as well as further consequences for public health. The available information on this topic is very limited. To the best of our knowledge only a few recent works were focused on the impact of specific ECs in DW bacterial communities (Gomes et al. 2018, 2019a, b; Wang et al. 2019; Huo et al. 2021; Arruda et al. 2022; Pereira et al. 2023; Pinto et al. 2023). Alterations in DW microbial behavior caused by ECs are undeniable. For example, Wang et al. (2019) demonstrated that ciprofloxacin and sulfadiazine, alone, were associated with an increase in the total number of bacteria

in multispecies DW biofilms, altering also their diversity (increased the abundance of *Hyphomicrobium* and decreased the abundance of *Sphingopyxis*). Also, the exposure to these two antibiotics increased proteases and dehydrogenase production, as well as an increase in the number of copies of resistance genes. More specifically, ciprofloxacin caused an increase in *mexA* and ciprofloxacin resistance genes (*qnrB* and *qnrS*). On the other hand, sulfadiazine increased the number of sulfadiazine resistance genes (*sul1*, *sul2*, and *sul3*) (Wang et al. 2019). Moreover, when multispecies DW biofilms were exposed to ciprofloxacin and sulfadiazine simultaneously, besides the already mentioned alterations, an increase in the EPS production by biofilms was observed (Wang et al. 2019). More recently, Huo et al. (2021) found that the exposure of multispecies DW biofilms to sulfadiazine induced an increase in bacterial diversity and richness, as well as in higher dehydrogenase and EPS production. Consequently, these characteristics may result in biofilms with higher tolerance to chlorine disinfection and also may contribute to the dissemination of antibiotic resistance genes (Huo et al. 2021).

Other six studies were conducted using single and mixed species biofilms formed with *Acinetobacter calcoaceticus*, *Stenotrophomonas maltophilia*, and *Burkholderia cepacia* isolated from DW (Gomes et al. 2018, 2019a, b; Arruda et al. 2022; Pereira et al. 2023; Pinto et al. 2023). Gomes et al. (2019a) evaluated the impact of 10 ECs (mainly pharmaceuticals and musk fragrances) in planktonic and sessile *B. cepacia*, demonstrating that the presence of some ECs may hinder the disinfection efficiency of residual chlorine along DWDS (Gomes et al. 2019a). Some of the tested ECs changed the behavior of the selected bacteria; however, some of the results did not seem concerning. For example, exposure to carbamazepine or to trimethoprim-sulfamethoxazole reduced the tolerance of *B. cepacia* biofilms to chlorine treatments (Gomes et al. 2019a). On the other hand, the presence of antipyrine, diclofenac, caffeine, and trimethoprim-sulfamethoxazole seems to hinder chlorine disinfection, increasing the minimum bactericidal concentration for sodium hypochlorite. Moreover, diclofenac and galaxolide were also responsible for an increase in *B. cepacia* swarming motility, which means that in the presence of diclofenac, *B. cepacia* has a higher ability to move on solid surfaces. On the other hand, the exposure to caffeine or trimethoprim-sulfamethoxazole induced a reduction on *B. cepacia* swarming motility (Gomes et al. 2019a).

In a different study, *S. maltophilia* biofilms were exposed for 26 days to 8 ECs, individually or in combination (Gomes et al. 2018). Most of the alterations observed in *S. maltophilia* behavior resulted from the simultaneous presence of different ECs, such as the previous exposure to the combination of clofibric acid and carbamazepine which induced biofilms tolerance to sodium hypochlorite. When ibuprofen was added to this combination, it was observed that *S. maltophilia* had a lower ability to form biofilms; however, those biofilms were also more tolerant to the disinfection with sodium hypochlorite. Regarding the impact of ECs individually, diclofenac, ibuprofen, and tylosin were responsible for an increase in the ability of *S. maltophilia* to produce biofilms (Gomes et al. 2018). Clofibric acid (singly) was also responsible for significant alterations in *S. maltophilia* behavior, but only when the exposure time was increased from 26 days to 12 weeks (Gomes et al. 2018, 2019b). Among

these alterations, it is possible to highlight the rule of clofibric acid on the increased tolerance of *S. maltophilia* biofilms to sodium hypochlorite and the tolerance of *S. maltophilia* to the antibiotic erythromycin. Moreover, after being exposed to clofibric acid, *S. maltophilia* had a reduced ability to invade human gastric cells (HT 29 cell line) (Gomes et al. 2019b). In sum, the impact of single ECs cannot be representative of the impact of the same EC in a mixture (real scenario), as demonstrated by Gomes et al. (2018), and the exposure time to a specific EC may also change the impact on microbial communities, as can be inferred through the studies of Gomes et al. (2018, 2019b) and Pereira et al. (2023). A recent study by Pereira et al. (2023) also evaluated the impact of ECs (specifically parabens, non-pharmaceutical compounds, and representative of preservatives class) at different exposure times. In that study, the exposure of single- and dual-species biofilms to four parabens solutions (methylparaben, propylparaben, butylparaben (singly), and a triple combination of all—MIX) was tested at 150 ng/L (representative of parabens concentration found in DW systems) for 7 and 26 days. The results showed that a lower period (7 days) of parabens exposure was sufficient to cause modifications in characteristics of single- and dual-species biofilms composed of *A. calcoaceticus* and *S. maltophilia*. These modifications include the potentiation of biofilm cellular culturability, density, and biofilm thickness in comparison to non-exposed biofilms. Curiously, these modifications were more pronounced for methylparaben in single-species biofilms. Methylparaben exposure was also able to potentiate the virulence of *S. maltophilia* bacterial cells from single biofilms, in terms of swimming motility and protease and gelatinase production.

Pinto et al. (2023) also revealed some modifications in *A. calcoaceticus* biofilm behavior after exposure to four ECs from different categories (caffeine, carbamazepine, ciprofloxacin, and ibuprofen). Curiously, individual ibuprofen exposure at trace concentrations found in DW decreased biofilm formation ability, whereas the exposure of all previously mentioned ECs in combination increased *A. calcoaceticus* biofilm formation ability. This highlights once again, that it is impossible to predict the impact of a mixture of ECs by assessing the effects of an isolated EC. Pinto et al. (2023) also found that exposure to residual levels of ciprofloxacin for 7 days decreased the susceptibility of *A. calcoaceticus* to ciprofloxacin and levofloxacin. The exposure to ibuprofen caused also a slight decrease in the susceptibility to levofloxacin and tetracycline. These different tendencies of alterations in antibiotic resistance by ECs exposure were also detected in relation to chlorine (NaOCl) susceptibility. Ciprofloxacin and ibuprofen exposure caused an increase in the tolerance of *A. calcoaceticus* to disinfection with NaOCl. On the other hand, carbamazepine induced an increase in the biofilm susceptibility to NaOCl. Moreover, Pinto et al. (2023) also demonstrated that the growth dynamic of *A. calcoaceticus* was also affected by exposure to ciprofloxacin for 7 days at residual concentrations, resulting in higher growth rates in relation to non-exposed bacteria.

The impact of other non-pharmaceuticals ECs (musk fragrances namely tonalide and galaxolide) on the DW microbial community was also recently evaluated by Arruda et al. (2022). Tonalide musk exposure for 7 days was found to increase the cellular density and viability of dual-species biofilms of *A. calcoaceticus* and

S. maltophilia, as well as the extracellular polysaccharides content of biofilms. However, bacterial susceptibility to chlorine and the ability to form new biofilms were significantly altered by galaxolide exposure in the same conditions (Arruda et al. 2022).

Attending all these results about the impact of specific ECs from different classes, or specific combinations of them on DW microbial communities, there are no doubts that these exposures, even at trace concentrations, are changing the bacterial behavior. Alterations in microbial diversity and quantity, increase in biofilm formation, and EPS content will probably have a direct correlation on the efficacy of DW residual disinfection along DWDS but also on the biofilm dynamics and the possibility of detachment and consequently on DW quality and safety. The dissemination of ARG was also demonstrated in association with the presence of antibiotic ECs, which is also defined as a global public health concern. Moreover, the direct relationship between the presence of specific ECs and the reduced activity of residual chlorine was demonstrated. Despite the lack of information and the significant difference in experimental design among the existing works, the impact of ECs on DW microbial communities and their possible relation to future problems in DW safety and consequences for public health is real and must be prioritized.

3.2 *One Water, One Health*

One Health is a transdisciplinary initiative that intends to preserve human, animal, and environmental health through surveillance, prevention, and mitigation. One Health has as the main idea that human health, animal health, and environmental health are all innately interrelated (O'Brien and Xagorarakis 2019; Prata et al. 2022). Water is a key factor in this approach since water is the main connection between all three elements of the One-Health approach (animals, humans, and environment) as exemplified in Fig. 2. Water may play an important role in the transport and transmission of pathogens between humans, animals, and plants. Anthropogenic activities can have widespread impacts on water and consequently interfere with human, animal, and environmental health. For example, nitrate leaching from agricultural fields to surface and groundwaters used as drinking water sources may affect human and animal health. For instance, methemoglobinemia may be caused by the uptake of nitrate in excess (from DW) which is reduced to nitrite and quickly absorbed in human and animal bodies. Methemoglobinemia results in the formation of methemoglobin which replaces hemoglobin in the blood and consequently reduces the transport of oxygen in the blood. Environmental health may also be affected by nitrates in water, which may result in eutrophication. Many other health problems could be avoided when water is taken into consideration in the One-Health approach.

A similar approach can be done for ECs in water, since emerging pollutants are not completely removed from water in WWTPs or in DWTPs, they will reach the most varied organisms, including animals, humans, and plants (as exemplified in

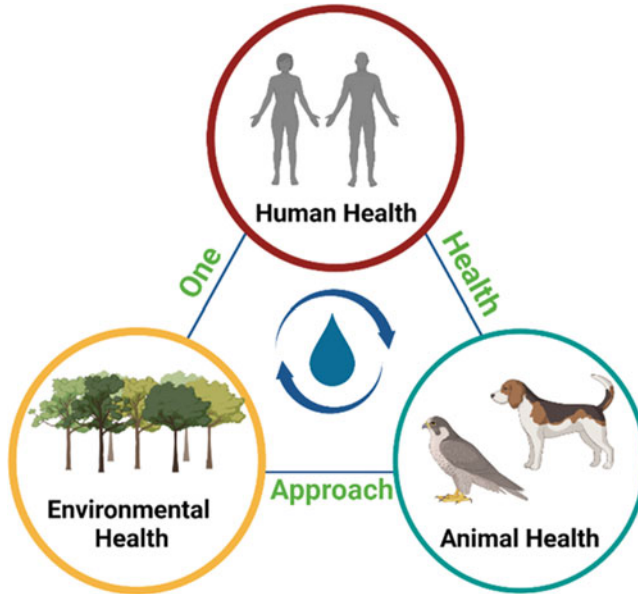


Fig. 2 Illustrative scheme of the interactions in the One-Health approach (Created with [BioRender.com](https://www.biorender.com))

Fig. 1). Therefore, their impact may be reflected in human, animal, and environmental health. Moreover, their consequences for microbial communities, such as alteration in the diversity and function of microbial communities, may cause a significant impact on animal and human health, as in the case of alteration in their natural microbial flora. Moreover, alterations in the microbial community in water bodies or soil may have consequences on the biogeochemical cycle, since aquatic biofilms have an important role in the removal of organic matter and nutrients (Yuan et al. 2023).

Additionally, exposure to specific ECs may result in the dissemination and increase of antimicrobial resistance (Alderton et al. 2021). Therefore, the dissemination of pathogens through water bodies or drinking water among animals, plants, and humans may result in infections that may be difficult to treat. These facts highlight the importance of water on public health and emphasize the need to manage water, attending that all water sources and all water uses are important and should be managed as a whole, as defended by the One-Water initiative (Fig. 3). The One-Water approach integrates each part of the water urban cycle (groundwater, surface water, drinking water, wastewater, stormwater, and recycled water) as a whole. These components are closely interconnected and will influence water characteristics in the following steps, that is, a change in the performance of one of these components/services will impact the others (Pokhrel et al. 2023). Therefore, the presence of concerning pollutants in one cycle component/service may cause consequences on the following components/services, which may also result in



Fig. 3 Illustrative scheme of One-Water approach interactions

different ecosystems (different microbial, animal, and plant communities) being affected. This approach is essential to ensure the correct use and management of all types of water resources.

4 Conclusions

The multitude of ECs simultaneously occurring in nature hinder the perception of their impact on the ecosystem. The presence of the combination of different ECs may represent antagonistic or synergic effects relative to the isolated compound. Attending to the high diversity of compounds in each ecosystem, it is difficult to simulate the reality and to predict the impact of all those ECs in the ecosystem. Moreover, the impact of non-pharmaceutical ECs in microbial communities has been disregarded and the accumulation of ECs in aquatic organisms, plants, and fruits may be the first step in the bioaccumulation and biomagnification phenomena. Additionally, the impact of ECs on the DW microbial community cannot be denied. However, the variability of experimental procedures, conditions, and design, and in most cases, the reduced similarity to reality are the main factors affecting the analysis of the impact of ECs in microbial communities. Attending to all these challenges, it is possible to understand that currently, the real impact of ECs on microbial communities and the main consequences for public health are difficult to predict. However, it is important to notice that the use of holistic approaches such as One

Health and One Water are crucial to access the global risks of ECs in water resources and reducing its impact on human, animal, and environmental health.

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