Hemen Sarma
Sanket Joshi *Editors*

Land Remediation and Management: Bioengineering Strategies

Springer

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Preface

In recent years, the growing concern over environmental pollution and its impact on human health has brought soil contamination to the forefront of scientific research and public attention. The presence of emerging contaminants, persistent organic pollutants, heavy metals, and other harmful substances in soil poses significant challenges to sustainable land management and ecosystem health. In order to address these pressing issues, innovative and efficient soil remediation techniques are urgently needed. This book aims to provide a comprehensive overview of the latest advancements in plant-based and microbial-assisted technologies for the reclamation of contaminated soil. Each chapter delves into specific aspects of soil remediation, exploring a range of strategies and applications. From the plantation-based reclamation of emerging contaminants to the biodegradation of endocrine-disrupting chemicals, this book covers a wide spectrum of topics to offer readers a holistic understanding of the field.

Chapter 1 focuses on the plantation-based soil reclamation of the emerging contaminants, highlighting the use of plants in the remediation process. Chapter 2 explores plant-based technologies for the removal of pharmaceutical and personal care products (PPCPs) from soil, shedding light on the potential of vegetation for detoxification purposes. In Chap. 3, the concept of rhizoremediation is examined as a powerful approach to address persistent organic pollutants in soil. Chapter 4 investigates the biotransformation of 1,4-dioxane, a hazardous compound, by bacteria in the soil, presenting a promising solution for its remediation. The persistence, toxicity, and strategies for remediating brominated flame retardants in soil and sedimentation in aquatic matrices under aerobic and anaerobic conditions are explored in Chap. 5, offering valuable insights into the complex challenges associated with these contaminants. Moving forward, Chap. 6 dives into the biodegradation of fungicides by bacteria in soil, while Chap. 7 explores the role of fungal enzymes in the bioremediation of environmental pollutants. Chapter 8 presents mycoremediation as a viable method for removing heavy metals and metalloids from soil, utilizing the remarkable abilities of fungi. In Chap. 9, the focus shifts to the bio-removal of analgesics and antibiotics by soil worms, uncovering the potential of these organisms in remediation efforts. Chapter 10 investigates vermiremediation, a process that employs earthworms to degrade pesticides and restore contaminated soil. The potential of biochar-assisted remediation for contaminated land is discussed in Chap. 11, highlighting the prospect and challenges associated with this innovative technique. Biomass-based engineered materials for soil remediation are explored in Chap. 12, emphasizing the importance of sustainable and eco-friendly approaches. Chapter 13 takes a closer look at the bioremediation of Asa River sediment using agricultural by-products, presenting a case study that demonstrates the practical application of such methods. The potential application of biochar for the efficient restoration of crude oil-contaminated sites is examined in Chap. 14, shedding light on the transformative power of this natural material. In Chap. 15, the focus turns to the biodegradation of low-density polyethylenes (LDPEs) using microbial consortia, offering a promising solution to address plastic pollution. Finally, Chap. 16 delves into the biodegradation aspects of endocrine-disrupting chemicals in soil, unravelling the complex interactions between these pollutants and soil microorganisms. By presenting a diverse range of topics and approaches, this book strives to foster a deeper understanding of soil remediation, encourage further research, and inspire innovative solutions to the pressing environmental challenges we face today.

We sincerely hope that this book serves as a valuable resource for researchers, scientists, environmental professionals, policymakers, and anyone interested in the field of soil remediation. Together, we can work towards a cleaner, healthier, and more sustainable future for our planet.

Kokrajhar, Assam, India Hemen Sarma
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About the Editors

Hemen Sarma earned a PhD in Botany from Gauhati University in 2008. He is currently an Associate Professor at Bodoland University. In 2022, he was elected as a Fellow of "The Linnean Society of London." Dr. Sarma's research focuses on plant-microbe interaction, microbial biotechnology, nanobiotechnology, and environmental sustainability. He has published over 100 articles in international journals, including conference papers, book chapters, and patents. He has also edited eight books. He has received several awards and fellowships for his academic contributions, including research projects sponsored by the Indian Government. Dr. Sarma has been a visiting scholar at the University of Texas at El Paso and has travelled to universities worldwide.

Sanket Joshi PhD Microbiology is currently serving as a Professor and Deputy Director, at Amity Institute of Microbial Technology, Amity University of Rajasthan, India. He served as Deputy Director Oil & Gas Research Centre (2018–2023), and an Application Specialist, Central Analytical and Applied Research Unit, at Sultan Qaboos University, Oman, from 2013–2023. Prof. Joshi has 18 years of academic research experience and 4 years of industrial R&D experience in India and Oman. His current research interests encompass energy, microbial products, and environmental bioremediation.

Prof. Joshi serves as an Academic/Associate/Guest Editor for some of the highly reputed journals and books. He was listed among the 2% of the researchers in the world, for 2022 and 2023, for excellence in scientific research in "energy" and "biotechnology" disciplines.

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1 Plantation-Based Soil Reclamation of Emerging Contaminants

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Abstract

Soil pollution with emerging contaminants such as human and veterinary pharmaceuticals, antibiotics, steroids, endocrine disruptors, perfluorinated compounds, water disinfection by-products, gasoline, industrial additives, and microplastics is one of the most persistent environmental problems, which poses a serious threat to the humans and the environment. Phytoremediation, one of the innovative strategies for remediating the soil polluted by such emerging contaminants, has been recognized as a powerful in situ approach to soil remediation. The synergistic actions of plants and their associated microorganisms can improve plant growth and enhance the biodegradation of emerging contaminants, thereby accelerating the removal of these pollutants from the soil. In view of the aforementioned discussion, this book chapter is designed to cover the plant species demonstrating higher removal efficiency of emerging contaminants from soil, explain different factors influencing phytoremediation of emerging contaminants in soil, and discuss the different fundamental mechanisms of endophyte-assisted phytoremediation of emerging contaminants. Finally, the advances, challenges, and new directions in the field of phytoremediation technology for the removal of selected emerging contaminants are also discussed.

Keywords

Phytoremediation · Emerging contaminants · Soil contamination · Constructed wetlands · Mechanism · Plant uptake

1.1 Introduction

A large array of emerging contaminants (ECs) are being recognized as a threat to the ecosystem, human health, and the environment, including water, soil, and air (Gomes et al. 2020). Pharmaceuticals and personal care products (PPCPs) such as antiseptics, fragrances, soaps, sunscreens, insect repellents, surfactants, fire retardants, plasticizers, disinfection by-products of urban and industrial origin, pesticides, industrial chemicals, and municipal waste are the primary sources of ECs into the environment (Kumar et al. 2022). Economic growth and consumer-centric lifestyle have largely contributed to the growing concern of ECs, which is likely to worsen in days to come. The use of ECs for health and general life quality is increasing globally, and complete removal from different environmental sources is almost impossible.

Hospitals, industrial-scale animal feeding operations, dairy farms, leaking sewer lines, landfills, and inappropriately disposed wastes are the primary sources of ECs, while wastewater treatment plants (WWTPs) are the main entry point into the aquatic environment in the urban water cycle (Pal et al. 2014). The pharmaceuticals such as analgesics, anti-inflammatory drugs, anti-epileptic drugs, blood lipid regulators, β-blockers, antibiotics, hormones, and cytostatic drugs are frequently encountered in surface water, groundwater, drinking water, and wastewater (Kurade et al. 2021). Different antibiotics, such as tetracycline, quinolones, penicillin, amoxicillin, and gentamicin, are widely used in livestock farming to treat diarrhea and bovine pneumonia. Increased usage of a variety of antibiotics, sulfonamide, and tetracycline group in particular also leads to accumulation of those ECs in environmental matrices, as a part of it excreted out is unaltered in urine and feces by animals. PPCPs and antibiotic traces are commonly found in sewage treatment plants with concentrations ranging from ng/L to μg/L (Chaturvedi et al. 2021). Table 1.1 provides a list of various emerging contaminants with their concentration, class, and sources.

Apart from analytical challenges for quantifying trace amounts (1–100 ng L^{-1}), ECs have gained little recognition in environmental legislative lists. With no regulatory framework, significant ecotoxicological effects of PPCPs on human health are well anticipated. An increased presence of ECs in the environment is likely to cause bioaccumulation in some organisms and biomagnification (propagated through the food chain). Lipophilic compounds or metabolites, with a log $K_{\mathrm{ow}} > 3$, tend to accumulate in the environment. Some ionophore veterinary antibiotics, gemfibrozil, ibuprofen, and diclofenac, have been known to bound to sewage sludge (Zenker et al. 2014). Pharmaceuticals can have very different bioconcentration factors depending on the aquatic environment, and relevant species when studied under environmentally relevant concentrations. The transformation product of ECs, though not extensively studied, can have even higher ecotoxicity and bioaccumulation potential (Maculewicz et al. 2022). A significant proportion of pharmaceuticals, possessing bioaccumulation potential, are not biodegradable and have a toxic effect on aquatic organisms. Bioaccumulation in aquatic organisms can have serious implications for top predators such as fish, birds, and humans (Richmond et al. 2018).

The presence of PPCPs in the aquatic ecosystem may exert a significant risk to human health and aquatic life. Though adverse effects of PPCPs on human health are not rigorously assessed, possible human health risks through ingestion of contaminated water (Pai et al. 2020) or food in the long term cannot be ignored. Negative effects of some model PPCPs, such as diclofenac, affecting the kidneys of

Table 1.1 Examples of various emerging contaminants with their concentration, class, and sources

Class	Contaminants and their concentration (ng L^{-1})	Location	References
Analgesics/anti-inflammatory drugs	Acetaminophen, 3610–119,000; ibuprofen, 300–63,000; diclofenac, 73–10,340	Hospital WWTP, South Africa	Kanama et al. (2018)
Antibiotics	Azithromycin, 26–991; carbamazepine, 10–113; estrone, 26–124; bisphenol A, <LOQ–450	Ahar River, India	Williams et al. (2019)
Antioxidants	Nonylphenols, 1519–2773; hexestrol, <LOQ-17; diethylstilbestrol, <LOQ-10; dienestrol, <LOQ-11; estrone, <LOQ-184; β-estradiol, <LOQ-62; 17α-ethynylestradiol, 4–51	WWTP, Guangdong Province, China	Jiang et al. (2020)
Antibacterial agents, disinfectants	N4-acetyl-sulfamethoxazole, 14–31; triclosan, 15–26	Wastewater, Beijing, China	Liu et al. (2020)
Analgesics/anti-inflammatory drugs	Metformin, 4–31; acetaminophen, 3–99; atenolol, <MDL–4; cephalexin, <MDL–3; norfluoxetine, <MDL–10 ng mL^{-1}	Wastewater, Saudi Arabia	Shraim et al. (2017)
Estrogen	17α-Ethinyl estradiol, 1.3–407; bisphenol A, 0.5–450; 17β-estradiol, 27–150; 4-nonylphenol, 0.3–5.4; 4-*tert*-octylphenol, 0.3–7	WWTP, Mexico	López-Velázquez et al. (2021)
Plasticizer	2-Ethylhexyl phthalate, 28–528 ng g^{-1}	Sediments, Jiangsu, China	Fan et al. (2021)

LOQ limit of quantification, *MDL* method detection limit

fish and anti-ovulation potential or antidiabetic drug metformin causing feminization of male fish, have now been established (Ambrosio-Albuquerque et al. 2021). Complications in the reproductive system; reduction in sperm count in humans; egg breakage of fishes, birds, and turtles; and structural and functional impairment of the immune system in marine animals have been attributed to acute and chronic exposure to ECs. Dietary intake of PPCP contaminated with vegetables and fruits can cause a potentially harmful impact on human health. The accumulation of PPCPs in crops irrigated with reclaimed wastewater in the long term poses a risk to human health (Liu et al. 2020). Few PPCPs are known to impact the host immune system, male fertility, and alterations in the gut microbiome, thereby impacting energy metabolism (Kumar et al. 2022). The consumption of antibiotic-contaminated foods and grains has been observed to develop antibiotic-resistant pathogens in the human body and can also aggravate estrogenic activity and immediate systemic hypersensitivity reactions (Keerthanan et al. 2021). The human risk associated with exposure to ECs is determined in terms of risk quotient (RQ), i.e., the ratio between estimated daily intake (EDI) and acceptable daily intake (ADI), and cumulative health hazard index (HI).

The EDI, body weight normalized daily intake of contaminant, is given by Eq. (1.1):

$$\mathrm{EDI} = \frac{\mathrm{CD}}{W}, \tag{1.1}$$

where D is the daily intake rate (g d^{-1}) of contaminated food/drinks containing C ng g^{-1} of EC by an individual with body weight W (kg). Then, the RQ is given as in Eq. (1.2):

$$\mathrm{RQ} = \frac{\mathrm{EDI}\left(\mathrm{ng\ kg}^{-1}\ \mathrm{d}^{-1}\right)}{\mathrm{ADI}\left(\mathrm{ng\ kg}^{-1}\ \mathrm{d}^{-1}\right)}. \tag{1.2}$$

The cumulative health HI is a reflection of the combined risk associated with each contaminant (Eq. 1.3):

$$\mathrm{HI} = \sum_{i=1}^{n} \mathrm{RQ}_i. \tag{1.3}$$

The value of RQ and HI >0.05 is considered to be a distinct human risk (Zhao et al. 2019). A recent study on screening-level risk assessment of 98 PPCPs, detected in the different water environments of India, suggested that a large proportion (47%) of the detected PPCPs possess a possible risk (RQ >1) to either aquatic species or human health. A few PPCPs with very high RQs (>1000) could potentially cause severe health concerns (Sengar and Vijayanandan 2022).

The complete removal of ECs in WWTPs is not possible. Several conventional and advanced treatment processes have been already investigated. However, low octanol/water partition coefficients of ECs make their partitioning out of the aqueous phase a significant challenge. The use of activated carbon and, to an extent, biochar has been effective for the adsorptive removal of some ECs to a moderate extent (Rodriguez-Narvaez et al. 2017). The success of microfiltration and nanofiltration technologies varies depending on the type of membrane and the characteristics of contaminants (Lidén and Persson 2015). Due to toxicity, most of the ECs cannot be utilized as a sole carbon source in the microbiological treatment process and require an additional source of electron acceptor in co-metabolism. Microalgae/fungal based treatments have been effective for PPCPs and endocrine-disrupting chemicals (EDCs) (Matamoros et al. 2015). Biodegradation in the activated sludge process is widely adopted for the removal of EDCs with excellent removal efficiency while being moderately effective against some pharmaceuticals, where adsorption plays the dominant role in the removal. The use of hybrid systems such as ozonation followed by biological activated carbon has been highly efficient in the removal of pesticides and PPCPs (Ahmed et al. 2017).

Environmental engineers have created more effective remediation techniques such as improved oxidation processes, microbial degradation, and enzymatic catalysis in response to the ineffectiveness of standard WWTPs and recalcitrant PPCPs.

However, the cost of these procedures is still debatable, preventing their use in large-scale commercial applications even though these technologies have been demonstrated to be effective and offer several benefits. Plant-based phytoremediation technologies are of immense interest due to their low-cost, eco-friendly biotic approach with low risks. The ubiquitous presence in almost every climatic region and the potential to take up organic and inorganic compounds from the soil-water system make phytoremediation a robust technology. Plants have been successfully utilized for the elimination of heavy metals and polychlorinated biphenyls from the contaminated environment (Passatore et al. 2014). Various removal mechanisms, such as phytostabilization, rhizodegradation, rhizofiltration, phytoextraction, phytoaccumulation, and phytodegradation, may be involved in the process (Wang et al. 2017).

In this chapter, the different plant species and the factors influencing the removal of emerging contaminants have been illustrated. The mechanism of the phytoremediation process and the involvement of the enzymatic system have been discussed. Appropriate modifications to phytoremediation systems have also been discussed.

1.2 Different Plant Species Demonstrating Higher Removal Efficiency of Emerging Contaminants from Soil

The plant-based bioremediation technology enables the plant to accumulate toxic substances in different parts of plants and mobilize them into plant tissues through various metabolism. The studies on molecular and physiological mechanisms of the phytoremediation process have been gaining momentum in recent years through recent engineering and biological strategies related to the optimization and augmentation of metabolic processes. Based on the availability of contaminants in different types, forms, and complexes, plants exploit different mechanisms in combination including degradation (e.g., rhizodegradation), accumulation (e.g., phytoextraction, rhizofiltration), dissipation (e.g., phytovolatilization), and immobilization (e.g., phytostabilization) to degrade, remove, or immobilize the toxic pollutants present in the soil environment. For phytoremediation, plant species are selected based on their adaptation to the regional climate, root depth, and nature and interaction with the contaminants. The ideal depth of different flora is reported as 3 ft., 10 ft., and 20 ft. for remediation using grasses, shrubs, and deep-rooting trees, respectively (Chirakkara and Reddy 2015). An ideal plant species to be employed in the phytoremediation process should possess the following characteristics: hard in nature, high biomass canopy, tolerant to toxic effects of contaminants, easy cultivation, high adsorption capacity, and non-attractive to herbivorous. Besides, the nature of contaminants is a very important factor that determines the different mechanisms and interactions with plant tissues and organs. Based on these interactions, the phytoremediation process can be described as phytoaccumulation (in plant tissues), rhizodegradation (in the root zone), and phytodegradation (metabolism in plant tissues). During metabolic disintegrations, contaminants are either degraded or transformed into other forms and get concentrated in the tissues and organs (Kafle et al. 2022) of hyperaccumulators. The plants have promising characteristics to transfer the contaminants from the root to the shoot and have capabilities of degradation, absorption, accumulation, and transfer to different parts of the plant. In recent years, phytoremediation of radionuclide-contaminated soils using different plant species through improving the soil environment by the addition of fertilizer, organic acids, or chelating agents has been reported extensively (Kafle et al. 2022).

The selection of these plants is based on their ability to survive in a different adverse climate of contaminated sites and the pollutant mobilization potential. The ideal plant used in the phytoremediation process should have the capability of mitigating oxidative stress, which is caused by the activation of the oxidation system by reactive oxygen species (ROS). However, excessive radical scavenger generation can shift the equilibrium between its production and scavenging, leading to damage of plant cells. The important enzymatic antioxidants are superoxide dismutase, catalase, and peroxidases such as ascorbate peroxidase and guaiacol peroxidase (Das and Mazumdar 2016). Besides, superoxide radicals (O_2) play the role of scavengers in the plant by converting it to hydrogen peroxide. These enzymes have the potential to cause severe oxidative stress in plants and can affect their growth and productivity (Rascio and Navari-Izzo 2011). The various physiological responses of plants used in phytoremediation under the influence of different emerging contaminant concentrations are summarized in Table 1.2.

1.3 Factors Influencing Phytoremediation of Emerging Contaminants in Soil

The type of plants and their morphology, environmental conditions, type of pollutants, and soil properties are the major factors that influence the translocation and absorption of emerging contaminants in plants.

1.3.1 Plant Species and Their Morphology

The selection of plant species and their morphological features play a critical role in influencing phytoremediation. The plant species that possess hyperaccumulation properties, high tolerance to onsite conditions, and short life cycles and plants that are easy to handle and harvest are suitable for the phytoremediation of soil. The bioaccumulation factor (BAF) determines whether the plant belongs to the hyperaccumulating species or non-hyperaccumulating species (Chaudhry et al. 2020). The BAF is determined as the ratio of pollutants accumulated in the plant species to the concentration of pollutants present in the soil (Lesmeister et al. 2021). When the calculated BAF is >1.0, it indicates that the plant species possess the ability to hyperaccumulate the pollutants present in the soil (Agarwal et al. 2022). For example, *Helianthus annus* (sunflower), *Zea mays* (corn), *Brassica campestris* (field mustard), and *Pisum sativum* (pea) are some of the hyperaccumulator plants

Table 1.2 The various physiological responses of plants during phytoremediation under the influence of different emerging pollutant concentrations

Common name	Scientific name	Contaminants	Phytoremediation method	Physiological response	References
Ryegrass	*Lolium perenne*	Halogenated flame retardants and Cd	Plant root absorption and bioaccumulation	– The plant assimilated a trace amount of dechlorane plus (DP) and tetrabromobisphenol A (TBBPA) and dissipated in soil with the help of root exudates and rhizosphere microorganisms – Total cadmium in soil was effectively reduced by ryegrass in an optimal bioremediation time of 60 days	Xie et al. (2021)
Water spinach	*I. aquatica*	Sulfamethoxazole	Absorption and accumulation in roots	Sulfamethoxazole is taken up rapidly in the roots of *I. aquatica* with an average accumulation of 18 μg g^{-1} in 24 h	Chen et al. (2017a)
Water spinach and Chinese cabbage	*I. aquatica* *B. rapa chinensis*	Tetracycline	Absorption and accumulation in roots	Tetracycline is taken up rapidly in the roots of *B. rapa chinensis* with an average accumulation of 160 μg g^{-1} in 24 h, and for *I. aquatica*, it is 18 μg g^{-1} in 24 h	Chen et al. (2017b)
Alfalfa	*M. sativa*	Sulfamethazine	Root uptake and translocation	Distribution of sulfamethazine into the root (8.58 μg kg^{-1}), top portion (1.89 μg kg^{-1}), middle portion (1.3 μg kg^{-1}), and sap (0.38 μg kg^{-1}) is done within 72 h of contact time	Kurwadkar et al. (2017)
Horemanii red sword	*E. horemanii*	Atenolol and triclosan	Root uptake and bioaccumulation	The bioconcentration factor of triclosan was 4390 L kg^{-1}, and for atenolol, 2660 L kg^{-1} was observed in 28 days; accumulation in the leaf was higher compared to the root, as leaves were submerged and having direct contact with the pollutant	Pi et al. (2017)
Common water hyacinth	*E. crassipes*		Root uptake and bioaccumulation	17β-Estradiol, 17α-ethinylestradiol, estrone, and bisphenol A accumulated in the roots in	Pi et al. (2017)

		17β-Estradiol, 17α-ethinylestradiol, estrone, and bisphenol A		28 days with average accumulation (2–150 L kg^{-1}) compared to other parts as roots were submerged in direct contact with the pollutants	
Umbrella sedge	*C. alternifolius*	Oxybenzone	Root uptake and accumulation in plant tissues	An antioxidative defense mechanism was adapted to counteract stress and biotransformation of oxybenzone into conjugates of lower toxicity and was observed in tissues after 120 h of study	Chen et al. (2017a)
Lettuce	*L. sativa*	Ibuprofen	Rhizosphere biofilm uptake and biodegradation	90% of ibuprofen was concentrated in the root with a biodegradation mechanism observed in the rhizosphere biofilm endophytic assistance in roots within a contact time of 10 weeks	Hurtado et al. (2016)

with BAF >1.0 (Eapen et al. 2007). The tolerance index (TI) is another factor that defines the ability of a plant to tolerate the pollutant concentration as well as to grow in conditions with longer periods in contaminated soil (Chaudhry et al. 2020). The TI is calculated by comparing the test plant group that is exposed to the pollutant conditions to that of the control (Samreen et al. 2021). When the TI is >1.0, it indicates that the plant can adapt to the pollutant stress conditions. On the other hand, when TI is <1.0, it indicates that the plant is under pollutant stress and cannot adapt to the polluted soil (Belouchrani et al. 2016). Therefore, it is important to select the species with higher BAF and TI values.

The plants absorb the pollutants mostly through roots, and the pollutants get translocated from the roots to the leaves, shoot, and other regions of the plant through transpiration, cohesion, adhesion, and osmosis mechanism (Madikizela et al. 2018). Plant species with a good root system (fibrous root) make more contact with the pollutants present in the soil and accumulate a higher concentration of pollutants as depicted in Fig. 1.1. The root concentration factor (RCF) for *Festuca pratense* (meadow fescue) ranges between 2 and 10 for the removal of metformin (antidiabetic drug) compared to the leaf concentration factor (LCF) due to the presence of a good fibrous root system in the plant (Eggen et al. 2011). Plant species such as *Oryza sativa* L. (rice) and *Glycine max* L. (soybeans) are known to accumulate antibiotics such as norfloxacin, oxytetracycline, and tetracycline via the root region because these species have limited translocation capacity (Bao et al. 2019; Khan et al. 2021). In contrast, certain plant species such as *Echinodorus horemanii* are known to accumulate carbamazepine, ibuprofen, atenolol, and triclosan in its leaf tissue compared to roots due to the fact that this plant belongs to submerged species and it is exposed to these pollutants through direct contact and has good translocation capacity (Bigott et al. 2021).

1.3.2 Type of Pollutants

The molecular weight, size, charge, hydrophobicity, and ratio between octanol-water coefficients (K_{ow}) and octanol air coefficients (K_{oa}), K_{ow}/K_{oa}, of the pollutant determine the translocation of pollutants in the various regions of the plant and its removal method. For pollutants such as PPCPs, the plant cell membrane lacks a specific transport system to accumulate the pollutants; rather, it is driven by the simple diffusion process (Keerthanan et al. 2021). This process mainly depends on the type of pollutants and their chemical properties such as K_{ow} and K_{oa} (Dowdy and Mckone 1997). When log K_{ow} values of the pollutant range between 0.5 and 3.5, these types of pollutants are effectively translocated and transported across the membrane through cell fluids (Rissato et al. 2015). Pollutants with lower K_{oa} values (1–3.5) are effectively absorbed and accumulated in the leaves (Zhu et al. 2020).

Highly hydrophilic pollutants such as caffeine are known to be absorbed and translocated into the roots easily by several plant species, e.g., *Scirpus validus, Elodea canadensis, and Salvinia molesta* (Hu et al. 2021). On the other hand, anionic and hydrophobic pollutants are partitioned into lipid membranes in the

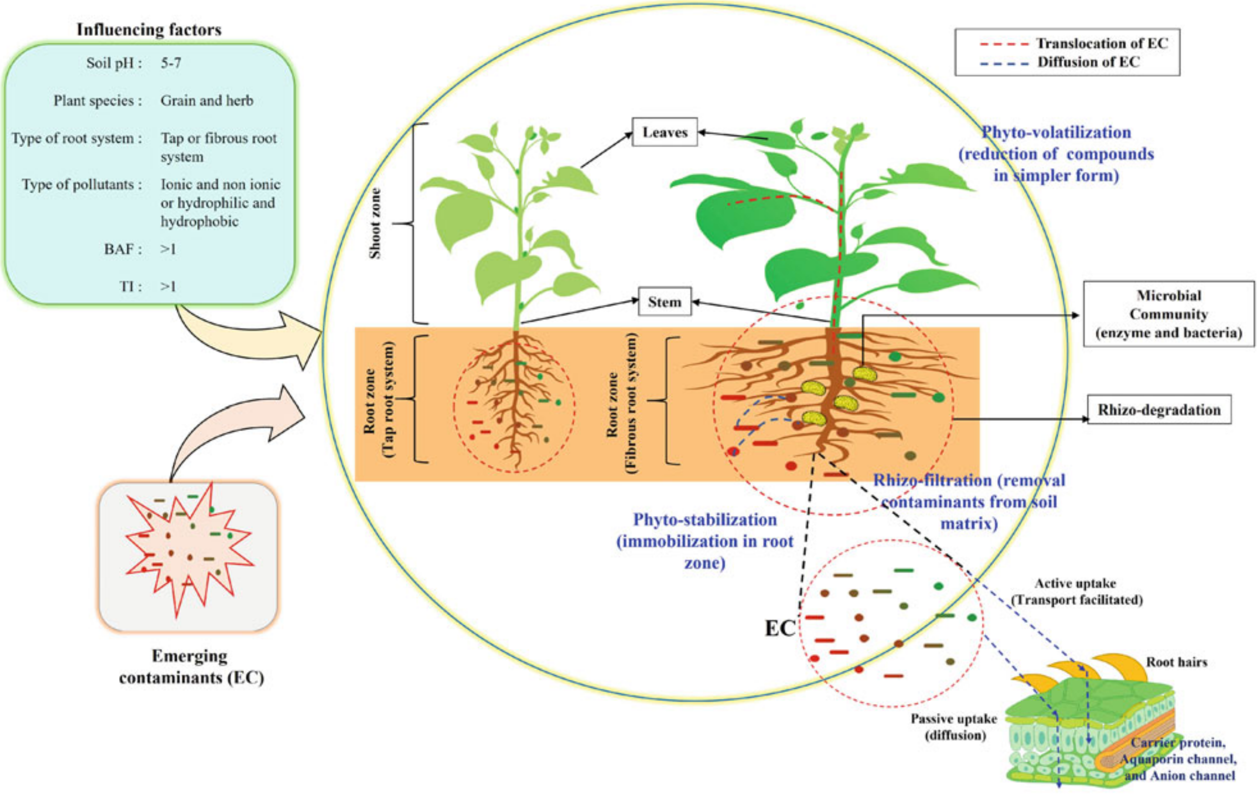

Fig. 1.1 Factors influencing the mechanism of emerging compounds in plants

root zone and are translocated from the roots. Cationic pollutants get accumulated in the leaves as they favor the translocation into other parts (Adeel et al. 2017). Nonionic contaminants are also known to be absorbed through the mechanism of chemical sorption into the membranes and cell walls of the roots (Zheng and Guo 2021). Ionic contaminants such as PPCPs are confined in the phloem and get accumulated in various tissues such as the fruit region of the plant due to the negatively charged cell wall and cytosol of the plant (Goldstein et al. 2014).

1.3.3 Environmental Conditions

Rainfall, sunlight, and temperature play a major role in seed germination and plant growth (Babu et al. 2021). Seasonal climatic variations (warm and cold season) greatly influence phytoremediation especially in tropical and subtropical regions as the conditions facilitate the removal mechanisms in plants (Cristina 2014). A temperate maritime climate zone enhances phytostabilization in plants for phytoremediation (Sherene 2010). The temperature conditions between 25 and 42 °C are known to favor rhizoremediation in the plants as they favor the growth of microorganisms that can enhance the reduction of pollutants. The microorganisms near the rhizosphere reduce the pyrene into phthalic acid in the soil for the phytoremediation to proceed (Gabriele et al. 2021). The microbial community in the roots that forms biofilm around the root zone greatly depends on the temperature conditions. However, with minor deviation from the optimum temperature conditions, the phytoremediation efficiency can significantly decrease, leading to the inhibition of plant growth (Wu et al. 2019).

Optimum rainfall or moisture content in the soil can enhance enzyme activity in the root zone. As a result, the removal of pollutants from the contaminated site becomes higher, and these conditions favor endophytic-assisted phytoremediation (He et al. 2020). In contrast to this, beyond the optimum conditions, water flooding and drought environmental conditions can harm the plant as well as the microbial community. Therefore, it is important to assess the type of plants that are suitable considering the environmental conditions for the better removal of pollutants from the soil.

1.3.4 Soil Physicochemical and Biological Properties

The pollutants can be strongly combined or adsorbed to the soil organic matter (SOM) present in the soil and can potentially reduce the availability of the pollutant for degradation since SOM is known to reduce the solubility of the contaminant (Bartrons and Peñuelas 2017; Nguyen et al. 2019). However, dissolved organic matter (DOM) is a part of SOM that increases the bioavailability of pollutants (Jayampathi et al. 2019). Pyrene bioavailability is greatly increased in the soil matrix when the DOM is present in the soil (Gabriele et al. 2021). Aged soil determines the type of organics present in the soil. Alfalfa phytoremediation studies have shown that an increase in SOM (8.5%) in the soil plays a vital role as a limiting factor for the plant (Wei et al. 2017). Even 6.3% of SOM in the soil can retain the pollutant in the soil and reduce the availability of pollutants in the soil for the plants (Chekol et al. 2002).

The soil pH values determine the availability of contaminants in the soil in neutral or ionic form. At a pH of 6.5–6.7, carbamazepine is known to be available in a neutral form, whereas sulfamethoxazole is present in an ionic form in the soil medium (Holling et al. 2012). Studies have shown that sulfamethoxazole is largely accumulated in the *Brassica campestris* (cabbage) tissue because the ionic form favors the adsorption and translocation of the pollutants from the root to the tissue (Herklotz et al. 2010).

Soil oxygenation is more important for the rhizosphere microbial community as well as for the plant tissues to take up and translocate the pollutants in the aerial parts via the root system (Zhu et al. 2019). Therefore, it is important to mix with porous soil that facilitates soil oxygenation in the soil-contaminated sites for better phytoremediation. Furthermore, the presence of nutrients in the soil can enhance phytoremediation by augmenting the growth of the microbial community as well as the biomass of plant species. These factors not only facilitate phytoremediation but also enhance the endophytic assistance to the plants for the better removal of pollutants in the soil.

1.4 Mechanisms of Endophyte-Assisted Phytoremediation of Emerging Contaminants in Soil

Phytoremediation is an inexpensive and environmentally benign solution that has attracted much attention due to its capacity to remove contaminants through biotic processes with few hazards. Plants use various techniques to eliminate toxins from the contaminated site, including phytostabilization (PS), rhizodegradation, rhizofiltration, phytodegradation, phytoextraction, and phytoaccumulation. Additionally, combinations of plants and microbes, either plant–endophytic or plant–rhizospheric relationships, are also exploited to promote phytoremediation (Kurade et al. 2021).

1.4.1 Mechanisms of PPCP Removal from Soil

PPCPs are a distinct group of contaminants of emerging concern with the innate ability to exert physiological effects on humans, even at low dosages. Most PPCPs are capable of changing biological processes in various organisms because they are unable to create physiological effects at low doses (Kar et al. 2020).

The three main biotic processes to remove organic chemicals are adsorption, bioaccumulation, and biodegradation. Furthermore, the PPCPs can reach plants in many different ways, such as through translocation and diffusion. In addition, PPCPs can diffuse through dissolved organics or enter the roots and aerial tissues in a mass stream. Plants can absorb organic pollutants from the air through their leaves and roots. Still, the roots are the primary pathway for PPCP exposure. Most PPCPs have low volatility. Thus, they are usually exposed to plants through water or soil, either passively or actively. Through either a passive or active transport mechanism, plants can absorb xenobiotic compounds into the plant vacuole along with nutrients. Most organic pollutants are thought to be absorbed via a common mechanism known as passive uptake, controlled by transpiration, except a few hormonelike chemicals (such as phenoxy acid herbicides).

The pollutants are mass-translocated upwards into the shoots, leaves, and fruits across the xylem. This is made possible by the pressure gradient created by transpiration, which is formed in the xylem. Stomata on the leaf surface require a continuous transpiration flow regulated by translocation by constant water evaporation. Water evaporation from plants generates a continuous interaction of water molecules and their adherence to xylem vessels. Osmosis is used to capture and transport water and PPCPs from the roots to the leaves, and a "transpiration–cohesion–adhesion" mechanism follows this process. Compared to xylem sap, the phloem includes a comparatively large number of dissolved organics. These important conduits are in charge of transporting the photosynthesis end products from the leaves to the roots. The contaminants' passing capacity through the endodermis cell membrane is based on the solubility of the contaminants in the aqueous phase (Kurade et al. 2021). The mechanism involved in the uptake of emerging organic contaminants through various phytoremediation processes is shown in Fig. 1.2.

The PPCPs can be potentially absorbed by the plants and have detrimental effects on the physiology and functions of the plant, with the most frequent effects on germination, and growth and development of the plant. Tetracyclines, lincosamides, β-lactams, and macrolides are hazardous to plants and their growth and development. They impair the uptake of phosphorus by numerous plant species, root activity, photosynthesis, chlorophyll content, seed germination, root length, and biomass (Bártíková et al. 2016). Table 1.3 shows the removal efficiency of different plant species for emerging compounds.

1.4.2 Biodegradation of PPCPs Through Enzyme Synthesis

Recent studies have demonstrated that enzymatic degradation is a required method by which plants remove PPCPs from the environment. Monooxygenases, cytochrome P450s, laccase, peroxidase, nitrilase, and other enzymes may be involved in the biodegradation or biotransformation of PPCPs through metabolic pathways. Phase I and II enzymes usually transform the PPCPs in plants. A terminal oxidase called cytochrome P450 (CYP) catalyzes the cleavage of a dioxygen molecule (Hurtado et al. 2016). This is one of the enzymes in the phase I group that integrates into the substrate by using a hydrogen abstraction-oxygen rebound process. These enzymes primarily carry out decarboxylation, hydroxylation, demethylation, dealkylation, epoxidation, and isomerization. On rare occasions, they can work as peroxidases in the presence of H_2O_2 and reductases in the absence of oxygen.

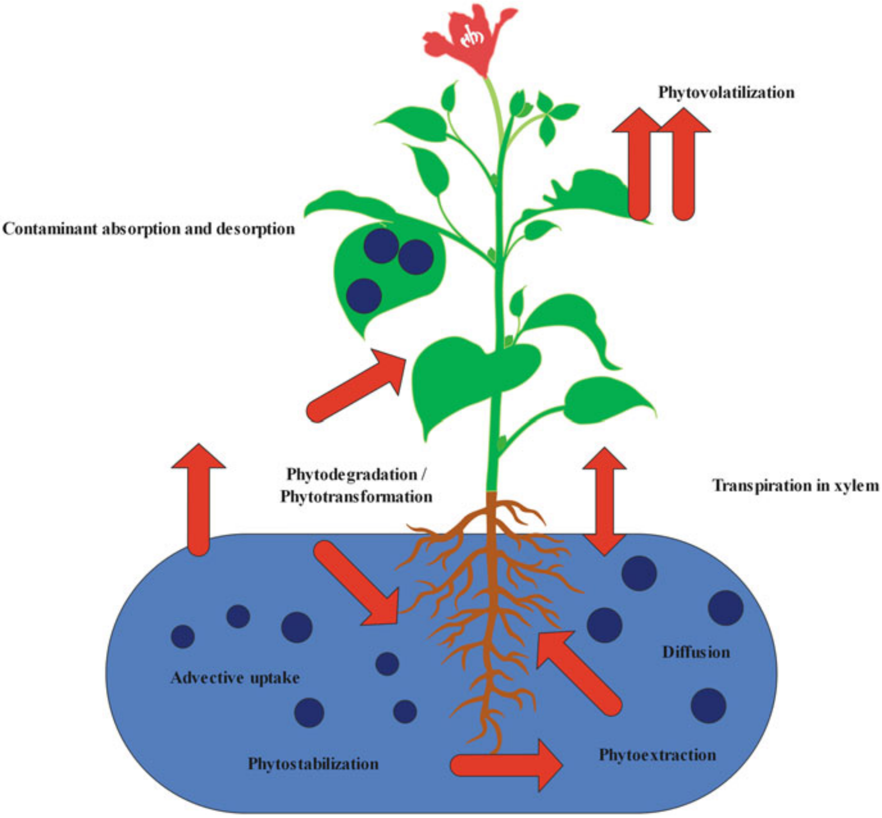

Fig. 1.2 Phytoremediation mechanism

The phase II biotransformation reactions alter PPCPs with hydrophilic functional groups to increase the polarity of the final products in phase I. Phase II metabolism in *A. thaliana* resulted in the acetylation and conjugation of the product of sulfamethoxazole hydrolysis with glutathione, glucuronic acid, and amino acids. These processes subsequently form non-extractable bound residues, which are sequestered most likely by integrating them into the cell walls or other cell components. In phase III, the conjugated metabolites are either deposited into vacuoles or bound to components of the cell wall (Kurade et al. 2021).

1.4.3 Constructed Wetland for the Removal of PPCPs

Constructed wetlands have gained popularity as a technology due to their excellent removal capacity of contaminants including PPCPs, simplicity of usage, low cost, and significant potential for recycling nutrients and water (Wang et al. 2017).

Table 1.3 Removal of emerging compounds (ECs) by plants

S. no.	ECs	EC category	Plant	Concentration (mg L^{-1})	Day	Removal (%)	Mean concentration in plants (μg g^{-1})			References
							Roots	Shoots	Leaves	
1	Sulfamethoxazole	Antibiotic	*I. aquatica*	100	1.5	NA	4.7	4.3	0.03	Chen et al. (2017a)
2	Tetracycline	Antibiotic	*I. aquatica* *B. rapa chinensis*	100 100	1.5 1.5	NA NA	28 640	4 35	9 80	Chen et al. (2017b)
3	Sulfamethazine	Antibiotic	*M. sativa*	10	5	NA	8.58	3.57	NA	Kurwadkar et al. (2017)
4	Atenolol	Beta-blocker drug	*E. horemanii*	0.002	14	NA	0.0026	NA	0.0097	Pi et al. (2017)
5	Oxybenzone	Sunscreen agent	*C. alternifolius*	50 μm	5	74	160	34	4	Chen et al. (2017a)
6	Caffeine	Psychoactive drug	*L. sativa*	0.004	70	43	0.398	NA	0.147	Hurtado et al. (2016)
7	Propranolol	Beta-blocker drug	*L. sativa*	0.004	70	75	0.393	NA	0.119	Hurtado et al. (2016)
8	Tonalide	Aromatic musk	*L. sativa*	0.004	70	61	0.587	NA	0.321	Hurtado et al. (2016)
9	Ibuprofen	Nonsteroidal anti-inflammatory drug	*E. horemanii*	0.002	14	NA	0.0005	NA	0.0025	Pi et al. (2017)
10	Triclosan	Antibacterial and antifungal agent	*E. horemanii*	0.002	18	NA	0.011	NA	0.126	Pi et al. (2017)

The free water surface (FWS) systems, one of the common techniques in tertiary treatment facilities for the removal of different pollutants from water, are composed of shallow basins with water up to 0.4 m in depth and a hydraulic loading rate (HLR) between 0.7 and 5.0 cm d^{-1}. Because vegetation and biofilms work in harmony, organic molecules are degraded aerobically close to the water's surface and anaerobically in deeper waters. It has been noted that the FWS systems have a high removal efficiency for PPCPs, such as naproxen, triclosan, and ketoprofen, as a result of exposure to sunshine (Hijosa-Valsero et al. 2010). Four FWS systems were merged and constructed using a range of vegetation, including *Glyceria maxima, Myriophyllum spicatum, Typha* spp.*, Carex* spp.*, Phragmites australis, Scirpus sylvaticus, and Schoenoplectus lacustris,* to assess the removal of 65 PPCPs. It showed normal anticipated clearance rates between 42 and 52%, which are lower than those of advanced treatment approaches (Naz et al. 2022). Although less dangerous than those treated with advanced tertiary treatments, PPCPs in water treated by FWS systems were nonetheless present. Therefore, it can be concluded that FWS systems can provide a supplemental treatment option for the treatment of PPCPs and that improved treatment technologies are required for their complete removal from wastewater.

1.4.4 Floating Treatment Wetland

Floating treatment wetlands (FTWs) are currently used to enhance water quality. FTW was first designed to improve the habitat and appearance of ornamental lakes and ponds. The FTW is made by developing emergent macrophytes with roots lying on a floating mat, which, in turn, inhabits deepwater. BOD, NH_4-N, TP, and organic contaminants are all drastically reduced in FTW systems. When roots, rhizomes, and root-bound biofilms are associated with organic pollutants, physical and biological processes transform the pollutants by filtering, entrapping, and biodegrading particulate matter. Several methods have been used to remove different PPCPs, including plant uptake, biofilm-related microbial degradation (salicylic acid, ibuprofen, galaxolide), adsorption onto particulate matter with subsequent sedimentation (tetracycline, triclosan), and photodegradation (triclosan, naproxen, ketoprofen, and diclofenac) (Hurtado et al. 2016).

The subsurface flow (SSF) systems, which are constructed using a porous media like sand, gravel, or small crushed pebbles with a typical bed depth of 0.6 m and an average HLR between 2 and 20 cm d^{-1}, are equal to a wetland of 0.5–5 ha with a flow of 1000 m^3 d^{-1}. The SSF system normally provides two configurations: vertical SSF systems and horizontal SSF systems. These systems have an integrated structure of aerobic, semi-aerobic, and anaerobic zones in the subsurface. The granular medium is traversed by the wastewater either vertically or horizontally. The aerobic zones of the SSF system, which provide oxygen to the substrate through oxidation, are represented by the surrounding region of plant roots and rhizomes. It has been amply demonstrated that SSF systems enhance the removal of BOD, COD, phosphate, and nitrogen and provide optimum denitrification conditions. In addition, by sticking to the organic material in the granular medium, polycyclic musks and other hydrophobic compounds may be successfully eliminated. Eliminating several of the regularly seen PPCPs in three separate rural horizontal SSF systems demonstrated substantial diversity (37–99% for β-blockers, 11–100% for anti-inflammatories, and 18–95% for diuretics) (Zhang et al. 2014).

1.5 Recent Advancements and Challenges in the Field of Phytoremediation Technology for the Removal of Emerging Contaminants

Recent advancements in research and challenges on phytoremediation for the removal of emerging contaminants were analyzed through bibliometric analysis. Bibliometrics is an approach to examining and analyzing the impact of research output through quantitative analysis using various computational and statistical tools. The various analyses such as citation analysis, co-citation analysis, keyword occurrences, and co-authorship analysis can be carried out using suitable software tools (e.g., VOSviewer). This analysis revealed the linkage of different articles published on different domains of phytoremediation and focused on a new dimension of future research on the phytoremediation of emerging pollutants (Narayana Prasad and Kalla 2021).

Literature on recent research on phytoremediation was collected using the Scopus database on 29th of October 2022 using the search terms "*Recent advancements AND challenges AND phytoremediation AND emerging contaminants*." The document type was restricted to research articles, conference proceedings, and review papers published during the last 5 years (2019–2023). A total of 157 articles were found to be relevant to the recent applications in the area of phytoremediation, and screening was done based on relevant information in the search areas. The bibliometric analysis of the exported data was carried out using VOSviewer software (ver. 1.6.18) developed by Leiden University, Netherlands. The keywords mentioned in a research paper provide information on which research work was carried out. Thus, keyword co-occurrence analysis is important in Scientometrics, which can help readers to get a better insight into the current research-focusing area. The collected data comprised 157 research papers including review articles. During the analysis, a total of 5051 keywords was obtained, out of which 351 keywords met the threshold limit (set as a minimum of occurrences of the term to 5). The keywords were further screened to remove the irrelevant occurrences, and a final map was created (Fig. 1.3). The constructed map can be understood in such a way that the size of the circle reflects the weightage of the occurrence, and the nodal color illustrated the different cluster (e.g., red, blue, and green) appearing in the research area. The transition in the cluster color is represented as the evaluation of different research domains of phytoremediation. The red color cluster, having the largest network, showed the major research development on phytoremediation research work in the past 5 years. These research areas included the development of genomics and metabolomics including plant–microbes interaction study, and bioaugmentation.

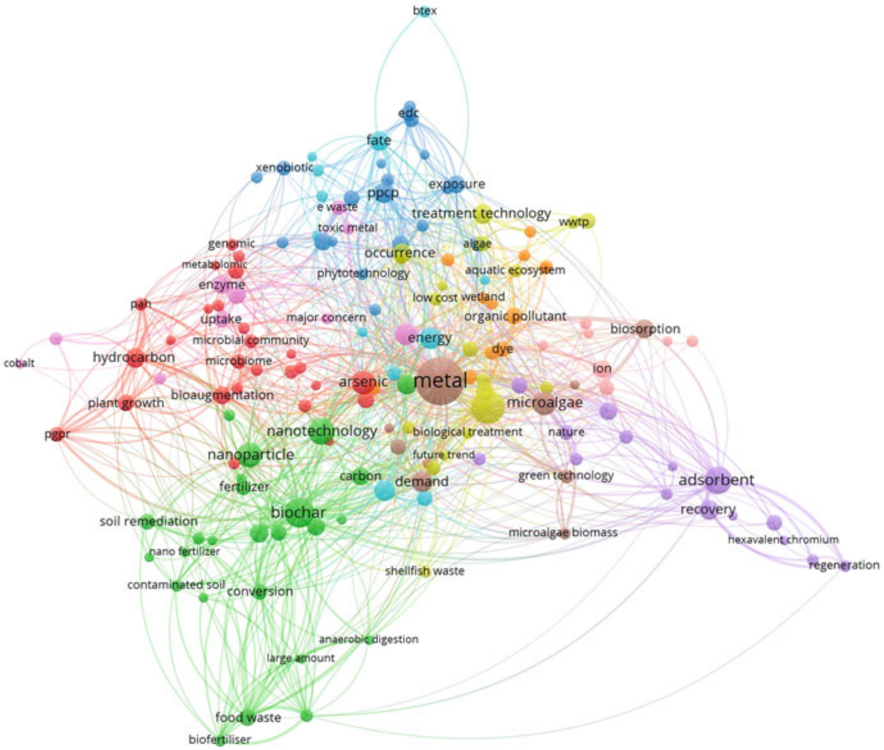

Fig. 1.3 Co-occurrence network visualization map of the key terms appeared during the search of advance research on phytoremediation in ScienceDirect (search terms: Recent advancements AND challenges AND phytoremediation AND emerging contaminants)

The green color cluster represents the research focus on the application of nanotechnology and soil amendments with biochar for enhancement of the phytoremediation process. Besides, the purple color cluster represents the recent application of microalgae in the area of phytoremediation as green technology.

In the recent times, sustainable genetic engineering has been playing an important role in the area of phytoremediation technology to cope up with the situation arising due to the advent of industrial revolution and resulting pollution. The research on phytoremediation techniques is focusing on various aspects of combinatorial genetic engineering tools in which the cluster repeats of spaced palindromic (CRISPR)-Cas9 have showed a greater potential for site-specific expression regulation and provide a new insight on plant functional genomics. The gene editing in plant growth, promoting rhizobacteria (PGPR) using the CRISPR-Cas9 technique, has improved the synthesis of bioactive compounds with simultaneous increase in biomass production, tolerance to pollutants, transportation, accumulation, and detoxification of critical pollutants (Naz et al. 2022). The CRISPR-Cas9 technique is recognized as a modern way to increase the potential of genotypes to perform phytoremediation.

Hyperaccumulator-based phytoremediation technologies have been improved successfully through the application of genetic engineering, which is known as "genoremediation," to overcome the limitation associated with the traditional way of toxin removal from soil. Thus, tremendous efforts have been made in recent years in the area of gene expression-derived transporters/enzymes, and molecular mechanisms have been exploited for augmentation of "genoremediation" of environmental contaminants (Rai et al. 2020). It has also been investigated that the molecular mechanism of phytoremediation and gene manipulations through overexpression of metal chelator and transporter genes resulted in the increase of plant biomass and reduced oxidative stress/phytotoxicity (Rai et al. 2019).

In addition, incorporation of omics tools such as metagenomics, metatranscriptomics, and metabolomics has remarkably revolutionized the potential of phytoremediation in recent years. A remarkable progress has been made using the next-generation sequencing (NGS) tool, as cutting-edge research through expression of alkB gene coding for alkane monooxygenase and CYP153 gene for P450 alkane hydroxylase in *Dietzia* genome, leading to phytoremediation of PHA (Alonso-Gutiérrez et al. 2011). The molecular and genetic prospects of copper accumulation in a hyperaccumulator plant of *Brassica napa* through the expression of ATPase gene system have also been investigated (Zhang et al. 2019).

Several broad-spectrum insecticides such as chlorfenapyr have been classified as hazardous materials and pose substantial risk to the reproductive ability of birds and threat to the environmental stability. Nowadays, integrated green and nanotechnology is focusing on eco-friendly phytoremediation of these toxic recalcitrant compounds and to overcome the challenges associated with the sustainable environmental management of plants used in phytoremediation. Besides, the green synthesis of Fe- and Ag-based nanoparticles is involved in the extraction of toxic compounds both as a stabilizer and as a reducing agent (Romeh et al. 2020). This approach is simple, eco-friendly, nonhazardous, economic, and time efficient and involves coating with natural organic compounds. The fast and efficient removal of chlorfenapyr using a combination of *Plantago major* and green nanoparticles of F-Fe^0, Ip-Ag^0, and Br-Ag^0 supported by activated charcoal has been investigated (Romeh et al. 2020). The effect of solubility-enhancing agents (e.g., SiO_2, argal, and ethanol) has been monitored and found effective for enhanced phytoremediation. Thus, these strategies can also be considered as an eco-friendly and cost-effective alternative approach to traditional remediation technologies for detoxification of contaminated soil.

Anew, biochar preparation is considered as an active research domain under environmental management of phytoremediation plants. Calcium silicate-coated nZVI/biochar composite (BOS) has been prepared using an industrial waste, and phytoremediation technique is employed for As(V) removal (Tan et al. 2022). In this way, the toxicity risk of BOS is greatly reduced compared to the toxicity of raw material. In addition, microalgae-based bioremediation technique has been emerging as a potential alternative in recent years and has been employed for the removal of a variety of toxic chemicals including PPCPs, pesticides, heavy metals, and oil-contaminated sites from water streams (Bhatt et al. 2022).

1.6 Conclusion

In recent years, phytoremediation technology has been proven as an environmentally benign, economically feasible, and sustainable remediation option for the removal of ECs from the soil matrices. Phytoremediation in combination with microbial remediation can be considered an eco-friendly technique as the microorganisms support the plant tolerance that overcomes toxicity in the form of less toxic form. The research on phytoremediation is focusing on plant genomics and proteomics approaches for improvement in the bioremediation potential of plants. The recent challenges, opportunities, and prospects in the area of phytoremediation of ECs lie in the improvement of plant stability and extraction efficiency through genetic engineering, microbial assistance, and chelation support approaches. With the help of molecular tools, adaptive phytoremediation ability can be improved in the current global conditions.

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Plant-Based Technologies for the Removal of Pharmaceutical and Personal Care Product (PPCP) in Soil

2

Şana Sungur

Contents

Abstract

The increase in people's living standards has also led to an increase in the use of pharmaceuticals and personal care products (PPCPs). Pollution caused by unmetabolized or partially metabolized PPCPs has emerged as a serious danger in recent years. This pollution can be carried to soil, underground waters, wastewater, and even drinking water in cases where serious treatment is not done. Removal of the pollution does not take place as soon as the participation of the pollutant in the nature; it takes much longer. Phytoremediation is a general name given to the technology of removing pollutants using plants, and there are many

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different technologies under this name. Phytoremediation is much more economical than traditional physical and chemical treatment methods and has many technical and environmental advantages. This review summarizes current information on the sources and transport of PPCPs, phytoremediation and its types, advantages and disadvantages, factors affecting the phytoremediation process, and removal of PPCPs in soil by plants.

Keywords

Pharmaceuticals and personal care products (PPCPs) · Soil · Environment · Phytoremediation · Plant-based technologies

2.1 Introduction

Nature and the environment are also affected by the negativities that arise as a result of industrialization, the development of technology and population growth, and the size of pollution that is increasing rapidly day by day. Soil pollution, which is a type of environmental pollution, appears to be a serious problem all over the world. As a result of soil pollution, the physical, chemical, biological, and geological structure of the soil is deteriorated (Menteşe 2017). Pharmaceuticals and personal care products (PPCPs) are also one of the important factors that play a role in these deteriorations. Since PPCPs are abundant in household, industrial, and hospital wastes, they cause pollution in both soil and water resources (Nguyen et al. 2019; Bhattacharyya et al. 2022).

A wide variety of methods are used to remove PPCPs from the environment. Advanced technologies are used in most of these methods, which necessitates the need for trained personnel as well as high investment and operating costs (Morone et al. 2019). However, phytoremediation is an environmentally friendly, cost-effective, and easy-to-apply new method used to remove both organic and inorganic pollutants from the environment by plants (Muszyńska et al. 2020). Today, the use of phytoremediation technology is becoming more and more widespread. Generally, plants suitable for accumulating pollutants in their roots and stems are preferred. Plants remove pollutants from the environment through various natural biophysical or biochemical processes such as adsorption, transport, hyperaccumulation, and transformation (Chandra and Kumar 2018).

In this chapter, current information on the sources and transport of PPCPs, phytoremediation and its types, advantages and disadvantages, factors affecting the phytoremediation process, and removal of PPCPs in soil by plants will be shared.

2.2 The Sources and Transport of PPCPs

PPCPs are a broad group of medicines, personal hygiene products, cosmetics, and household chemicals (Arias 2019). The intensive use and unconscious disposal of PPCPs, whose varieties and numbers are increasing day by day, have been a serious concern in recent years (Liu and Wong 2013; Chacon et al. 2022). Half-lives of PPCPs are short. However, they are included in the so-called pseudo-persistent class because they are continuously discharged into the environment, albeit in low concentrations (Yang et al. 2020). Degradation times in the environment vary depending on their chemical structure and metabolic process (Chen et al. 2015). The classification of PPCPs based on their purpose and properties is shown schematically in Fig. 2.1 (Perez-Lemus et al. 2019).

Medical and personal waste, sewage, industrial and agricultural activities, aquaculture studies, veterinary uses, and livestock urine and feces are the main sources of PPCPs (Keerthanan et al. 2021). Pharmaceuticals are biologically active compounds and are excreted from the body without being fully metabolized (Bottoni and Caroli 2018). Pharmaceuticals excreted from both human and animal bodies through urine and feces cause water and soil pollution (Tasho and Cho 2016). Personal care products, on the other hand, are dispersed to the environment through sewage without undergoing any metabolic changes (Yang et al. 2017). Domestic, industrial, and hospital wastewater discharged into sewage systems is treated by passing through various physical and biochemical processes. Treated urban wastewater is

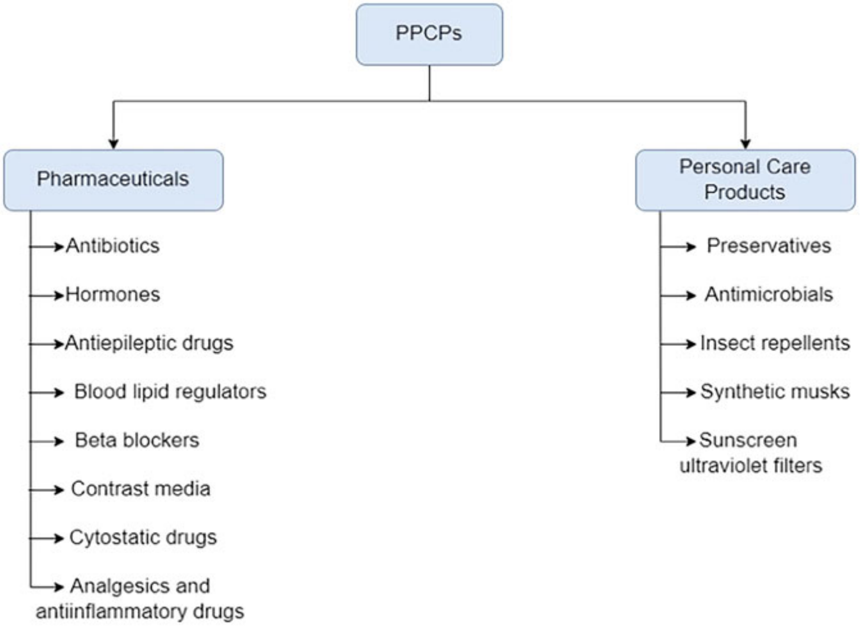

Fig. 2.1 The classification of PPCPs based on their purpose and properties

considered among the best sources of irrigation water for sustainable water management due to its high volume, applicability, and well-known quality characteristics (Can Doğan et al. 2016). In addition, the obtained sludge is used as a fertilizer. However, PPCPs found in these sources and which cannot be removed with conventional systems at sufficient rates are released into the environment (Wang et al. 2018). Studies have shown that PPCPs are found in concentrations ranging from ng to μg in the effluent and the resulting treatment sludge after treatment (Bartrons and Penuelas 2017; Rosman et al. 2018).

PPCPs can accumulate in water and soil environments, as they generally dissolve easily in aqueous environments and do not evaporate at normal temperature and pressure (Wang et al. 2019). They can leak from the soil and mix with groundwater and drinking water, causing serious pollution (Shraim et al. 2017). They can also enter the food chain when they are in the soil for a long time and are not biodegradable (Bhattacharyya et al. 2022). Since the number and types of PPCPs are very large, their behavior in the environment also differs. Their behavior is influenced by their physicochemical properties and environmental conditions (Xing et al. 2016). Environmental distribution of PPCPs with low volatility, high polarity, and hydrophilic character occurs primarily through aqueous transport, and they are rapidly dispersed into the environment (Dhir 2022). Hydrophobic ones prefer to accumulate in soil or sediments (Caliman and Gavrilescu 2009; Ebele et al. 2017).

2.3 Phytoremediation and Its Types

Phytoremediation is derived from the words "phyto" meaning plant and "remediation" meaning improvement and entered the terminology in 1991. It is also called bioremediation or green remediation (EPA (Environmental Protection Agency) 2000). With the phytoremediation method, organic and inorganic substances can be removed from the area where they cause pollution by using plants (Misra and Misra 2019). The main reason for using plants for cleaning the soil is to convert the impurities held by the soil into a more controllable and portable form by accumulating in the roots, stems, and leaves of the plant (Bhandari 2018; Can 2020). Remediation methods used to remove organic and inorganic pollutants from soil are shown schematically in Fig. 2.2.

There are six types of phytoremediation methods: phytoextraction, phytostabilization, phytovolatilization, rhizodegradation, phytodegradation, and rhizofiltration. The phytoextraction (phytoaccumulation) method is based on the principle that especially inorganic pollutants are taken from the soil by the plant roots, transported to the aboveground parts (stem and leaf) by moving within the plant tissues, and stored there (Pedron et al. 2021). Phytoextraction is a method mostly used to remove metals from contaminated soils. Since plant growth cannot be sustained in heavily polluted areas, it can be applied to areas with low or moderate metal pollution (Terzi and Yıldız 2011). The plant to be used in the phytoextraction method should have a high tolerance to heavy metals, have high biomass per hectare, show rapid growth, store heavy metals in the leaves, and have a strong and extensive

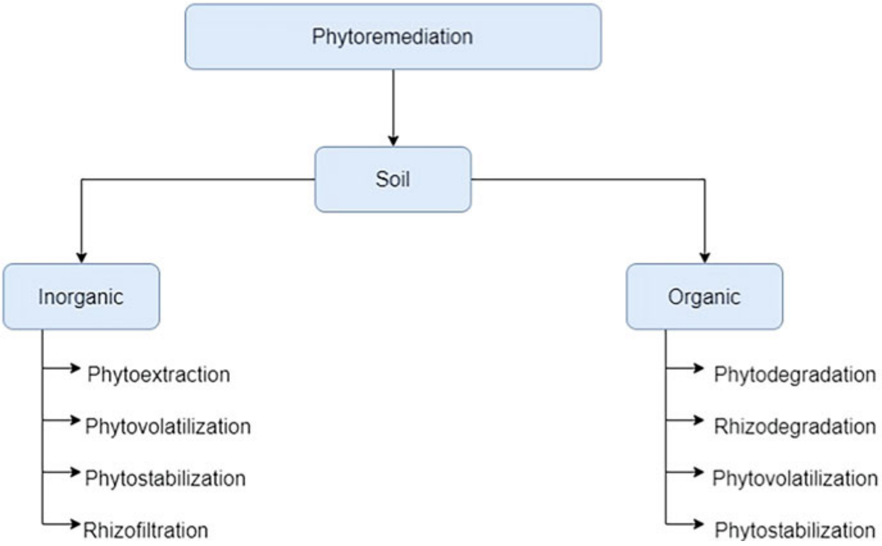

Fig. 2.2 Remediation methods used to remove organic and inorganic pollutants from soil

root system (Jadia and Fulekar 2008; Ijaz et al. 2016). The harvested plant can be used for biogas production, or it can be burned to recover heavy metal. The main advantages of phytoextraction are that it is environmentally friendly, does not cause any damage to soil quality, is inexpensive, and permanently extracts toxic pollutants from the soil (Etim 2012). Because the process is controlled by plants, it takes longer than traditional soil-clearing processes. This is the disadvantage of the method (Ali et al. 2017). The process of limiting the movement of pollutants in the soil with the help of plants is called phytostabilization or phytoimmobilization (Hrynkiewicz et al. 2018). Immobilization of pollutants is achieved by their deposition by the roots, their adherence to the surface of the roots, or their precipitation in the root zone of the plant. This technique is used to prevent erosion, reduce the pollutant load in groundwater, and prevent direct interaction with contaminated soil (Schwitzguebel et al. 2011). It is an important advantage that it does not require soil transportation. Its main disadvantage is that the pollution remains in the soil. Fertilization and soil improvement studies are needed to ensure maximum stabilization efficiency. Root depth is also extremely important for the efficiency of the system (Grzegorska et al. 2020). Phytovolatilization occurs in two ways, direct and indirect. In direct phytovolatilization, organic and inorganic pollutants are absorbed by the plant roots and then transported along the shoots and released into the atmosphere during the transpiration process of the leaves. This process is also called phytovolatilization for short. Phytovolatilization depends on the physical properties of pollutants such as polarity, solubility, and hydrophobicity. Volatile compounds with high solubility in water can be easily removed. Furthermore, root depth of plants is also very important in this method (Pedron et al. 2021; Limmer and Burken 2016). In indirect phytovolatilization, an increase in the amount of volatile pollutants removed by increasing the activities of plant roots is provided. The activities of plant roots can be increased by methods such as chemical transport by hydraulic redistribution, increasing soil permeability, advection with water towards the surface, lowering the water table (Limmer and Burken 2016). The most important advantage of the phytovolatilization method is that many toxic compounds such as mercury compounds can be converted into less toxic forms. However, releasing very harmful or toxic substances into the atmosphere is also a disadvantage (Farraji et al. 2020). If the degradation takes place by microorganisms or by the effect of plant roots, this event is called rhizodegradation (Kafle et al. 2022). Microorganisms take pollutants into their body with the help of root system after their chemical structure has changed. This association keeps microorganisms at an optimum level for them to continue their vital activities and ensures the continuous breakdown of toxic pollutants. Thus, microorganisms in the soil break down organic pollutants and accumulate them in their bodies (Naeem et al. 2020). Plant roots activate sugars, alcohols, and organic acids as sources of carbohydrates for the soil microflora. Thus, they increase microbial formation and activity (Dominguez et al. 2020). The biggest advantage of rhizodegradation is that the pollutants are destroyed in the natural environment. However, they are transported to plants and the atmosphere, albeit to a lesser extent (Aybar et al. 2015). Compared to phytodegradation, rhizodegradation provides a very rapid purification due to the microbial community association (Farraji et al. 2020). Phytodegradation is also called phytotransformation. The basic mechanism in this method is the uptake of organic pollutants by plants and their metabolization in the plant structure (Spaczyński et al. 2012). Plant enzymes such as dehalogenase, nitroreductase, peroxidase, laccase, and nitrilase play an active role in the metabolism of pollutants (Asante-Badu et al. 2020). The incorporation of organic compounds into the plant is affected by the type of plant, the residence time of the pollution in the soil, and the physical and chemical structure of the soil (Arıkan 2021). The most important advantage of the method is that reduction or degradation takes place in the plant in line with physiological events and is not dependent on microorganisms. The disadvantages of the method are that toxic intermediates and end products can be formed during deterioration and their detection is very difficult (Sharma and Pathak 2014). Depending on the abiotic, biotic, and filtration processes with the roots, the process of taking the pollutants into the structure of the roots or keeping them on the plant roots is called rhizofiltration. During these processes, pollutants can be taken to the plant and transported. The pollutants can then be removed from the plant in different ways. The plants to be used in this method must have advanced root systems that act as filters (Kristanti et al. 2021). Rhizofiltration method is generally applied for metals and mixed wastes (Galal et al. 2018). It is an advantage of the system that it allows the use of terrestrial and aquatic plants. In addition to its applicability in natural environments, the system can also be applied in artificial areas such as pools, tanks, and ponds. The most important disadvantages of this method are the need for a constant pH range and placing the plants in the rhizofiltration system after they are grown in a greenhouse. In addition, periodic harvesting and plant disposal are required (Sharma and Pathak

Table 2.1 Some of the plants frequently used in phytoremediation studies

Application	Plants	References
Phytoextraction	Indian mustard (*Brassica juncea*), sunflowers (*Helianthus annuus*), grass (*Cynodon dactylon*)	Rathore et al. (2019); Alaboudi et al. (2018); Gajaje et al. (2021)
Phytostabilization	Phreatophytic trees, grasses (*Bromus tomentellus, Chloris virgata, Calamagrostis epigejos)*	Ferro et al. (2013); Roohi et al. (2020); Mishra et al. (2020); Teodoro et al. (2020)
Phytovolatilization	Giant reed (*Arundo donax* L.), annual beard grass (*Polypogon monspeliensis*), reed (*Phragmites australis*)	Guarino et al. (2020); Ruppert et al. (2013); Miguel et al. (2013)
Rhizodegradation	Sesbania (*Sesbania cannabina*), Cucurbits (*Cucurbita sp.*), Chinaberry tree (*Melia azedarach*)	Maqbool et al. (2012); Ely and Smets (2017); Kotoky and Pandey (2020)
Phytodegradation	Red mangrove *(Rhizophora mangle* L.), willows (*Salix viminalis*), broadleaf cattail (*Typha latifolia* L.)	Sampaio et al. (2019); Clausen et al. (2017); Papadopoulos and Zalidis (2019)
Rhizofiltration	Water hyacinth *(Eichhornia crassipes*), duckweed (*Lemna minor*), water lettuce (*Pistia stratiotes*)	Kodituwakku and Yatawara (2020); Singh et al. (2021)

2014). Some of the plants frequently used in phytoremediation studies are shown in Table 2.1.

2.4 Advantages and Disadvantages of Phytoremediation

Phytoremediation has become a highly preferred method today because it is a natural method that provides cleaning of the soil and has many advantages. The main advantages of phytoremediation are as follows:

- It is much easier to implement than physicochemical technologies.
- It does not require special equipment during the application.
- It is effective in many organic and inorganic pollutants.
- It does not require specialized personnel.
- It can fight the reaper pollutant at the same time.
- The cost of breeding is much cheaper compared to other technologies.
- It allows the reusable area of application.
- It reduces erosion of soils.
- When the maintenance and renewal of the plants are done regularly, the system has a very long life.
- The spread of pollution to the environment is very low in on-site applications.
- It has an aesthetic appearance, creates habitat, and restores ecological function (Ekta and Modi 2018; Mohammed and M-Ridha 2019).

Phytoremediation also has some disadvantages. The effectiveness of the system is limited by root depths and climatic conditions. In heavily polluted areas, plants do not show their effectiveness in a short time. Phytoremediation takes longer breeding time compared to other breeding methods. Since the survival and growth of plants are affected by soil and climatic conditions, it cannot be applied in every environment. It is not suitable for all compounds. The use of plants that are not in the ecosystem of the application area may adversely affect biodiversity (Chaudhry et al. 2002; Aybar et al. 2015; Ekta and Modi 2018).

2.5 The Factors Affecting the Phytoremediation Process

It is of great importance to consider the factors affecting phytoremediation in the successful application of the phytoremediation method. The main factors affecting the phytoremediation process can be listed as follows:

- Physical and chemical properties of pollutants (such as solubility in water, octanol water distribution coefficient, vapor pressure)
- Environmental characteristics (such as temperature, pH, organic structure, soil moisture content)
- Plant characteristics (such as root system, plant types) (Srivastav et al. 2018)

2.5.1 Physical and Chemical Properties of Pollutants

Chemical properties of pollutants such as hydrophobicity and volatility affect their movement in the soil. Hydrophobicity is expressed by the octanol-water distribution coefficient (log K_{ow}). Pollutants with high hydrophobicity also have high log K_{ow} values. Hydrophobic molecules (log K_{ow} >3) are tightly bound to the organic structure of the soil and do not dissolve in the water in the soil pores (Huang et al. 2004). The volatility of the pollutant is expressed by Henry's law (H_i) and shows the tendency of the compound to disperse in the air relative to water. Pollutants with a H_i value greater than 10^{-4} have a tendency to move in air spaces between soil particles. Those with a H_i value of less than 10^{-6} tend to move in water and can be broken down by phytodegradation. Those with a H_i value between 10^{-4} and 10^{-6} can move both in air and in water. They can also pass from the soil to the atmosphere via transpiration stream (Zand and Hoveidi 2016). The extent to which substances in the environment enter living organisms is expressed by bioavailability. The bioavailability of pollutants is affected by environmental conditions, soil structure, biological activity, and chemical properties of pollutants (Gourlay-France and Tusseau-Vuillemin 2013). By making some improvements in the soil, the uptake of pollutants by the plants can be increased. For example, the bioavailability of hydrophobic molecules can be reduced by adding organic matter to the soil, or the bioavailability of pollutants can be increased by adding surfactant. Since organic compounds can be in more or less protonated forms at different charges, the solubility of pollutants can be changed by changing the pH of the soil. This affects the uptake of pollutants by the plant (Biswas et al. 2018). Uptake of organic and inorganic pollutants by plant roots differs. Since the majority of organic pollutants are man-made, plants perceive these substances as xenobiotics. For this reason, they do not have carriers in plant membranes, and they tend to enter the plant by simple diffusion. Differences in root structure, biomass, transpiration, and growth rates of plant species differently affect the biochemistry of the soil environment and microbial community. It is preferred that the plants to be used in the phytoremediation of organic pollutants are fast growing, durable, and tolerant to pollution and have a wide root structure and high biomass (Chen et al. 2019).

2.5.2 Environmental Characteristics

The texture of the soil affects the bioavailability of the pollutants. Since clay soils have smaller particle structure and higher exchange capacity compared to silty and sandy soils, the bioavailability of pollutants in soils with high clay content is lower (Brady and Weil 2016). Soil moisture and temperature affect microbial activity (Kim et al. 2012). In soils with low moisture content, both microbial activity losses occur and plants become dehydrated. In soils with high moisture content, the movement of air and gases in the soil is prevented and anoxic zones are formed as a result of deterioration in which anaerobic microorganisms are dominant (Schimel 2018). Oxygen transfer from the root to the plant varies depending on the type of plant. Herbaceous wetland plants convert carbon dioxide, which their leaves absorb through photosynthesis, into oxygen and then carry them to the roots and then to the rhizosphere (Faußer et al. 2016). They also support bacterial populations in the rhizosphere, which can aid in the degradation of organic pollutants. Unlike wetland plants, woody plants have a weak capacity to transport oxygen from the leaves to the root (Dong et al. 2016). Temperature affects the speed of the mechanisms involved in phytoremediation. At temperatures between 10 and 40 °C, every 10 °C increase in temperature increases the rate of microbial degradation two times (Wright et al. 1997). Both plants and rhizosphere microorganisms need nutrients to survive and grow in contaminated soils. The main nutrients required are macronutrients (such as carbon, nitrogen, phosphorus, potassium), micronutrients (such as calcium, magnesium, sulfur), and trace nutrients (such as manganese, zinc, iron, cobalt, copper) (Zand and Hoveidi 2016). Fertilization is applied in order to supplement the missing nutrients in the soil. For this purpose, organic fertilizers containing nitrogen, phosphorus, or potassium and carbon dioxide fertilizers are used (Wu et al. 2017). The amount of fertilizer to be used in fertilization processes is also very important. Studies have shown that excessive fertilizer application reduces phytoremediation efficiency (Xiong et al. 2012). In addition, it has been determined that the use of carbon dioxide fertilizers in phytoremediation increases the resistance of plants to pollution and improves plant biomass (Tang et al. 2003).

2.5.3 Plant Characteristics

Plant species selection is extremely important for the successful implementation of the phytoremediation process. The plant characteristics to be considered can be listed as follows:

- It should be resistant to the climatic conditions of the area where the pollution is located.
- It should be able to tolerate pollution.
- It should be resistant to the pH and salinity of the soil.
- It should grow fast.
- It should have a broad root structure.
- It should be resistant to drought and poor drainage conditions.
- It should have the capacity to take up and transport pollution.

In addition to these, it is necessary to evaluate whether it is evergreen, sold commercially, and domestic (Ghavzan and Trivedy 2005; Laghlimi et al. 2015).

2.6 Removal of PPCPs in Soil by Plants

2.6.1 The Factors Affecting Uptake of PPCPs by Plants

Since PPCPs are a large group, their physicochemical properties vary. Accordingly, the log K_{ow} values are also different. Hydrophilic ones have low K_{ow} values (between 1 and 4), while hydrophobic ones have high K_{ow} values (>4). As a result, hydrophilic PPCPs tend to pass into the plant, while hydrophobic ones tend to stay in the soil (Colon and Toor 2016). PPCPs with a half-life of more than 14 days are taken up by plants, while those with a half-life of less than 14 days are degraded (Bondarenko et al. 2012). The organic carbon content of the soil is also effective on the degradation of PPCPs. Soil absorption of PPCPs is increased in soils with high organic carbon content. Therefore, their bioavailability is reduced (Li et al. 2013). PPCPs with a molecular weight of less than 1000 g mol^{-1} are easily absorbed by plant roots (Zhang et al. 2017). PPCPs can be acidic, basic, or neutral (Ohoro et al. 2019). Acidic PPCPs decompose in aqueous media and form anions and undissociated acids. Since the cell membranes of plants have negative electrical potential, they repel anions and thus anions are difficult to be taken up by plants. Basic PPCPs dissolve in aqueous media and form neutral and cationic molecules. Cations are easily taken up by plants as they will be attracted by the negative electrical potential in plant cell membranes. Neutral molecules pass through plant cell biomembranes faster than charged molecules because the bioaccumulation of charged molecules is reduced by the roots (Guasch et al. 2012).

Plants absorb organic pollutants from the air through their leaves and from the soil through their roots (Kurade et al. 2021). Because PPCPs generally have low volatility, they are transported from the soil to plants by being absorbed by plant roots (Zhang et al. 2017). Plants carry the nutrients they receive from the soil through their roots to the upper parts with active and passive transport mechanisms (Brundrett et al. 2018). In active transport, biochemicals are transported from a region of low concentration to a region of high concentration. Therefore, chemical energy is needed. In contrast, in passive transport, biochemicals are transported from a region of high concentration to a region of low concentration. Therefore, there is no need for chemical energy (Trapp and Legind 2011). It has been determined that plants carry organic pollutants in the same way as nutrients, and they generally use the passive transport mechanism in this process (Madikizela et al. 2018). Molecular sizes of PPCPs taken from the soil by plants are highly effective on their transport mechanisms. While PPCPs with small molecular size easily pass through cell membranes and are transported to upper tissues via the xylem, those with large molecular size show resistance (Kvesitadze et al. 2015). Basic PPCPs have a larger translocation factor than acidic and neutral ones. Therefore, they are more easily transported from the roots towards the leaf tissues (Dodgen et al. 2015; Sungur 2022).

2.6.2 Uptake of PPCPs from Soil by Plants

Studies have shown that PPCPs from contaminated soils are taken up by plants and carried to the upper parts of the plant. People are exposed to these substances, which pose a health risk, especially as a result of the transfer of PPCPs to edible plants. Therefore, there are many studies on this subject. Some of these studies are summarized in Table 2.2.

2.6.3 Remediation Methods Applied to Remove PPCPs in Soil

Studies showing that PPCPs pass to edible plants have formed the idea that they can also pass to plants that are not consumed as food. Subsequently, an increasing number of studies have begun to be conducted on the removal of PPCPs, which cause soil and water pollution, by plants. These studies have shown that more than 100 PPCPs can be removed. However, most of the work on this topic is concerned with the removal of PPCPs from aqueous media (Topal et al. 2018; Li et al. 2020a, b; Mohammed et al. 2021; Deng et al. 2022; Maldonado et al. 2022). The number of studies on the removal of PPCPs from the soil is currently very limited. Some of these studies were carried out under hydroponic conditions in soilless environments, and some of them were carried out in greenhouses (Carvalho et al. 2014). Hydroponic studies can provide insight into plant-soil interactions regarding PPCP uptake, but hydroponically grown plants have physiological differences compared to soil-grown plants (Miller et al. 2016; Kurwadkar et al. 2017). Some studies carried out in recent years on the removal of PPCPs by plants in both hydroponic and greenhouse conditions are briefly mentioned below.

Table 2.2 Uptake of PPCPs from contaminated soil by edible plants

PPCP	Plant	Concentration range in plant (μg g^{-1})	References
Atenolol, ciprofloxacin, metformin, minocycline, norfloxacin, naproxen, glyburide, sulfamerazine, penicillin G, triamterene, trimethoprim	Tomato, carrot, potato, sweet corn	2×10^{-5}–0.014	Sabourin et al. (2012)
Triclosan	Cucumber, radish	Up to 5.2×10^{-3}	Prosser et al. (2014)
Triclocarban	Carrot, green pepper, tomato, cucumber	Up to 5.7×10^{-3}	Prosser et al. (2014)
Carbamazepine, diclofenac, fluoxetine, propranolol, sulfamethazine, triclosan	Radish, ryegrass	0.01–65.26	Carter et al. (2014)
Carbamazepine, meprobamate, dilantin, naproxen	Lettuce, spinach, cabbage	3×10^{-5}–1.4×10^{-3}	Wu et al. (2014)
Carbamazepine, diclofenac, acesulfame lamotrigine, ciprofloxacin, benzotriazole, gabapentin, acridone	Potato, lettuce, carrot, zucchini, cabbage, pepper, eggplant, tomato, parsley, rucola	$3.8.10^{-3}$–0.216	Riemenschneider et al. (2016)
Diclofenac, sulfamethoxazole, trimethoprim	Tomato	3.4×10^{-3}–0.012	Christou et al. (2017)
Acetaminophen, antipyrine, propranolol, carbamazepine, trimethoprim, venlafaxine	Tomato	3×10^{-4}–2×10^{-3}	Martinez-Piernas et al. (2019)
Tetracycline, tylosin, norfloxacin, oxytetracycline, sulfamethoxazole, sulfamethazine, chlortetracycline, erythromycin, enrofloxacin, ciprofloxacin	Peanut	7×10^{-5}–0.023	Zhao et al. (2019)
Atenolol, carbamazepine, triclosan	Lettuce, radish, maize	1.8×10^{-3}–0.424	Beltrán et al. (2020)
Sulfamethoxazole, triclosan, ibuprofen, chloramphenicol, sulfamethazine, trimethoprim	Eggplant, wheat, cucumber, long bean	2×10^{-5}–0.028	Liu et al. (2020)

Adesanya et al. (2021) investigated the phytoextraction of ciprofloxacin (CIP) and sulfamethoxazole (SMX) by cattail (*Typha latifolia L*) and switchgrass (*Panicum virgatum L*) under hydroponic conditions. They stated that after a 21-day growth period, cattail takes up 34% of ciprofloxacin and 20% of sulfamethoxazole, while switchgrass takes up 10% of both antimicrobial drugs. Furthermore, they emphasized that it would be beneficial to carry out a similar study in non-hydroponic conditions, and the results may be different. Gahlawat and Gauba (2016) examined the phytoremediation potential of *Brassica juncea* for aspirin and tetracycline under hydroponic conditions. The study was continued for 28 days for aspirin and 24 days for tetracycline. Phytoremediation rate of *Brassica juncea* was determined as 90% for aspirin and 71% for tetracycline. Zhang et al. (2016) investigated whether four different plants (*Typha, Phragmites, Iris, Juncus*) could remove ibuprofen and iohexol in hydroponic culture. The plants were grown in the greenhouse until they reached a length of 200 mm and then transferred to glass vessels containing culture solution. Ibuprofen and iohexol were added to the culture solution. After a 24-day study, ibuprofen was almost completely removed by all plant species studied. Iohexol could be removed between 13 and 80% depending on the plant species. *Typha* and *Phragmites* plants removed both pharmaceuticals with the highest efficiency. Pierattini et al. (2016) studied the erythromycin uptake potential of *Populus alba Villafranca* under hydroponic conditions. They continued the study for 28 days, and 0.01, 0.1, and 1 mg L^{-1} erythromycin was poured into the Hoagland's nutrient solution. The results obtained showed that erythrosine was found in all organs of the plant. They stated that more erythrosine was detected in the root of the plant compared to the leaves in all three applied erythrosine concentrations.

Lei et al. (2022) studied the use of *Phragmites australis, Typha angustifolia,* and *Juncus effusus* in the phytoremediation of micropollutants. The plants were grown in pots containing gravel in greenhouse conditions for 6–9 weeks. During this period, they applied 300 mL of the mixture solution containing 8 μg L^{-1} of each micropollutant (trimethoprim, metoprolol, benzotriazole, carbamazepine, propranolol, sulfamethoxazole, furosemide, mecoprop, diclofenac, and irbesartan) three times. Based on the results they obtained, they stated that *Typha angustifolia* and *Juncus effusus* have higher tolerance to the micropollutants they examined compared to the *Phragmites australis*, and they can be used successfully in the phytoremediation of these pollutants. Bhatt and Gauba (2021) investigated the tetracycline removal potential of basil (*Ocimum basilicum*) from the soil in a greenhouse environment. Basil plants were grown in plastic pots containing 1 kg of soil and grown at 36 °C, with 12 h of light and 12 h of darkness, by watering twice a week. 200, 400, and 600 mg kg^{-1} tetracycline was poured into the soil in the pot. After 4 weeks, the highest remediation capacity (97%) was detected in plants exposed to 200 mg kg^{-1} tetracycline. Basil exposed to 400 mg kg^{-1} tetracycline showed 77.8% remediation capacity, while basil exposed to 600 mg kg^{-1} tetracycline showed 67.7% remediation capacity. Martins and Teixeira (2021) investigated whether the *Solanum nigrum* L. plant could be used to clean sites contaminated with paracetamol. After germinating the plants, they were transferred to containers containing vermiculite:perlite (2:1). They continued the study for 4 weeks and added 0.25 and 0.5 mg L^{-1} paracetamol to the dietary supplement. They stated that the applied paracetamol concentration did not make a difference on plant growth but caused differences at biochemical and molecular levels. As a result, they emphasized that the *Solanum nigrum* L. plant can be used to clean paracetamol pollution, but plants with higher tolerance should also be examined. Li et al. (2020a, b) investigated the phytoremediation of tetracycline-group antibiotics (tetracycline, oxytetracycline, chlortetracycline) from contaminated alkaline soils using *Mirabilis jalapa* L. and *Tagetes patula* L. plants. They continued the study in a greenhouse environment for 4 weeks. The antibiotics were applied to the soil, where the plants were located between 0.5 and 2 mg kg^{-1}. They found that both plants removed 99% of tetracycline-group antibiotics. Zhang et al. (2019a, b) examined the suitability of *Bougainvillea spectabilis* for the removal of galaxolide (HHCB) from contaminated soils. *Bougainvillea spectabilis* seedlings were planted in pots containing 1 kg of soil, and 50 and 100 mg kg^{-1} HHCB was applied to the soil. The study was continued for 6 weeks. Furthermore, some of the pots were ventilated with ambient air, while others were exposed to high CO_2 levels (750 and 950 μL L^{-1}). Based on their results, they stated that *Bougainvillea spectabilis* is an extremely suitable plant for removing HHCB even from contaminated soil under high CO_2.

2.7 Conclusion

Soil has an important place in the food chain. In addition, it is home to vegetation and many species of living things. The most important feature that distinguishes the soil from air and water ecosystems is that it is more resistant to pollutants. However, in case of soil pollution, removing the pollutants from the soil and returning the soil to its former structure are much more difficult and costly than other systems (Mishra et al. 2016). Anthropogenic activities cause an increase in soil pollution day by day. Traditional methods used to clean the soil are expensive as well as destroy the environment (Dhanwal et al. 2017). Phytoremediation is an innovative, cost-effective, and green environmental biotechnology that uses plants to clean contaminated areas (Bansal and Wani 2022). Nowadays, plants are frequently used to remove or render harmless pollutants in soil, water, and air. In order for the polluted environment to be successfully cleaned by plants, first of all, it is necessary to determine the characteristics of the environment, which pollutant it is contaminated with, and which plants will be more successful in cleaning this pollutant (Malik et al. 2015).

There are many studies on phytoremediation in the literature. However, the majority of these studies focused on the removal of heavy metals from the environment by plants (Nikolić and Stevović 2015; Mahar et al. 2016; Zhang et al. 2019a, b; Yan et al. 2020). Recently, studies on the removal of PPCPs from the environment by plants have also started. However, as mentioned in Sect. 2.6.3, most of them are for the removal of PPCPs from aqueous media. The number of studies on the removal of PPCPs from the soil by plants is very few, and these studies are carried out in a laboratory or greenhouse environment. As a result of the examinations, it has been seen that there is an important gap in the literature that needs to be filled in this regard. Considering the plant diversity, there are many studies that can be carried out. Particular attention should be paid to actual field studies because actual field conditions differ from laboratory and greenhouse environments (Ali et al. 2013). Phytoremediation applied in actual areas is affected by many factors such as temperature, precipitation, humidity, plant pathogens, nutrients, uneven distribution of pollutants, and changes in soil type and pH (Ji et al. 2011).

Although the mechanisms of uptake of PPCPs by plant roots are known, there are still some unclear aspects regarding the transport of both PPCPs and their metabolites into plant tissues (Kurade et al. 2021). A large number of studies on the phytoremediation of PPCPs in soil are needed to both clarify the uncertainties and fill the gaps in the literature. It is also of great importance that these studies be carried out as interdisciplinary because it is necessary to have knowledge in a wide variety of fields such as plant biology, ecology, soil chemistry, and microbiology. As a result, it can be said that phytoremediation techniques are one of the most effective and innovative techniques to be used in order to significantly reduce the pollution caused by PPCPs, which are widely used all over the world, and the number of studies on this subject should be increased.

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Rhizoremediation of Persistent Organic Pollutants (POPs) from the Soil

3

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Abstract

Persistent organic pollutants (POPs) are highly toxic chemical substances infiltrated into the environment due to rapid innovation of new products for personal and industrial use. POPs have unique characteristics, such as rapid bioaccumulation, biomagnification, and transport, causing irreversible damage to our ecosystem. Significantly, these pollutants jeopardize organisms survival by affecting all ecological components, including soil, air, and water. The existing physical and chemical eradication methods of POPs are expensive and are not cost effective. Therefore, eco-friendly and sustainable alternative technology is urgently required. Rhizoremediation, along with various potential approaches like the addition of nanoparticles, charcoal, and compost, is shown to be promising in eliminating POPs from the environment. Some other approaches like a transgenic plant and genetically modified microorganisms are also promising, effective, and eco-friendly, which are still under research and development for the remediation of POPs.

Keywords

POPs · Rhizoremediation · Assisted rhizoremediation · PAHs · OCPs · PCBs

3.1 Introduction

The rapid growth of industries and human-related activities have all contributed to the worsening of the environment, considered a major problem in recent decades. The paper and pulp, pharmaceutical, textile, leather, agrochemical, and petroleum industries are the most important because they have improved our lives although polluting the environment as a whole. As mentioned earlier, pollution generated due to anthropogenic activity has contaminated the land, which has resulted in a loss of soil quality and productivity. The drying of rivers, holes in the ozone layer, and increased global warming are some other consequences of environmental pollution. This could be the reason that the ecosystem gradually lost its equilibrium. The impact of land pollution was severe, and as a result, we have lost many floras and faunas. It has been repeatedly observed to endanger living organicism by causing natural disasters such as landscapes, floods, droughts, earthquakes, storms, tornadoes, and acid rains.

Several studies show that persistent organic pollutants (POPs) have been released into the environment at an alarming rate in recent years. According to the United States Environmental Protection Agency (EPA), “POPs have a global impact on human health and the environment because POPs can be transported by wind and water, and contaminated soil. They have the potential to have an impact on people and wildlife far from where they are generated and released” (USEPA 2002). POPs were defined by Hanedar et al. (2019) as “organic compounds of natural or anthropogenic origin that are resistant to photolytic, chemical, and biological degradation and thus persist in the environment for long periods" (Hanedar et al. 2019). Examples are polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and organochlorine pesticides (OCPs) that are the primary persistent organic pollutants in the environment (Neale et al. 2015). According to the Stockholm Convention 2019 report, the environment contains 28 most robust and hazardous POPs. Pesticides (chlordecone, lindane, aldrin, dieldrin, chlordane, toxaphene, endrin, hexachlorobenzene, dichlorodiphenyltrichloroethane (DDT), mirex, and heptachlor), industrial chemicals (hexachlorobutadiene, polychlorinated naphthalenes, and polychlorinated biphenyls), and byproducts (polychlorinated dibenzo-para-dioxins, and polychlorinated dibenzofurans) are among them (Stockholm Convention—Home page n.d.). These chemicals remain in the environment for a long time after being introduced into nature due to their bioaccumulation and slow biodegradation in natural environment. According to Gaur et al. (2022), many POPs, such as PCBs and OCPs, are used in developing Asian countries for agricultural, industrial, and vector control purposes. In India, approximately 87,000 tonnes of pesticides, primarily malathion and hexachlorocyclohexanes, are used yearly (Gaur et al. 2022). These POPs are in the soil due to a lack of facilities, managements, and concerns to remove and clean them up (Sarma et al. 2016). They coexist in soil by influencing soil polarity, molecular structure, soil-microbial community, solubility, hydrophobicity, pH, and other factors (Gaur et al. 2022; Varjani et al. 2017). Humans develop immunogenic, carcinogenic, mutagenic, genotoxic, and teratogenic health problems when exposed to these pollutants through ingestion, inhalation, or dermal routes (World Health Organization 2020). The characteristics and health effects of various POPs are listed in Table 3.1.

According to Tiwari et al. (2016), physical, chemical, and thermal remediation strategies have been developed and implemented to address this global issue. These include conventional methods like flocculation, incineration, membrane separation, filtration, reverse osmosis, solvent extraction, chemical precipitation, electrodialysis, ion exchange, electrochemical treatments, alkali metal reduction, gas-phase chemical reduction, and dumping (Saravanan et al. 2020). Many advanced technologies have been developed in recent years but consume too much energy, are too expensive, are not selective enough, become clogged, produce too much slime, or affect nearby resources (Sarwar et al. 2017).

Some existing biological remediation procedures are gaining popularity due to their numerous benefits, such as high-quality, cost-effective, and environmentally friendly services, particularly for removing POPs from the environment (Jeevanantham et al. 2019). Phytoremediation is derived from the Greek prefix phyto, which means plant, and the Latin word "remediation," which means to repair or eliminate (Jeevanantham et al. 2019). Thus, phytoremediation is a green and sustainable method that uses plants to remove, stabilize, and degrade POPs via hydrolysis, redox, and compartmentalization (Malik et al. 2022). This method has a minor impact on the environment. According to Jeevanantham et al. (2019), the critical components of phytoremediation are phytostabilization, phytovolatilization, phytodegradation, phytoextraction, and rhizoremediation. Despite the fact that plants help with this technique, combining it with the influence of microbes provided

Table 3.1 Characteristics and consequences of some different types of POPs

POPs	Chemical formula	Application/source of origin	Effect	References
Aldrin	$C_{12}H_8Cl_6$	Used as pesticides	Malaise, hyperexcitability, myoclonic jerking, and gastrointestinal disease	Honeycutt and Shirley (2014)
Chlordane	$C_{10}H_6Cl_8$	Used as broad-spectrum insecticides	Tremors, stomach pain, and convulsion	Koshlukova and Reed (2014)
DDT	$C_{14}H_9Cl_5$	Used as insecticides	Tremors, vomiting, endocrine disruption, and seizures	Burgos-Aceves et al. (2021)
Dieldrin	$C_{12}H_8Cl_6O$	Used as insecticides	Liver damage, headache, vomiting, irritability, and dizziness	CDC (2017)
Heptachlor	$C_{10}H_5Cl_7$	Used as insecticides	Liver damage, endocrine disruption, and seizures	CDC (2017)
Mirex	$C_{10}Cl_{12}$	Used as insecticides	Liver damage, abdominal pain, anemia, nausea, and vomiting	Waters et al. (1977)
Polychlorinated biphenyls	$C_{12}H_{10\text{-}n}Cl_n$ $(1 \leq n \geq 10)$	Applied as heat-exchange fluids, capacitors, and also additives in paint and plastic	Endocrine disruption, suppressed immune system, and hepatic damage	Buha Djordjevic et al. (2020)
Polychlorinated dibenzo-p-dioxins	$C_{12}H_nCl_mO_2$ $(0 \leq n \geq 7;$ $(1 \leq m \geq 8))$	Formed as byproduct during pesticides manufacture	Endocrine disruption, liver damage, hyperpigmentation, and chloracne	Akinola et al. (2021)
Alpha-hexachlorocyclohexane	$C_6H_6Cl_6$	Used as insecticides	Liver damage, headache, vomiting, seizures, and dizziness	Chen (2014)
Chlordecone	$C_{10}H_{10}O$	Used as insecticides	Hepatotoxicity, endocrine disruption, and neurotoxicity	Multigner et al. (2016)
Polychlorinated naphthalenes	$C_{10}H_nCl_m$ $\{(0 \leq n \geq 7;$ $(1 \leq m \geq 8)\}$	Applied as wood preservatives and coatings of electrical wires	Liver and central nervous system damage, suppressed immunity, and endocrine disruption	Fernandes et al. (2022)

Lindane	ClCH (CHCl)$_4$CHCl	Used as insecticides	Liver and central nervous system damage, and endocrine disruption	Zhang et al. (2020a, b)
Pentachlorobenzene	C_5HCl_5	Applied as fire retardants, used in PCBs and fungicides production	Headache, coughing, liver and kidney damage	Linder et al. (1980)
Dicofol	$C_{14}H_9Cl_5O$	Used as pesticides	Immunological, neurological, and reproductive disorders	Salcedo-Bellido et al. (2022)
Hexachlorobutadiene	C_4Cl_6	Used as solvent, and for making rubber compounds	Immunological, neurological, and liver disorders	ATSDR (2014)

us with greater efficiency; this is how rhizoremediation technology was developed (Sarma et al. 2017). Rhizoremediation is a subset of phytoremediation that involves the biodegradation of organic pollutants in the rhizosphere by selective plants or plants that grow naturally on polluted soil where microbes assist the plants in accelerating the rhizoremediation process (Thijs and Vangronsveld 2015). Microbial activity in the rhizosphere improves plant mineral absorption and water absorption, promotes plant growth, protects against pathogens, and causes plant roots to release secondary metabolites used by microorganisms to break down pollutants (Hoang et al. 2021). In this sense, rhizoremediation is a symbiotic relationship between plants and microorganisms.

A plant-microbe meta-transcriptomic study published recently discovered that POPs' degradation genes expressed in the rhizosphere were primarily associated with bacteria. As a result, the bacteria that degrade POPs through rhizoremediation are thought to be the most important rhizosphere microorganisms (Correa-García et al. 2018). Rhizoremediation is accomplished through three processes, according to Oberai and Khanna (2018): biosurfactant production, organic acid synthesis, and biofilm development (Oberai and Khanna 2018). Both abiotic and biotic factors also influence rhizoremediation in the natural environment.

Recent research has focused on increasing the rate of degradation of POPs through various strategies. This chapter focuses on how different assisted rhizoremediation strategies can help remove POPs from the environment and how they work together. Furthermore, various enhancing strategies and rhizoremediation challenges are addressed (Fig. 3.1).

3.2 POPs in Soil

Pollutants can infiltrate the environment in either a natural or an anthropogenic activity, but either way, their continued presence is detrimental to both human and environmental health (Fuller et al. 2022). According to the Indian Environment (Protection) Act of 1986, a pollutant is "any solid, liquid, or gas that is present in such a way that it may be harmful to the environment or tends to be." This definition covers POPs that have the potential to harm the environment. POPs are a class of hazardous compounds that have been dumped into the environment at an alarming rate in recent decades. POPs are semi-volatile and poisonous and are released into the environment due to excessive use of agrochemicals, industrial chemicals, and fossil fuels and their inappropriate disposal (Hanedar et al. 2019; Ukalska-Jaruga et al. 2020). Since the middle of the eighteenth century, the industrial revolution has contributed to the steady but consistent release of POPs into the environment. The wind carries the vast majority of POPs from its source point to further distant sites, where they are deposited in the soil and water (Evangeliou et al. 2020). POPs can enter the atmosphere in one of the two ways: either by a single hop or by multiple hops. Once there, they can accumulate in the ground through precipitation and condensation and contaminate the soil (Evangeliou et al. 2020). Because of their large surface areas and long retention times, the majority of POPs are able to remain

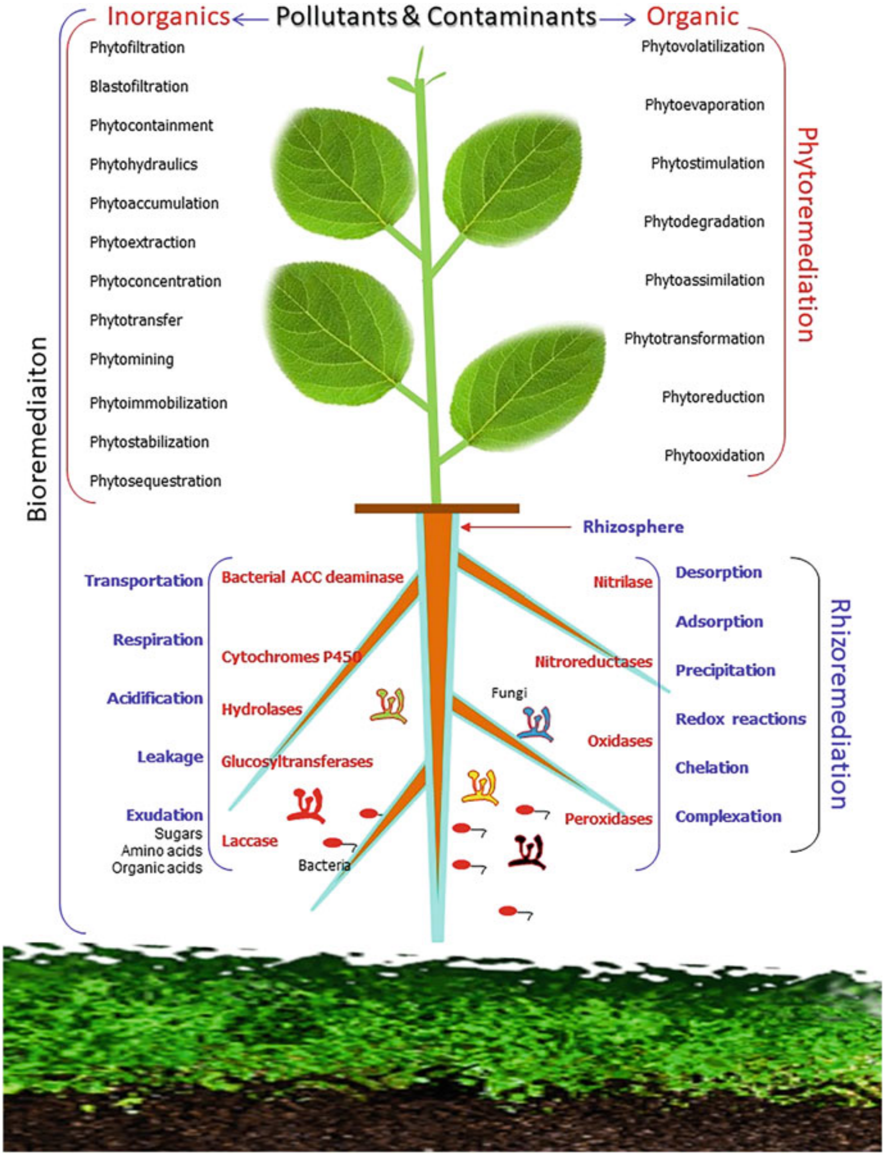

Fig. 3.1 The overall phytoremediation approaches to the restoration of contaminated soil (Sarma et al., 2019b).

in the soil matrix (Hanedar et al. 2019). As a direct consequence, they are rapidly taken up by the ground and enter into the food chain, which jeopardizes the ecosystem.

Organochlorine pesticides (OCPs) are one of the most frequent types of persistent organic pollutants (POPs) that are used in agriculture to protect crops from insects and to prevent diseases that are transmitted by vectors (Jayaraj et al. 2016). Later, it was outlawed because of its adverse effects on human health and the environment; nonetheless, it is still utilized in economically marginalized nations. In such countries, OCPs such as DDT, dieldrin, endosulfan, hexachlorocyclohexane, chloropropylene, and dicofol are commonly used (Jayaraj et al. 2016). Because of the strong and durable covalent link between the Cl and C atoms, they have various characteristics, such as low polarity, high persistence, and ability to drive through and move along with water. Pesticides that are volatile or chlorinated enter the biosphere and finally react with soil particles (Tzanetou and Karasali 2022). Organochlorine pesticides change the critical elements in the soil, which are phosphorus and nitrogen. Contaminants, on the other hand, change the nitrogen and carbon levels in the soil reversely (Egbe et al. 2021). OCPs also affect the biogeochemical cycle, behavior, richness, biochemical characteristics, and soil macro- and microorganism distribution. This can cause problems for plants' growth and development, making plants more susceptible to diseases and pests (Egbe et al. 2021).

PAHs are organic colloids that can be colorless, light yellow, or white. They are made of two or more benzene rings and are released into the environment by industries such as power plants, vehicles, and oil refineries (Abdel-Shafy and Mansour 2016; Sarma et al. 2019b). PAHs can move from one site to another because of the movement of water and air that originates from their source. Bortey-Sam et al. (2014) discovered that after a cascade of biological processes deposit PAHs in the top layer of soil, the compounds then accumulates in plants and makes its way into the food chain. PAHs can enter the body of a human through the lungs, the digestive tract, or the skin, which can lead to various ailments. There have been hundreds of different PAHs found. Because of the potential for PAHs to cause cancer, the EPA has categorized 16 of these compounds as priority pollutants (Hussar et al. 2012).

Polychlorinated biphenyls (PCBs) are a type of highly toxic aromatic chlorinated benzene that is frequently found in soil and has become a major source of concern in recent years. Throughout the 1800s, PCBs were extensively used in the leather, paper, and pulp industries as both a coolant and a dielectric liquid (Jing et al. 2018). PCBs can make their way into the environment through landfills, leachate, and dumping of waste containing PCBs. From the environment, PCBs can be ingested, inhaled, or absorbed via the skin if a person is close to contaminated soil (Kumar et al. 2014). Under the Stockholm Convention on POPs, PCBs have been made illegal worldwide because they are poisonous, lipophilic, and carcinogenic; have poor chemical and biological degradation; and have a significant potential for bioaccumulation (Vandana et al. 2022).

3.3 Mechanism of Rhizoremediation

Rhizoremediation is a sustainable remediation technique for eliminating soil pollutants by using plants and rhizosphere microbes. The plants and rhizosphere microbes release nutrients, enzymes, and biosurfactants into the rhizosphere by their symbiotic and co-metabolic activities, which helps the soil's organic contaminants to be cleaned up (Poonam and Kumar 2019). Members of the plant families, e.g., Asteraceae, Brassicaceae, Cunoniaceae, Caryophyllaceae, Euphorbiaceae, Poaceae, Lamiaceae, and Fabaceae, among others, have been identified as rhizoremediation candidates (Ojuederie and Babalola 2017). The rhizosphere of such plants attracts a large number of bacteria, actinomycetes, and fungi that aid in rhizoremediation (Mendes et al. 2013). The reason for this is that plant root exudates provide nutritional support to rhizosphere microbes, while the plants get protection and aid with nitrogen fixation (Upadhyay et al. 2022; Sarma and Sarma 2010). Plant roots integrate nutrients, enhance redox conditions, and give oxygen, all of which contribute to promoting and activating rhizosphere microorganisms. Plant roots can also disperse rhizosphere microbes throughout the soil and into strata that microbes would otherwise be unable to reach (Backer et al. 2018). Plant root exudates are also reported to promote microbial respiration (Adamczyk et al. 2021). The process of rhizoremediation may be divided into two phases. First, the pollutants-degrading microbes start inoculation in the rhizosphere zone, and later the pollutants are degraded by respective microbes in the rhizosphere (Poonam and Kumar 2019). In both the phases, POPs are eliminated from soil (Mohanan et al. 2020). The three primary mechanisms in the breakdown of POPs via the microbe-mediated rhizoremediation process are biosurfactant synthesis, biofilm development, and organic acid production (Saravanan et al. 2020). Aside from those three mechanisms, rhizoremediation involves adsorption, redox reaction, desorption, precipitation, acidification, chelation, transportation, respiration, and exudation (Jeevanantham et al. 2019).

3.3.1 Biosurfactant Production

In the influence of root exudates, the rhizosphere microbes are stimulated for the synthesis of biosurfactants. Biosurfactants are amphiphilic biopolymers formed extracellularly or as part of microbe cells (Santos et al. 2016). Their hydrophobic and hydrophilic moieties aid in the reduction of fluid surface and interfacial tension (Patowary et al. 2022b). Recently, four biosurfactants with chemical and microbiological origins have been identified. Glycolipids, lipopeptides, phospholipids, and polymeric biosurfactants are examples of these types (Patowary et al. 2022a; Shu et al. 2021). The creation of micelles increased the solubility of hydrocarbon contaminants, resulting in their degradation by rhizosphere microbes (Bordoloi and Konwar 2009). POPs are challenging to remove from soil due to strong hydrophobicity, high water partition coefficient, high electronegativity, and low polarity (Kookana and Navarro 2022). The biosurfactant disrupts these qualities, which moves the pollutants into the aqueous phase. This allows for the mobilization and removal of persistent contaminants in the soil matrix (Ławniczak et al. 2013). Biosurfactants, in general, emulsify hydrophobic contaminants into micro- and macro-emulsion forms and reduce the interfacial tension between the aqueous and nonaqueous phases (Sarma et al. 2021). Finally, increasing surface area increases the pollutants transfer rate to the aqueous phase and increases mobilization of adsorbent liquid-phase persistent pollutants (Cameotra and Makkar 2010). Overall, biosurfactants change the physiochemical properties of pollutants, making POPs more flexible and adaptable to further breakdown processes.

3.3.2 Biofilm Production

A biofilm is a microorganisms aggregation in which cells are typically trapped inside a self-producing matrix. Generally, microbes adhere to other surfaces by secreting extracellular polysaccharides, which results in the formation of biofilms (Alotaibi 2021). William Costerton (1995) defined biofilms as “a matrix-enclosed bacterial population adherent to each other and surfaces or interfaces” (Costerton 1995). Those microorganisms present in the biofilm have a better chance of survival since the matrix shields them and aids in the immobilization and breakdown of pollutant persistence compounds (Alotaibi 2021; Donlan 2002; Yin et al. 2019).

3.3.3 Organic Acid Production

The symbiotic interaction of plants and microbes has released acid-like molecules (organic acid) in the rhizosphere (Vishwakarma et al. 2020). Different plant species may produce a variety of organic acids (citric acids, oxalic acids, malic acids, succinic acids, and formic acids), which provide a carbon-rich habitat for microorganisms and can stimulate root colonization by establishing molecular communication with rhizosphere microbes (Macias-Benitez et al. 2020; Li et al. 2021). These acids can act as chelating agents by providing protons and organic anions. Negatively charged anions can form complexes with positively charged metal ions such as Ca^{2+}, Fe^{2+}, and Al^{2+} to chelate them from the soil (Flora and Pachauri 2010). Organic acids reduce soil pH, improving POPs solubility, mobility, and fate and promoting POPs breakdown (Shah et al. 2022). For example, citric acid and glutaric acid alter intracellular redox equilibrium and boost microorganisms growth rates and enzymatic and oxygenase status, resulting in higher POPs biodegradation (Zhang et al. 2021).

3.4 Mechanism of PAHs Rhizoremediation

Because PAHs include complex heterocyclic aromatic rings in their skeletons, it can be challenging to remedy polluted locations (Huang and Penning 2014). In the rhizosphere, PAH degradation is predominantly caused by microorganisms having specific PAH-degrading genes and enzymes (Correa-García et al. 2018). There are a variety of microorganisms that have been implicated in the PAHs rhizoremediation process, including bacteria, actinomycetes, and fungus (Ghosal et al. 2016). These rhizomicrobes are classified as either aerobic or anaerobic depending on their mode of respiration. Aerobic bacteria such as *Pseudomonas, Mycobacterium, Sphingomonas, Alcaligenes, and Rhodococcus*, among others, have been demonstrated to break down PAHs (Vidali 2001). In the rhizosphere, microorganisms reduce the hydrocarbons to produce carbon dioxide (CO_2), reducing electron acceptors by a single species (Widdel et al. 2010). The breakdown of PAHs occurs in both aerobic and anaerobic environments (Premnath et al. 2021). In both cases, several aromatic molecules are first transformed into a few basic substrates (benzoate, phloroglucinol, and resorcinol). The aromatic rings are then activated and cleaved to generate a noncyclic molecules, which is later transformed into central intermediates. Carboxylation, decarboxylation, reduction, hydroxylation, dihydroxylation, deamination, aryl ether cleavages, and lyase reactions are all engaged in the rhizoremediation process that leads to the core intermediates, which then enter oxidation pathways and create CO_2 and energy molecules (Widdel et al. 2010). Many enzymes released by bacteria, fungi, actinomycetes, yeast, and plants have been found to aid in the rhizodegradation of PAHs. For example, specific hydrocarbon-degrading enzymes like alkyl dehydroxylate (alkB and CYP153) are secreted by a variety of bactrial species including *Rhodobacter*, *Mycobacterium*, *Frankia*, and *Bacteroidetes* (Nie et al. 2014). Furthermore, *Mycobacterium fortuitum* produces catechol 1,2-dioxygenase (Silva et al. 2013), while *Pseudomonas cepacia* G40 and *Pseudomonas* sp. JS150 produces toluene-2-monooxygenase, and *Pseudomonas pickettii* PK01 produces toluene-3-monooxygenase, all of which play important roles in PAHs degradation (Bertoni et al. 1998).

3.5 OCPs Rhizoremediation Mechanism

One of today's primary challenges is the accidental and purposeful discharge of OCPs into the environment, which must be retrieved using eco-friendly, cost-effective reclamation technologies. Rhizoremediation stands out as a viable approach where in rhizomicrobes collaborate with plants to degrade pollutants within the rhizosphere offering an effective means of addressing this challenge. (Shukla et al. 2013). Different species of rhizobacteria, such as *Acinetobacter, Alcaligenes, Bacillus, Pseudomonas, Serratia, Rhizobium, Streptococcus,* and *Stenotrophomonas*, and fungi, including Mycorrhizae, *Phanerochaete chrysosporium, Didemnum ligulum basidiomycetes, Ganoderma austral,* *Coprinellus radians*, etc., in collaboration with plants (*Pisum sativum, Zea mays, Pinus pinea, Cucurbita pepo, Ricinus communis, Holcus lanatus, Cytisus striatus, Vigna radiata, and Zinnia angustifolia*) may successfully ameliorate OCPs without causing harm to surrounding environmental entities (Wang et al. 2022; Arora and Kumar 2019). These possible organisms have been widely utilized to remediate OCPs throughout the last few decades. OCPs rhizoremediation is accomplished in two phases. Microorganisms first absorb the pollutants and then form a microbial film around it. Later, the microorganisms metabolized the OCPs through a sequence of the enzymatic process (Huang et al. 2018). The essential chemical steps in breaking down the intricate structure of OCPs include hydrolysis, oxidation, reduction, and expansion (Sarker et al. 2021). A pesticide's hydrolysis is aided by hydrophilic environmental conditions, followed by oxidation/reduction, which modifies the compound's redox state. The primary chemical group of a substance dictates whether it will be oxidized or reduced. The final stage is to expand a novel reaction product (Sarker et al. 2021; Rao et al. 2010). A diverse group of rhizomicrobes have been found to produced various enzymes such as monooxygenases, hydrolases, dehalogenase esterases, NADPH-cytochrome P450 reductases, and oxidoreductases. These enzymes play a crucial role in catalyzing the abovementioned reactions and are responsible for formation of highly soluble, less toxic intermediate compounds. Also, these enzymes are present in plants, aiding in the production of growth and other secondary metabolites to decrease pollution-induced stress (Mishra and Arora 2019). In the presence of glutathione S578 transferases, these intermediate products conjugated with sugar and amino acid molecules are transformed into CO_2 and H_2O in subsequent phases of cellular respiration (Gaur et al. 2018). For example, carboxylesterases accelerated the hydrolysis of the carboxyl ester link of carbamate, resulting in the formation of CO_2 and methylamine, both of which may be utilized as a carbon source by microbes (Malhotra et al. 2021). According to Huang et al. (2018), *Pseudomonas* sp. degraded atrazine via the AtzA, AtzB, and AtzC enzymes. The AtzA enzyme catalyzes atrazine hydrolysis dichlorination to form hydroxyl atrazine. The hydroxyl atrazine was then transformed to N-isopropyl cyanuric amide via a dichlorination reaction mediated by the AtzB enzyme. The third intermediate compound is generated by hydrolyzing N-isopropyl cyanuric amide in the presence of the AtzC enzyme and then splitting into CO_2 and NH_3 (Huang et al. 2018).

3.6 Mechanism of PCBs Rhizoremediation

Rhizoremediation has been considered a sustainable strategy for eliminating the toxic PCBs attached to soil particles or lowering their toxicity (Bala et al. 2022; Jing et al. 2018). It is easier to correctly retrieve PCBs from the rhizosphere by collaborating with plants and microorganisms. The influence of plants (root exudates) stimulates the breakdown capacity of rhizomicrobes or boosts the microbes' ability to attenuate the complicated structure of PCBs (Rohrbacher and St-Arnaud 2016; Upadhyay et al. 2022). Meanwhile, the microorganisms can help the plants for an extension of the root system as well as lowers the toxicity level of contaminated soil by lessening the plant's vulnerability to abiotic stress (Vergani et al. 2019). *Pseudomonas sp., Clostridium sp., Sphingomonas sp., Bacillus sp., Bradyrhizobium sp.*, *Ralstonia sp.*, *Alcaligenes xylosoxidan*s, *Candidatus saccharibacteria, Ochrobactrum anthropi*, *Rhodococcus sp*., and *Ralstonia sp*. are prospective rhizomicrobes capable of removing PCBs from soil under the influence of plants (Ancona et al. 2021). However, there are significant limitations to the approaches; due to the highly poisonous nature of PCBs, most rhizosphere microorganisms assume a non-culturable condition, and mortality of both plants and microorganisms is seen when exposed to PCBs (Iqbal et al. 2022; Ren et al. 2022). PCBs are rhizoremediated in both aerobic and anaerobic environments. High-chlorinated PCB compounds (e.g., PCB-47, PCB-77, PCB-153, and PCB-157) typically have high water partition coefficient (K_{OW}); thus, organohalide anaerobic respiration may degrade these pollutants more efficiently by anaerobic microbes such as *Achromobacter* sp., *Lysinibacillus* sp.*, Desulfomonile tiedjei, Dehalobium chlorocoercia, Dehalococcoides mccartyi*, and *Desulfitobacterium dehalogenase* (Pathiraja et al. 2019; Jing et al. 2019). The microbes halopriming of the meta and para positions of halogenated aromatic rings is done in the absence of oxygen. During this process, a chlorine atom is exchanged for a hydrogen atom, making it less toxic and more available for subsequent aerobic breakdown (Sharma et al. 2018). *Dehalococcoides* sp. strain CBDB1 is a highly efficient bacterial species for accelerating the dechlorination of a wide variety of PCBs (Agulló et al. 2017; Jing et al. 2019). However, the root exudates act as a stimulant of the PCBs' dichlorination process.

Through aerobic respiration, the aerobic microbes decomposed the dechlorinated product into chlorogenic acids, predominantly utlizing biphenyl catabolic enzymes. The three types of enzymes belong to the biphenyl catabolic enzyme cluster, i.e., dioxygenase encoded by bphA, dehydrogenase encoded by the bphB gene, and ring cleavage dioxygenase encoded by the bphC genes (Contreras et al. 2021).

Dioxygenase enzyme catalysis is the formation of dihydrodiol from dechlorinated PCBs through the deoxygenation of the benzyl ring (Pimviriyakul et al. 2020). The oxidation of 2,3-dihydrodiol to 2,3-dihydroxybiphenyl is catalyzed by dehydrogenase. The ring cleavage dioxygenase is responsible for cleaving the biphenyl ring to generate less toxic phenyl catechol, which is then converted into CO_2 and H_2O (Furukawa 2000; Jing et al. 2018).

3.7 Factors That Affect the Rhizoremediation

The rhizoremediation process involves oxidation, reduction, carboxylation, decarboxylation, hydroxylation, dihydroxylation, and deamination of POPs in the soil environment via synergistic associations between plants and microbes. Rhizosphere and endophytic microorganisms in plant roots play a crucial role in accelerating all biochemical reactions by functioning as biocatalysts in the POPs rhizoremediation reactions via enzymatic pathways (Agarwal et al. 2020). However, as enzymes are very selective and often function under modest reaction conditions, the rhizoremediation process ultimately depends on several biotic and abiotic variables (Jegannathan and Nielsen 2013; Kumar et al. 2021). Furthermore, the following characteristics influence POPs' degradation process (Kebede et al. 2021). This suggests that rhizoremediation might be more successful and efficient if these elements are manipulated, adjusted, and regulated (Kebede et al. 2021). This includes the following factors cited below:

3.7.1 Plant Root Exudates

Plant root exudates are a complex array of organic (low-molecular-weight and high-molecular-weight metabolites) and inorganic chemicals (carbon dioxide and water) emitted into the rhizosphere environment by the root system during plant development (Garriga et al. 2018). These chemical substances are essential ecological drivers that hasten the composition, variety, and numerous metabolic activities of the rhizosphere's microbial population (Correa-García et al. 2018) by offering carbon- and energy-rich habitat for rhizomicrobes (Ma et al. 2022). In addition, these compounds can select and attract specific microbial communities to protect and improve plant growth from soil pollutants. Exudation not only earns benefits to the microbes, but the plant also gets a direct benefit for itself. For example, organic acids are one of the constituents of root exudates that offer microorganisms a carbon-rich environment that aids plants in nutrient acquisition, stress relief, and pollutant mineralization (Correa-García et al. 2018). Exudates can also aid in the microbial deterioration of soil organic contamination (Lu et al. 2017). As a result, the higher the concentration of exudates, the faster the POPs rhizodegradation. Phillips and his colleagues reported in 2012 that root exudates increased the bioavailability of dichlorodiphenyldichloroethylene (DDE), DDT, PCBs, and PAHs (Phillips et al. 2012). Gao et al. (2010) also concluded that low-molecular-weight root exudates (citric acid and oxalic acid) promoted the desorption of POPs (phenanthrene and pyrene) from soil particles (Gao et al. 2010). In addition, the production of protocatechuate 3 and 4 dioxygenases, an aromatic ring breakage enzyme, was increased by root exudates (Yergeau et al. 2014). As a result, the pace of POPs breakdown has increased. On the other hand, the age of the plant, the amount of moisture in the soil, the species of plant, and the type of soil all affect the quality, quantity, and nature of root exudates, which in turn determines the rate at which organic pollutants are broken down (Maurer et al. 2021).

3.7.2 Microbial Population

It is one of the most important factor that govern the rhizoremediation process by increasing the humification of organic pollutants. POP-degrading microorganisms can digest, metabolize, or mineralize pollutants from the soil environment such as OCPs, PAHs, and PCBs (Seo et al. 2009). The degradation process takes place within a well-coordinated rhizomicrobial community. It involves transferring a functional group or thoroughly degraded pollutants into less hazardous products (water, carbon dioxide, and inorganic salt) via aerobic and anaerobic environments. These communities, which comprise bacteria, fungi, and algae, have the power to eliminate POPs. According to previous research, *Cyanobacteria sp., Alcaligenes sp.*, Bacillus *sp.*, Staphylococcus *sp.*, *Enterobacter sp., Corynebacterium sp.*, Gemmatimonadetes *sp.*, Streptococcus *sp.*, *Escherichia* sp., etc. and others generate pollutant-degrading enzymes that are widely employed in POPs rhizoremediation (Gaur et al. 2018). The abundance of naturally occurring POP-degrading microorganisms in polluted soil shows a positive correlation to the rate of POPs rhizoremediation (Kebede et al. 2021). Their accessibility in terms of species diversity, evenness, and richness, on the other hand, is intimately tied to the types and nature of hydrocarbon contaminats and the surrounding environmental conditions. A vast microbial population performs better than a single strain in terms of the degradation rate because a single strain can only process a certain number of enzymes, but a diversified microbial community can process a wide range of POP-degrading enzymes (Kebede et al. 2021; Mishra et al. 2021).

3.7.3 Contamination Types and Concentration

Significant considerations in the rhizoremediation process to remove pollutants from soil include the structure and concentration of contaminants (Tang et al. 2010). Pollutant's physiochemical properties and concentration have an effect on the biodegradation, mineralization, metabolic capacities, and diversity of the rhizomicrobial population (Alori et al. 2022; Wassie 2017). In most situations, biodegradable genes are suppressed at low concentrations, resulting in a low removal of pollutants despite their biodegradability (Kebede et al. 2021; Seo et al. 2009). Similarly, excessively high concentration are known to be harmful to the root's microbiome, and biodegradation rates are decreasing (Poznyak et al. 2019). As a result, at an optimal concentration of pollutants, complete mineralization of POPs from polluted surroundings occurs (Kebede et al. 2021).

3.7.4 Soil Properties and Soil Organic Matters

The biochemical and physiochemical processes of soil such as water and nutrient transport, air accessibility, root penetration, soil drainage, pollutant ageing, and POPs dispersion within the soil are affected by soil physiochemical parameters such as moistures, redox conditions, temperatures, pH, organic matter, nutrients, and amount of clay, among others (Sarkar et al. 2020; Zhang et al. 2020a, b). The soil's organic matter, which controls the soil's characteristics and gives microorganisms an energy-rich home, is made up of a variety of bacteria, metabolites, and humic substances that emerge through the chemical and microbiological alteration of organic pollutants. (Bashir et al. 2021). High soil organic matter provides a good environment for rhizomicrobes, allowing them to quickly increase their population and degrade pollutants since microorganisms act as a main catalyst for POPs breakdown in the rhizosphere (Masciandaro et al. 2013). The degradation rate varies according to the type and structure of the soil. Sandy soil exhibits greater degradation efficiency than clay soil. Clay soil particles obstruct the movement of oxygen and nutrients to microorganisms and promote the development of humic acid, lowering the effectiveness of POPs degradation (Haghollahi et al. 2016).

Furthermore, the most prevalent rate-limiting variables are soil temperature, moistures, and soil nutrients (Onwuka 2018; Stark and Firestone 1995). When they are above or below the limit, they negatively influence the rate of deterioration. For the POPs degradation process to be successful, adequate concentrations of these components must be present in polluted soil.

3.7.5 Temperature

The important abiotic factor, i.e., temperature, have a varied effect on the variety of the microorganism population, which is the driving force behind POPs rhizoremediation (Scofield et al. 2015). Temperature regulates degradation rates by influencing microbial enzymes activity, pollutants chemistry, and oxygen solubility (Kebede et al. 2021). As a result, temperature is regarded as a key element in rhizoremediation, and the efficacy of eliminating POPs is directly proportional to temperature. The ideal temperature for efficient remediation is determined by the microbial species and the nature of the pollutants (Abdel-Shafy and Mansour 2016; Das and Chandran 2011). In general, the rate of deterioration slows with decreasing temperature and speeds up with increasing temperature (Sihag Pathak et al. 2014). According to Ribicic et al. (2018), organic pollutants' breakdown processes are especially slow at low temperature (Ribicic et al. 2018). Furthermore, Liu et al. (2017) revealed that temperature significantly influences the selection of petroleum hydrocarbon-degrading bacteria, and the population of bacteria participating in hydrocarbon degradation is related to temperature change (Liu et al. 2017). Consequently, for full POPs rhizodegradation, prospective bacteria require an ideal temperature range.

3.8 Enhancement of Rhizoremediation

Rhizoremediation rates are often sluggish in natural conditions due to the effect of abovementioned abiotic and biotic factors (Hoang et al. 2021). Researchers are looking at the impact of various "catalyst approaches" on rhizoremediation capabilities, such as genetic engineering, nanoparticle assisted, and biochar assisted (Malik et al. 2022; Sarma et al. 2022). The combination of multiple techniques is critical for the remediation of particularly contaminated sites. It can become a highly efficient, environmentally friendly, and low-cost bioremediation technology in the future (Oberai and Khanna 2018). The following subsection describes several rhizoremediation catalyst approaches.

3.8.1 Bio-stimulation Assisted

Bio-stimulation is an addition of any stimulatory materials, bulking dealers, nutrient amendments, bio-surfactants, biopolymers, and slow-launch fertilizers to decorate and guide microbial increase and enzymatic activities of the autochthonous microorganisms in the infected soil for remediation activities (Wu et al. 2016). In addition to the common liming elements like nitrogen, phosphorus, potassium, carbon, and oxygen, which are often present in low quantities in soil, the process bio-stimulation involves not only adding or adjusting those elements, but it also address other types of limiting factors, micronutrients, and electron acceptors (Sayed et al. 2021). The trouble related to chemical nutrient addition to contaminated soil and groundwater differs from microbial addition. Bio-stimulation is the most successful and efficient bioremediation approach compared with different in-situ remediation in simulated soil infected with POPs (Myazin et al. 2021). The prerequisites for bio-stimulation include the presence of specific microorganisms, the ability to stimulate target microorganisms, and the ability to supply nutrients, C:N:P, 30:5:1, for stability growth (Simpanen et al. 2016).

3.8.2 Bioaugmentation Assisted

Bioaugmentation is the advent of microorganisms with specific catabolic talents into the tainted environment so that it will complement the indigenous population and increase up or enable the degradation of pollutants (Nzila et al. 2016). Bioaugmentation has validated success for remediation of PAHs in sediments with poor or lacking intrinsic degradation capability. Other studies also demonstrated that bioaugmentation did not decorate biodegradation notably compared to natural attenuation (Nzila et al. 2016; Omokhagbor Adams et al. 2020). One of the significant problems in applying bioaugmentation is to ensure the survival and pastime of the delivered organisms in the environment (Nzila et al. 2016). However, the critical issue for achieving the bioaugmentation procedure is the selection of the best microbial candidates (Nwankwegu and Onwosi 2017). When selecting the strain for augmentation, it is important to take into account the types of microbial groups that are present in the supply habitat. Bioaugmentation technique can also prove successful, specifically in the remediation of POPs (Nzila et al. 2016). This involves the addition of exogenous microbial cultures, autochthonous microbial communities, or genetically engineered microbes with a specific catabolic hobby that has adapted and been established to degrade contaminants to beautify degradation or increase the fee of degradation (Nzila et al. 2016; Thakare et al. 2021). Varjani et al. (2015) validated in-situ bioaugmentation of POPs using a microorganism consortium comprising six bacterial isolates for degradation of petroleum hydrocarbon contaminants. They reported removal performance of 83.7% over 75 days (Varjani et al. 2015). Covino et al. (2015) additionally confirmed bioaugmentation by using the autochthonous fungi from a petroleum hydrocarbon-infected soil to degrade clay soil contaminated with petroleum hydrocarbons and achieve a removal performance of 79.7% after a 60-day period (Covino et al. 2015).

3.8.3 Transgenic Plant Assisted

Overexpression of several types of genes (that help in POPs breakdown) in transgenic plants is one way to increase the rate of POPs rhizoremediation (Doty 2008). Transgenic plants typically have modified DNA, and many plant species may be transformed into transgenic plants using recombinant DNA technology (Jhansi Rani and Usha 2013). Transgenic plants are employed as hyperaccumulators of POPs, and their application in the bioremediation of POPs from contaminated soil is seen as a cost-effective strategy (Kumar et al. 2022a, b; Ojuederie et al. 2022). Transgenic plants were found to improve the overall phytoremediation approaches (Yan et al. 2020).

For the successful remediation of POPs from the soil environment, POP-degrading genes like bph, CYP, alkB, alkB1, nahAc, and $C_{12}O$ encode the degrading enzymes such as biphenyl dioxygenase, cytochrome P450 monooxygenase, nitroreductase, glutathione-S-transferase, and biphenyl catabolic enzymes that are introduced into the plant, which increases the degradation rate of POPs into the rhizosphere (Abhilash et al. 2009).

3.8.4 Nanoparticle Assisted

Nanoparticle-assisted rhizoremediation is an emerging approach for removing POPs from polluted soil. Due to its unique properties, smaller sizes, and wide surface area, this strategy has occupied a substantial area of study attention in the bioremediation sector over the last few years (Baruah et al. 2019; Chowdhury et al. 2022). Nanoparticles with these properties can efficiently adsorb and permeate POPs (Malik et al. 2022). Adding NPs to the rhizoremediation process first incorporates the physiochemical reactions as a catalyst that alter the physiochemical characteristics of pollutants such as absorption, adsorption, and dissolution, among others (Abebe et al. 2018; Rajput et al. 2022). The second phase instigates the contaminants to bioaccumulate, bio-stimulate, bio-transform, and mineralize (Desiante et al. 2021; Rajput et al. 2022). Most nanoparticle-assisted rhizoremediation technologies followed the steps mentioned earlier (Hidangmayum et al. 2022). Nanoparticles can be synthesized via physical, chemical, or biological techniques. However, several studies have shown that biologically synthesized nanoparticles in bioremediation are environmentally friendly, cost effective, and safe (Ahmed et al. 2022; Patel et al. 2020). Various biosynthesized nanoparticles are used for sequential POPs cleanup from the rhizosphere zone. However, the most commonly investigated nanoparticles include carbon-based nanoparticles, nano-zerovalent iron nanoparticles, metal oxide-based nanoparticles, and chitosan nanoparticles (Ghahari et al. 2022).

3.8.5 Biochar Assisted

Biochar contributes to the expedited completion of the POPs rhizoremediation process. Biochar is an aromatic carbon-rich alkaline adsorbent synthesized from biomass by pyrolysis at 350–700 °C in an anaerobic atmosphere (Guo et al. 2022). In POP soils, biochar adjuvant rhizoremediation mechanisms include pore filling, ion exchange, hydrophobic interactions, electrostatic interactions, pi-electron interactions, physical adsorption, fission, complex formation, and precipitation (Lu et al. 2022; Malik et al. 2022; Xiang et al. 2022). In addition, these processes decrease the bioavailability and bioaccessibility of pollutants (Ejileugha 2022). Various biochars, including bamboo biochar, banana trunk biochar, wheat straw biochar, etc., have been reported to improve PCBs remediation from the rhizosphere zone (Valizadeh et al. 2021). Hayat et al. (2019) demonstrated that application of biochar in conjunction with ryegrass-aided rhizoremediation enhanced PCBs remediation effectiveness by 85% (Hayat et al. 2019). Zhao et al. (2022) reported that rape straw biochar accelerated the rhizoremediation of PAHs and increased the production of PAH-RHDα GN genes in soil bacteria (Zhao et al. 2022). Biochar-assisted phytoremediation lowers soil pH; improves soil organic content, soil microbial population, and water-holding capacity; and increases the rate of POPs disintegration (Sarma et al. 2019a) (Fig. 3.2).

3.9 Conclusion

POPs are organic pollutants that can be formed either naturally or artificially. It was widely produced commercially in the 1990s to fulfill the food demands. These are extensively used as a pesticides in the agriculture sector. The manufacturing and use of 16 most deadly POPs were prohibited globally in the late 1990s. However, the number has now risen to 28. Furthermore, numerous forms of POPs, such as PCBs and PAHs, are introduced into the environment by anthropogenic activity, causing soil, water, and air pollution, as well as acute and chronic impacts on flora and fauna.

Consequently, numerous physical, chemical, and biological remediation approaches have been widely used to remove these contaminants from soil. Various investigations reveal that rhizoremediation, i.e., a plant-microbe-assisted bioremediation technology, is a sustainable and eco-friendly remedial technique for POPs. However, the rate of this approach is limited in the natural state due to various abiotic and biotic factors. Therefore, an in-depth investigation is necessary to cooperatively expedite remediation utilizing various approaches such as nanoparticles and biochar and to develop an eco-friendly, highly efficient rhizoremediation technology.

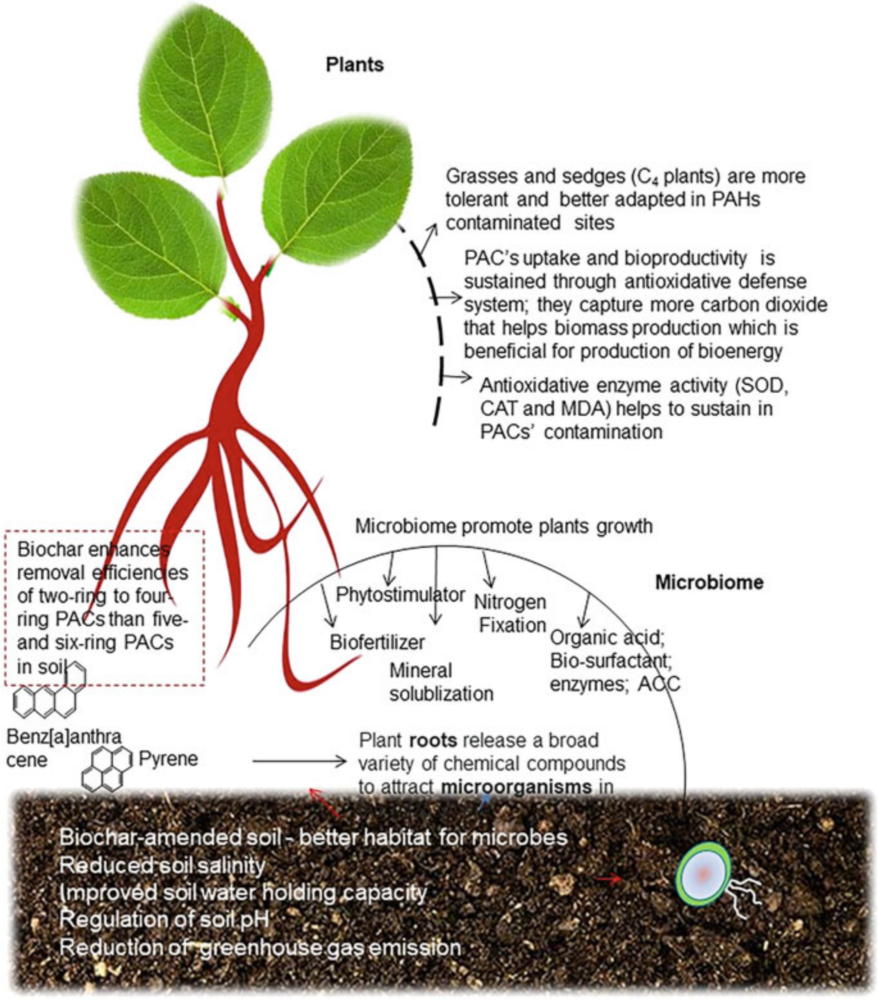

Fig. 3.2 Biochar-assisted rhizoremediation of POPs from contaminated soil (Sarma et al., 2019b).

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Biotransformation of 1,4-Dioxane by the Use of Bacteria in the Soil

4

Hossein Miraji, Asha Ripanda, Ramadhani Bakari, and Hemen Sarma

Contents

Abstract

Background: 1,4-Dioxane, also known as dioxane, is a water-miscible synthetic industrial chemical used as a stabilizer for chlorinated solvents and feedstock

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chemical for a wide range of industrial consumer products. It is a heterocyclic organic ether that, through consumer products and industrial, municipal, and domestic effluents, can get into the environment. Due to its volatility and miscibility, short-term exposure results in irritation of the nose, eyes, and throat, while excessive amounts damage the liver and kidney. Long-term exposure results in carcinogenicity to humans that may associate with death. **Statement of problem:** 1,4-Dioxane is nonbiodegradable in nature and hence persists in the environmental compartments; some methods such as UV peroxide oxidation, direct UV photolysis, and activated carbon adsorption were reported to be effective in the removal of dioxane in the environment. Yet, their adaptation challenges such as complex matrices, running costs, mass balance, and stoichiometry limitations hinder their efficiency. **Finding:** Mimicking natural or integrated techniques such as bacteriological transformation of dioxane via aerobic, anaerobic, microcosm, integrated microbial community, and co-metabolic techniques is among the robust eco-friendly technologies against these limitations. Soil matrix offers enormous microbial consortium for nature-based remediation of dioxane with high turnup than single microbial strains. Since bacteriological remediation offers adoptable, flexible, and quick implementation strategies that minimizes the use of synthetic chemicals, its fundamental understanding will be inevitable. **Conclusion:** Nature-based remediation of dioxane is an undoubtable future since apart from the natural occurrence of soil bacteria responsible for degradation, their natural adaptation flexibility, energy conservation, and release of harmless by-products without formation of secondary synergic harmful contaminants present a relatively affordable technique.

Keywords

Biotransformation · 1,4-Dioxane · Dioxin · Soil bacteria · Emerging contaminants · Eco-friendly

4.1 Introduction

1,4-Dioxane ($C_4H_8O_2$) is an industrial solvent produced for diverse direct applications including raw material and as a solvent. Its chemical abstract service number (CAS no.) assigned by the American Chemical Society is 123-91-1 with synonyms including dioxan, diethylene dioxide, dioxane, *p*-dioxane, diethylene oxide, glycol ethylene ether, or diethylene ether (McFee et al. 1994). At laboratory scale, this colorless and flammable liquid is used as a stable reaction media and as an extraction liquid for vegetable and animal oils (ATSDR 2006). Dioxane is useful as a growth substrate in organisms (Barajas-Rodriguez et al. 2019) and solvent in paints, ink, cosmetics, detergent, varnishes, and cleaning and shining fluids. With its nonpolar and aprotic solvent as it is presented in Fig. 4.1, dioxane is in addition utilized in the processing of petrochemicals, pesticide, pharmaceuticals, plastics and rubber, explosives, polishing, and pulp and paper as a solvent (DES 2018).

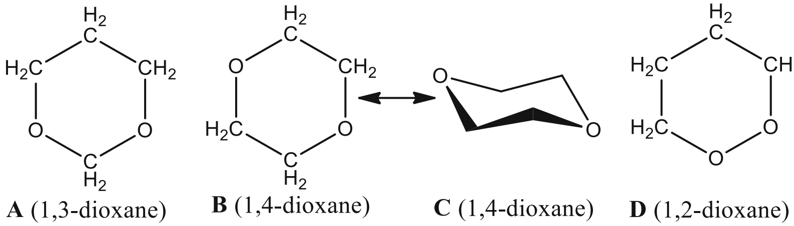

Fig. 4.1 Chemical structures of 1,4-dioxane (88.11 g/mol)

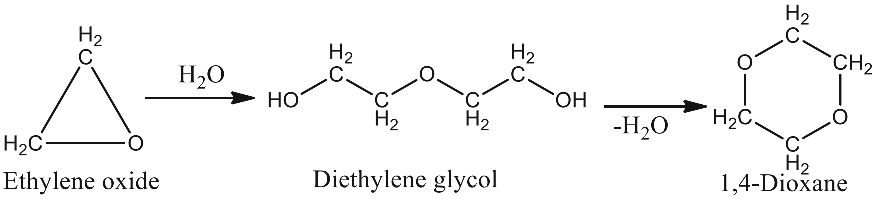

Fig. 4.2 Laboratory production of 1,4-dioxane (van Buskirk 2014)

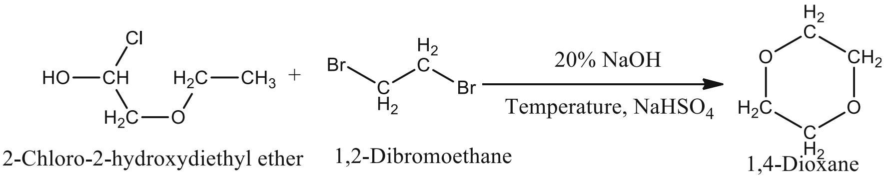

Fig. 4.3 Industrial production of 1,4-dioxane (Wilbur and Jones 2012)

Among the chemical structures presented in Fig. 4.1, structure B containing two planes of symmetry is the most stable due to minimum atomic constraints. The laboratory-scale production is shown in Fig. 4.2, while the commercial production of dioxane follows reaction root shown in Fig. 4.3.

Through literature survey, there are no industries in the world that directly produce 1,4-dioxane, implying that its production might be sporadic. The produced dioxane above undergoes heating with acids, distillation, salting out with $CaCl_2$, and distillation again in order to attain high level of purity. More than 90% of the produced dioxane is used for stabilization of chlorinated solvents (US EPA 2014a) such as trichloroethene and 1,1,1-trichloroethane (Milavec et al. 2020).

4.1.1 Properties of 1,4-Dioxane

Dioxane forms an adduct with 1,1,1-trichloroethane (TCE) that inhibits through poisoning the catalytic reaction between TCE and aluminum containers used for

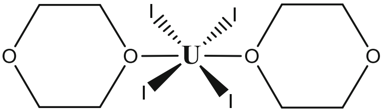

Fig. 4.4 Stable compounds of uranium-containing dioxane. [Image adopted with permission from Monreal et al. (2011)]

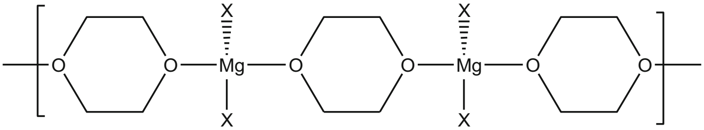

Fig. 4.5 Polymeric reaction of 1,4-dioxane

transportation of chlorinated solvents (Adamson et al. 2015). In most reactions and solvent requirements, dioxane has replaced tetrahydrofuran, which has high toxicity level than dioxane (Madhu 2018), high boiling point, hygroscopicity, diether chelating ligand (Tusher et al. 2021), and high water miscibility. According to the hard and soft Lewis acids and bases (HSAB) theory (Pinter et al. 2013), dioxane is a hard base implying that it is weakly polarizable, has high charge states, is less volatile, is nonpolar, and has small molecule (Davarani et al. 2012). Dioxane can react as a monodentate with uranium to produce useful materials (Fig. 4.4) for nuclear chemistry (Monreal et al. 2011).

However, the bidentate ligand is complex due to bond constraints. The possible reaction reported in Fig. 4.5 indicates the reaction between dioxane and Grignard reagent to form a polymer (Che-revision Administrator 2014).

4.1.2 Sources and Occurrence of 1,4-Dioxane

Reports on the direct production of 1,4-dioxane are rare; however, it occurs in most consumer products such as in cosmetics as a trace contaminant (Hossein et al. 2022) that can penetrate human and animal skin (U.S. FDA 2016). Industrial manufacturing of chlorinated solvents, papers and pulp, agricultural pesticides, organic chemical, dyes, and rubber and textile processing are potential sources of dioxane (Sun et al. 2016). It is a by-product during the manufacturing of aircraft deicing fluids, dyes, antifreeze, greases, paint strippers, and other consumer products (Hossein et al. 2022). Its high water miscibility and use in domestic activities including cleansing and bathing, recreational swimming, industrial production, and automobile activities release substantial amount of dioxane in terrestrial and marine ecosystem (Karges et al. 2018). Through its environmental partitioning, dioxane is rarely available in the atmosphere due to low volatility (Adamson et al. 2021), surface water (Karges et al. 2020), soil (Hinchee et al. 2018), and groundwater (Yamamoto et al. 2018a). The oceanic occurrence of dioxane is also reported by

Scaratti et al. (2020). The occurrence of dioxane in the body is rare since it is transformed to β-hydroxyethoxyacetic acid and eliminated through urination (ITRC 2020a). Its occurrence in the drinking water (Adamson et al. 2021), food (Broughton et al. 2019), and particulate matters (Lee and Choo 2013) has proved the occurrence of dioxane in all ecosystem compartments. Thus, mostly use and disposal of chlorinated compounds and consumer products, water and wastewater treatment plants, accidental releases, landfills, and pipe leakages are the major sources of dioxane to the environment.

The LD_{50} of dioxane in rats is 5170 mg/kg, while the no-observed adverse effect to human being is 400 mg/m^3 (Supprenant 2012). Dioxane falls among EPA's unregulated contaminant monitoring rule (UCMR) that qualifies it as an emerging contaminant (Suthersan et al. 2016; Sarma 2022), and in addition dioxins are classified as persistent organic pollutants (Miraji et al. 2021).

4.1.3 Effects and Fate of 1,4-Dioxane

Compared to other solvents such as ethanol whereby the USA alone produced 84% (6.3 million m^3) of the world in the year 2020 (AFDC 2022), recent data of 1,4-dioxane production are limited. For example, in the year 1985, global production of dioxane was 14,000 tons (13.6 million liters) (Wiki 2022); in the year 1990, about 18 million pounds was produced (7.9 million liters); and in the year 2002, the USA alone produced ten million pounds (4.4 million liters) (Wilbur and Jones 2012) indicating a gradual decrease. The absence of recent data on the direct global production of dioxane is not clear, yet most consumer products such as automotive coolants, chemical manufacturing, and textile contain dioxane. Dioxane is volatile (EPA 2010) with atmospheric half-life of 1–3 days (US EPA 2014b). There are several federal standard guidelines for dioxane exposure. Some of them are shown in Table 4.1 (US EPA 2014a).

Breathing of contaminated air (ATSDR 2006); skin adsorption via use of shampoo, toothpaste, and other cosmetics (Alsohaimi et al. 2020); ingestion via packaging material (Gi et al. 2018); food and food supplements/additives (Mo et al. 2022); pesticide remnants in agricultural products (Begum et al. 2016); groundwater (Chu et al. 2018); occupational exposure (US EPA 2014a); industrial effluents (Stepien

Table 4.1 Federal standard guidelines for 1,4-dioxane

Root of exposure	Amount	Exposure duration (days)	Status
Inhalation	2.00 ppm	<14	Acute
Inhalation	0.20 ppm	15–364	Intermediate
Respiration	0.03 ppm	>365	Chronic
Oral	5 mg/kg	1	Acute
Oral	0.5 mg/kg	1	Intermediate
Oral	0.1 mg/kg	1	Chronic

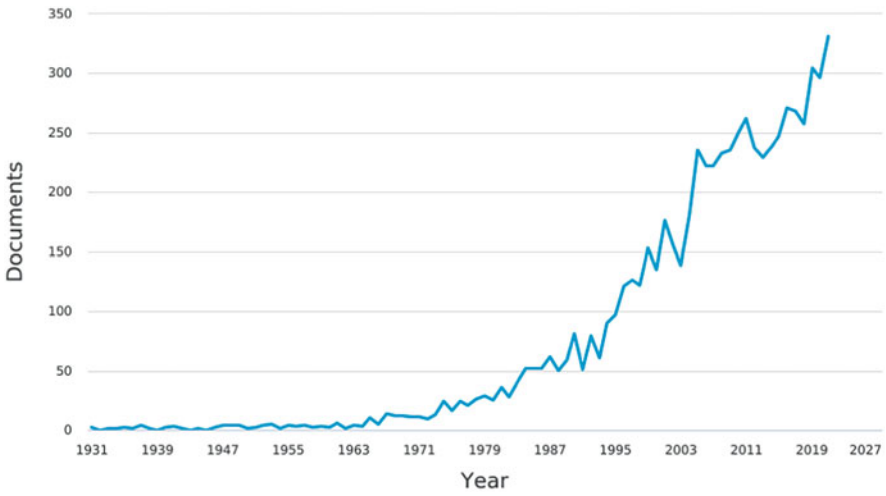

Fig. 4.6 Scopus analytic for the published papers mentioned 1,4-dioxane from 1931 to 2021

et al. 2014); and use of spermicidal sponge (ATSDR 2012) are the potential roots of exposure to dioxane.

Experimental research on dioxane has established LD_{50} of about 2 g/kg for cats and rabbits, 5.7–5.9 g/kg in mice, and 3.15–4 g/kg in guinea pigs. In this study, kidney and liver were the chronic affected organs (OEHHA 1998). The United States Environmental Protection Agency (US EPA) has reported 35 µg/L of dioxane as a cancer risk level (US EPA 2012) and classified it as group B2 chemical that probably causes human carcinogenic effect (McElroy et al. 2019). The Office of Environmental Health Hazard Assessment (OEHHA) has recommended 3 ppb of dioxane as a maximum level in the drinking water (OEHHA 1998). Evidence of dioxane carcinogenicity is reported and summarized by the Scientific Committee on Consumer Safety in its report number SCCS/1570/15 indicating that while the EU classifies it as a carcinogen category 2, the IARC classifies it as a group 2B carcinogen chemical. The SCCS recommends 55 µg/day; Australia has the highest recommendation of 420 µg/day, while Japan has the lowest recommendation of 4.3 µg/day (US EPA 2012).

Short-term or acute exposure to 1,4-dioxane may result in various effects, but the common ones are drowsiness; nausea; irritation of the eyes, throat, and nose; and headache (ATSDR 2012; US EPA 2014a). Long-term chronic exposure is associated with drying and cracking of skin and liver, dermatitis, eczema, and kidney damage (ATSDR 2012; US EPA 2014a). Recently, there has been an exponential growth in the global reports regarding 1,4-dioxane as indicated in Fig. 4.6.

Exponential growth is an indication of global awareness on the environmental impact of 1,4-dioxane, with the leading research area being chemistry as indicated in Fig. 4.7.

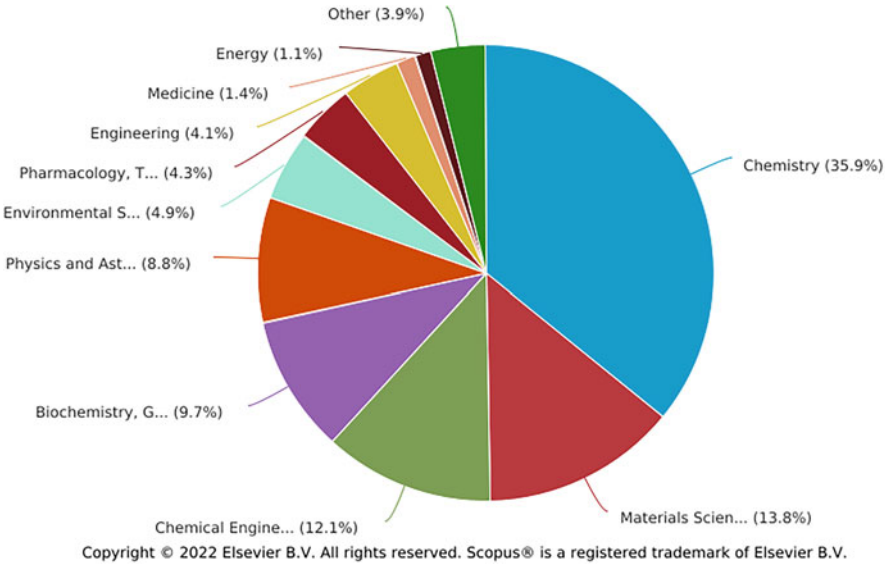

Fig. 4.7 Scopus analytic for the subject areas mentioned 1,4-dioxane from 1931 to 2021

Its occurrence as an impurity in most consumer products (Fuh et al. 2005) presents a challenge in its roots and mitigation approaches. Thus, apart from dioxane that will enter living organisms and causes adverse effects, the remaining will be contaminant in the environmental ecosystem that requires natural remediation for the ecosystem safety.

4.2 Remediation of 1,4-Dioxane

Chemical and physical properties of 1,4-dioxane lead to ineffective traditional remediation especially through chemical treatment methods (ITRC 2020b). Furthermore, these properties render conventional unit processes involved in drinking and wastewater treatment ineffective too (ITRC 2020b). Although under aerobic conditions 1,4-dioxane is biodegradable via direct metabolism or co-metabolism, the relative roles of these processes are dependent on both the concentration of 1,4-dioxane and the presence of co-contaminants (Zhang et al. 2017; He et al. 2018; Broughton et al. 2019; Polasko et al. 2019; ITRC 2020b; Johnson et al. 2020; Metabolism A, Cometabolism A, Biodegradation A, Tools MB 2021). Inhibitory co-contaminants frequently complicate the biological treatment of 1,4-dioxane (Johnson et al. 2020). Because of its uses as a solvent, wetting agent, and stabilizer for chlorinated solvents, used in metal vapor degreasing, 1,4-dioxane is frequently found with a variety of co-contaminants, including heavy metals like hexavalent chromium [Cr(VI)] (Zhang et al. 2017; He et al. 2018; Broughton et al. 2019; Polasko et al. 2019; ITRC 2020b; Johnson et al. 2020). Cr(VI) occurs naturally in groundwater due to geological formations, but it also has anthropogenic sources that can overlap with 1,4-dioxane.

Microbes that use 1,4-dioxane as a carbon or energy source, as well as those that co-metabolize it after growth on other organic substrates, can biodegrade it (Zhang et al. 2017; He et al. 2018; Broughton et al. 2019; Polasko et al. 2019; ITRC 2020b; Johnson et al. 2020). In this case, using microbes such as bacterial strains for biodegradation of 1,4-dioxane is of interest for environmental and public health safety. These techniques may be used to remediate 1,4-dioxane in contaminated water, wastewater, and soil. The composition of soil microbial community in contaminated soils is potential for the effectiveness of the remediation processes.

4.3 Soil Microbial Constituents

Soil comprises organic matters, minerals, gases, liquids, and living things, which contribute to supporting life (Haumaier et al. 2001; Pettit 2004; Amundson et al. 1998). In addition to a porous phase containing water and gases, soil consists of a solid phase comprised of minerals and organic matter (Haumaier et al. 2001; Amundson et al. 1998) as presented in Fig. 4.8. The solid, liquid, and gaseous states may coexist in the soil depending on the climatic conditions (Haumaier et al. 2001; Amundson et al. 1998). Climate; relief such as elevation, orientation, and slope of the terrain; organisms; and soil's parent materials interact over time to produce soil. The produced soil continuously changes due to various physical, chemical, and biological processes, including weathering and related erosion (Velde 2013; Okon and Antia 2022). Soil ecologists view soil as an ecosystem having deep internal connections and complexity (Hopp and McDonnell 2009; Häring et al. 2012; Velde 2013; Reinhold-Hurek et al. 2015; Okon and Antia 2022).

Soil microbial constituents are the main factor that determines the functions of soil microorganisms and how they impact soil characteristics and nutrient constituents (Haumaier et al. 2001; Amundson et al. 1998; Reinhold-Hurek et al. 2015). The first known bacteria and microbes on earth are thought to have originated

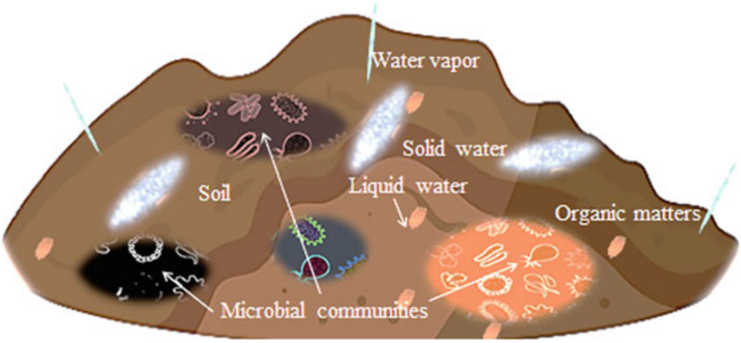

Fig. 4.8 Soil structure and some of its constituents

in the waters between two and four billion years ago (Margulis and Sagan 1997; Nisbet and Sleep 2001; Altermann et al. 2006).

These bacteria could fix nitrogen, and as they grew over time, they released oxygen into the environment (Margulis and Sagan 1997; Nisbet and Sleep 2001; Altermann et al. 2006). This process is crucial because it impacts soil fertility and structure. There are several soil microorganisms including bacteria, actinomycetes, fungus, algae, and protozoa (Edwards and Fletcher 1988; Belnap 2001; Bhattarai et al. 2015; Balasubramanian 2017). Each group has traits that characterize and define their roles in the soil (Lopez de Ceballos et al. 1983; Shormanov et al. 2012; Sei et al. 2013; Li et al. 2018; Yamamoto et al. 2018b; Tusher et al. 2021; Wang et al. 2021b). Each gram of soil around and surrounding plant roots, or the rhizosphere, contains up to ten billion bacteria (Liu et al. 2007; Sei et al. 2013; Miao et al. 2019; Polasko et al. 2019), which can be utilized for remediation purposes and restoration of natural environments.

4.4 Bacteriological Transformation of 1,4-Dioxane in the Soil

In most environments, 1,4-dioxane does not biodegrade easily possibly due to their chemical stability and high miscibility to water (Klečka and Gonsior 1986; Suh and Mohseni 2004; Ghosh et al. 2010; Stepien et al. 2014). However, several microorganisms have been identified that can biodegrade 1,4-dioxane, either directly or through co-metabolism (Altermann et al. 2006; Inoue et al. 2016, 2018; Zhang et al. 2017; Li et al. 2020; Johnson et al. 2020; Ramalingam and Cupples 2020a; Zippilli et al. 2021; Murnane et al. 2021b; Kikani et al. 2021; Wang et al. 2021a). Microorganisms use 1,4-dioxane as a growth substrate during metabolic biodegradation, but growth is slow unless 1,4-dioxane concentrations are high to levels greater than 100 mg/L (Ramalingam and Cupples 2020a; Metabolism A, Cometabolism A, Biodegradation A, Tools MB 2021). An additional growth substrate such as methane must be supplied during co-metabolic biodegradation to support biomass growth and induce the appropriate 1,4-dioxane-degrading enzymes (Gedalanga et al. 2014; US EPA 2017; Zhang et al. 2017; Aoyagi et al. 2018; He et al. 2018; Hamid et al. 2020; Ramalingam and Cupples 2020a, b; Murnane et al. 2021b). Unlike metabolic degradation, co-metabolic processes can reduce 1,4-dioxane to very low concentrations, which is important for greener ecosystems. These processes may be used separately or in combination based on needs. Details of 1,4-dioxane degradation conditions are presented in Table 4.2.

Some bacterial strains such as *Amycolata* sp. CB1190 and *P. carboxydivorans* RM-31 are capable of degradation of 1,4-dioxane in various reaction conditions. The utility of these microbes for environmental remediation of contaminants is undeniable. For example, Mahendra and colleagues investigated 1,4-dioxane, a probable human carcinogen and an important emerging contaminant (Mahendra and Alvarez-Cohen 2006). Their results revealed that among 20 bacteria strains, 13 were capable of biodegrading dioxane (Mahendra and Alvarez-Cohen 2006), indicating potential utility in remediation purposes.

Table 4.2 1,4-Dioxane degradation conditions

Bacterial strain	Reaction condition	Implication	Remarks	References
Pseudonocardia dioxanivorans CB1190	Metabolic process, the addition of THFMO	The microbes may potentially improve ecosystem health	Future improvement and use in remediation of other contaminants	Mahendra and Alvarez-Cohen (2005, 2006)
P. benzenivorans B5	Metabolic process, the addition of THFMO	The use of the microbes for the remediation of other contaminants	Future use in remediation of other contaminants	Parales et al. (1994)
Mycobacterium sp. PH-06	Metabolic process, the addition of PrMO			Kim et al. (2009)
Actinomycete CB1190	Metabolic process	Apart from established efficacy, the need for research on potential conditions necessary for degradation of 1,4-dioxane and other contaminants	Utilization for remediation of 1,4-dioxane and other contaminants	Kelley et al. (2001), Nakamiya et al. (2005), Mahendra et al. (2013), Sei et al. (2013), Zhou et al. (2016) and Murnane et al. (2021b)
Amycolata sp. *CB1190*				
P. carboxydivorans RM-31				
Afipia sp. *D1*				
A. baumannii DD1				
X. flavus DT8				
Pseudonocardia K1	Co-metabolism with the addition of THFMO	Most areas are contaminated with a mixture of contaminants. The use of these processes will potentially aid in keeping the environment clean	Utilization of these processes for remediation purposes	Mahendra and Alvarez-Cohen (2006)
B. cepacian G4	Co-metabolism with the addition of T2MO			
R. pickettii PKO1	Co-metabolism with the addition of T3MO			
P. mendocina KR1	Co-metabolism with the addition of T4MO			
Flavobacterium	Co-metabolism		Improvement and utilization of	Sun et al. (2011)
				Patt and Abebe (1995)

(continued)

Table 4.2 (continued)

Bacterial strain	Reaction condition	Implication	Remarks	References
Aureobasidium pullulans NRRL 21064			these processes for remediation purposes	
R. ruber ENV425				Hand et al. (2015)
M. austroafricanum JOB5				DeRosa et al. (1996), House and Hyman (2010), Nam et al. (2016) and Miao et al. (2019)

THFMO tetrahydrofuran monooxygenase, *PrMO* propane monooxygenase, *T2MO* toluene 2-monooxygenase, *T3MO* toluene 3-monooxygenase, *T4MO* toluene 4-monooxygenase

The application of bacteria strains in the biodegradation of contaminants, including 1,4-dioxane, was also reported by several researchers (Metsä-Ketelä et al. 2013; Hamid et al. 2020; Murnane et al. 2021b).

4.4.1 Aerobic Biotransformation

Although they are uncommon, several microorganisms that can metabolize 1,4-dioxane in aerobic conditions have been isolated. Among the microbes that can biotransform 1,4-dioxane in aerobic conditions, *Pseudonocardia dioxanivorans* CB1190 is the best studied strain (Arve 2015; Isaka et al. 2016; Zhang et al. 2017; Aoyagi et al. 2018; Guan et al. 2018; He et al. 2018; Miao et al. 2018; Barajas-Rodriguez et al. 2019; Ramalingam and Cupples 2020b; Johnson et al. 2020; Dang and Cupples 2021; Metabolism A, Cometabolism A, Biodegradation A, Tools MB 2021). Industrial activated sludge was used to enrich the bacterium and then fed with tetrahydrofuran and finally 1,4-dioxane. Studies indicate that high levels of chlorinated solvents, their by-products, and some metals may inhibit 1,4-dioxane CB1190 strain degradation (Arve 2015; Isaka et al. 2016; Zhang et al. 2017; Aoyagi et al. 2018; Guan et al. 2018; He et al. 2018; Miao et al. 2018; Barajas-Rodriguez et al. 2019; Ramalingam and Cupples 2020b; Johnson et al. 2020; Dang and Cupples 2021; Metabolism A, Cometabolism A, Biodegradation A, Tools MB 2021). The most effective inhibitors of 1,4-dioxane degradation are presented in Fig. 4.9.

It is reported that about 5 mg/L of 1,1-dichloroethene is an inhibitor of 1,4-dioxane biodegradation (Arve 2015; Isaka et al. 2016; Zhang et al. 2017; Aoyagi et al. 2018; Guan et al. 2018; He et al. 2018; Miao et al. 2018; Barajas-Rodriguez et al. 2019; Ramalingam and Cupples 2020b; Johnson et al. 2020; Dang and Cupples 2021; Metabolism A, Cometabolism A, Biodegradation A, Tools MB 2021). The most effective metal inhibitor of 1,4-dioxane degradation by CB1190 was Cu(II), which lengthened the lag time at 1 mg/L and significantly decreased

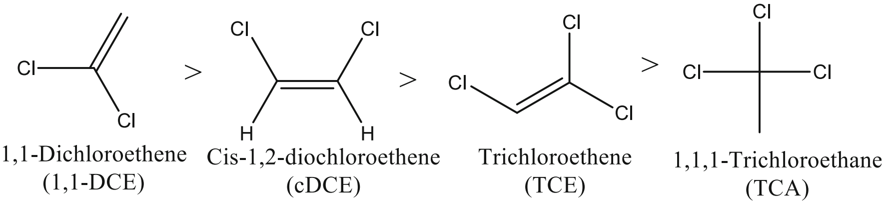

Fig. 4.9 Chemical structures of 1,4-dioxane degradation inhibitors (Source: Tomo Aoyagi et al.)

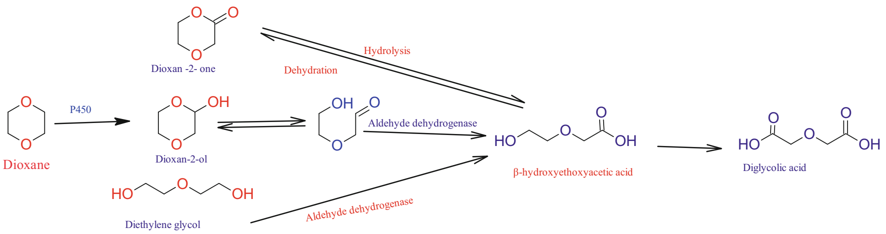

Fig. 4.10 Series of chemical processes occurring during aerobic biotransformation of 1,4-dioxane (released under CC by 4)

1,4-dioxane degradation rates at 10 and 20 mg/L Cu(II). While Zn(II) did not impact biodegradation of 1,4-dioxane at the highest test concentration (20 mg/L Zn), Cd(II), Ni(II), and Ni(II) were less sensitive to 1,4-dioxane degradation (Arve 2015; Isaka et al. 2016; Zhang et al. 2017; Aoyagi et al. 2018; Guan et al. 2018; He et al. 2018; Miao et al. 2018; Barajas-Rodriguez et al. 2019; Ramalingam and Cupples 2020b; Johnson et al. 2020; Dang and Cupples 2021; Metabolism A, Cometabolism A, Biodegradation A, Tools MB 2021). This result indicates that 1,4-dioxane occurs as a mixture of several contaminants; therefore, the more effective approach will be to propose and improve techniques for co-biotransformation of 1,4-dioxane and its co-contaminants in the environments. For the treatment of industrial wastewater contaminated with 1,4-dioxane, biodegradation is a viable, economical, and environmentally benign solution. A schematic and proposed chemical equation for aerobic biotransformation is presented in Fig. 4.10.

In a study, Tusher and colleagues explored metabolic bacteria from a stable microbial community that degrades 1,4-dioxane (Tusher et al. 2021). *Pseudonocardia* sp. (TS28), *Dokdonella* sp. (TS32), and *Afipia* sp. (TS43) were three bacterial strains that were discovered to be capable to use 1,4-dioxane as their only source of carbon and energy to break down organic compounds (Tusher et al. 2021). This was a pioneer study that detailed the participation of the genus Dokdonella in the biodegradation of 1,4-dioxane as presented in Fig. 4.11. Genus Dokdonella possesses inducible 1,4-dioxane-degrading enzymes' potential for remediation purposes (Tusher et al. 2021).

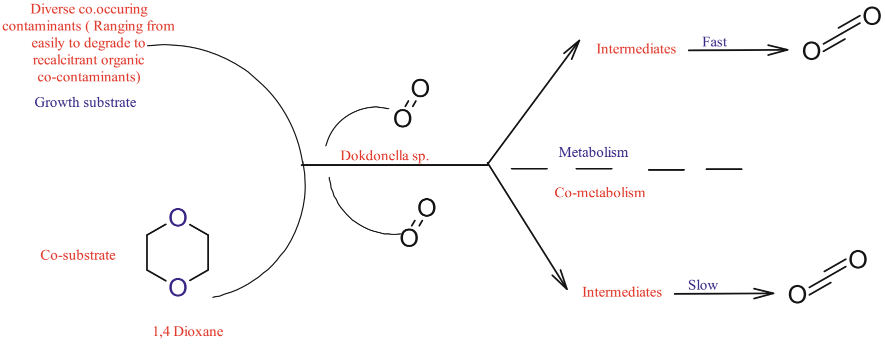

Fig. 4.11 Biodegradation of 1,4-dioxane by Dokdonella bacterium (released under CC by 4)

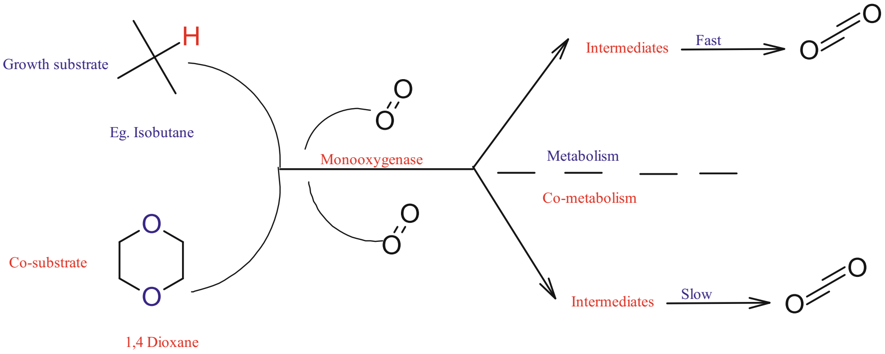

Fig. 4.12 Some main processes involved in co-metabolism (Mahendra et al. 2013)

The findings of this study also contributed to our understanding of how various 1,4-dioxane degraders interact and cohabit in a consortium while utilizing a single carbon supply to create an effective biological 1,4-dioxane treatment system.

4.4.2 Aerobic Co-metabolic Biotransformation of 1,4-Dioxane

A simultaneous degradation method of two compounds is known as co-metabolism, whereby the degradation of a second compound always depends on the presence of the first compound. Organisms involved in co-metabolizing 1,4-dioxane, in contrast to 1,4-dioxane-metabolizing microorganisms, can break down 1,4-dioxane after growing on a main growth-supporting substrate (Kashimoto et al. 1989; Mahendra et al. 2013; US EPA 2014a, 2017; Arve 2015; Zhang et al. 2017, b; Johnson et al. 2020; Miao et al. 2020; Metabolism A, Cometabolism A, Biodegradation A, Tools MB 2021; Tusher et al. 2021). Figure 4.12 shows some main processes involved in co-metabolism.

Co-metabolic active bacteria such as *R. rhodochrous* ATCC 21198 can often break down co-substrates at lower concentrations below those attained by organisms that metabolize and thrive on them since co-substrate is not utilized as either primary carbon or energy sources (Kashimoto et al. 1989; Mahendra et al. 2013; US EPA 2014a, 2017; Arve 2015; Zhang et al. 2017, b; Johnson et al. 2020; Miao et al. 2020; Metabolism A, Cometabolism A, Biodegradation A, Tools MB 2021; Tusher et al. 2021). Numerous bacteria such as *Mycobacterium austroafricanum* JOB5 (Arve 2015; Zhang et al. 2017; Johnson et al. 2020; Tusher et al. 2021) can co-metabolize 1,4-dioxane in various conditions. These include model organisms that utilize well-characterized enzymes like soluble methane monooxygenase (sMMO) and grow on primary substrates like toluene or methane, and other 1,4-dioxane co-metabolizing strains reported to thrive on THF, ethane, and isobutane. Numerous bacterial monooxygenases have the capacity to oxidize numerous co-substrates at once; if fully studied and utilized, this may have a promising future in the remediation of environmental contaminants.

Hatzinger and colleagues assessed methane and ethane capacity to promote the aerobic co-metabolism that breaks down 1,4-dioxane in groundwater aquifers (Hatzinger et al. 2017). Ethane encouraged *M. sphagni ENV482*, which was isolated from a separate aquifer, to aerobically break down 1,4-dioxane (Hatzinger et al. 2017). According to this study, ethane, a common by-product of the biotic or abiotic reductive dechlorination of chlorinated ethanes and ethenes, may act as a substrate to speed up the breakdown of 1,4-dioxane in aquifers, especially in areas where these by-products combine with aerobic groundwater (Hatzinger et al. 2017). A similar study was conducted by Murnane and colleagues on co-metabolic transformation of 1,1,1-trichloroethane and 1,4-dioxane by pure cultures of *R. rhodochrous* (ATCC strain 21198) (Murnane et al. 2021a). Results indicated that the transformation of dioxane occurred without a lag phase for cells grown on 2-butanol, while an induction period of several hours was required for 1-butanol-grown cells (Murnane et al. 2021a). A similar observation was archived with activity-based labelling patterns for monooxygenase hydroxylase components and specific rates of tetrahydrofuran degradation (Murnane et al. 2021a). The study further reported lower rates of oxygen gas consumption in the reactors containing *tetra*-s-butylorthosilicate, which has benefits for in situ bioremediation. Indicating the structure of SRC is important when developing passive aerobic co-metabolic treatment systems.

4.4.3 Anaerobic Biotransformation of 1,4-Dioxane

Little metabolic or co-metabolic anaerobic 1,4-dioxane biodegradation has been observed thus far (Skinner et al. 2009; Göen et al. 2016; Guan et al. 2018). There was no evidence of 1,4-dioxane biodegradation in microcosm research employing samples of aquifer material from several 1,4-dioxane-impacted sites. On 1,4-dioxane, an iron-reducing bacterium did grow anaerobically with chemical processes (Arve 2015; Zhang et al. 2017; Hamid et al. 2020; Ramalingam and Cupples 2020a; Dang and Cupples 2021; Sengupta and Dhal 2021). Fe(III)-reducing

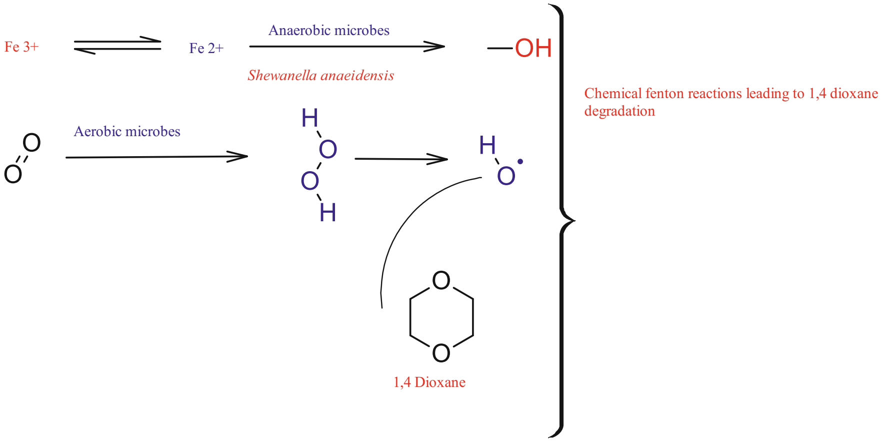

Fig. 4.13 Facultative anaerobe transformation of 1,4-dioxane by *S. oneidensis*

facultative anaerobe *S. oneidensis* can produce hydroxyl radicals, which degrade 1,4-dioxane as indicated in Fig. 4.13 (Sekar and DiChristina 2014; Sekar et al. 2016).

S. oneidensis produces Fe(II) in anaerobic circumstances, which interacts chemically with H_2O_2 to yield hydroxyl radicals that can result in oxidative 1,4-dioxane breakdown (Sekar and DiChristina 2014; Sekar et al. 2016).

4.5 Roles of Soil Bacteria in the Biotransformation of 1,4-Dioxane

A cyclic molecule such as 1,4-dioxane with two ether moieties was thought to be relatively unmanageable to biodegradation, until a recent study that demonstrated that it may be efficiently biotransformed (Zhang et al. 2016, 2017; He et al. 2018). Dioxane-degrading bacteria are promising in situ bioremediation agents for cleaning up 1,4-dioxane-contaminated soils because it is less expensive than using advanced technologies. Several strains that may co-metabolically degrade dioxane have been isolated from wastewater treatment facilities or dioxane-affected areas (He et al. 2018). Numerous research emphasized the significance of monooxygenase enzymes in dioxane breakdown, and a gene cluster and sequence identified in *P. dioxanivorans* CB1190 that can aid in this process (i.e., thmADBC) (Mahendra and Alvarez-Cohen 2006; Kim et al. 2009; Sales et al. 2011). The gene cluster encodes dioxane monooxygenases, the dissolving di-iron (SDIMO) that initiates the breakdown of dioxane. The di-iron monooxygenase contains multiple bacterial enzyme components that can catalyze the oxidation of a variety of priority pollutants such as chlorinated solvents and aromatic hydrocarbons, among other contaminants, implying that they have inherent bioremediation potential (Notomista et al. 2003; Grostern et al. 2012).

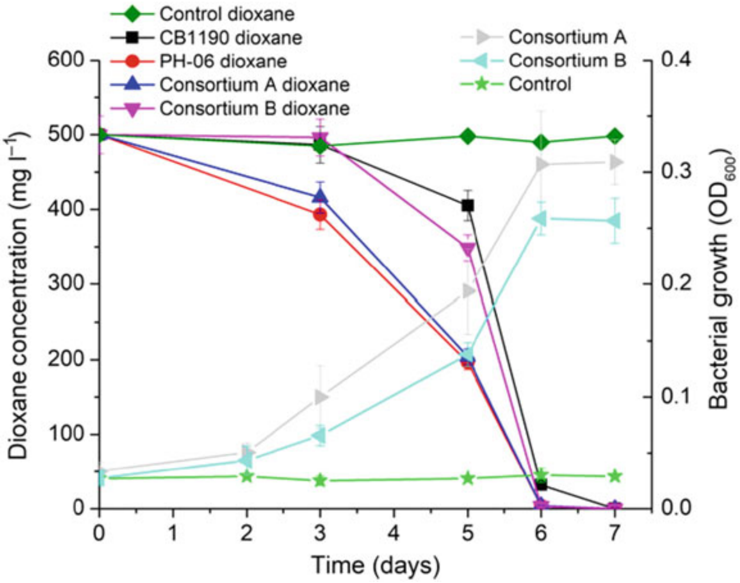

Fig. 4.14 Degradation of dioxane-enriched consortia and two archetypes (left) and concurrent growth of consortia (right). [Source: He et al. (2018)]

A garden soil with unknown history of exposure to dioxane has shown a capability to degrade 500 mg/L dioxane as the sole source of carbon and energy to non-detectable levels within a week (He et al. 2018). Filtering through the aquifer material hinders the subsurface dispersion of inoculated bacteria, which is particularly problematic when the cultures aggregate. The archetypal dioxane degraders, which aggregate in suspension and include *P. dioxanivorans* (CB1190) and *M. dioxanotrophicus* (PH-06), are severely constrained by this (Grostern et al. 2012). Remarkably, the SDIMO consortia (A and B) enriched by He et al. (2018) from garden soil did not clump as much as the archetype, making them better candidates for in situ bioaugmentation at areas with inadequate indigenous dioxane biodegradation ability. Figure 4.14 shows findings indicating that there is a substantial growth of bacteria when exposed in the dioxane, while simultaneous decrease in dioxane concurrently occurs.

Tenfold serial dilution was adopted during conduction of experiments in Fig. 4.14 where ammonium mineral salts were used as growth medium with an initial dioxane concentration of 500 mg/L, while autoclaved bacteria were used as control.

4.6 Fate of 1,4-Dioxane Biotransformation Products

Numerous intermediates produced by the biotransformation of 1,4-dioxane in environmental matrices have the potential to interact with the environment and result in secondary pollution issues. Therefore, it is crucial to comprehend their fate and the

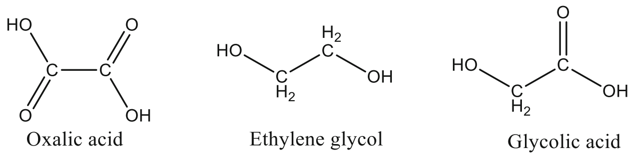

Fig. 4.15 Some intermediate compounds produced by *Cordyceps sinensis* during biodegradation of 1,4-dioxane

effects of these items. Spectrometry, chromatography, nuclear magnetic resonance spectroscopy (NMR), gas chromatography-mass spectroscopy (GC-MS), high-pressure liquid chromatography (HPLC), and gas chromatography-flame ionization detection (GC-FID) are some techniques that can be used to quantify and qualitatively estimate the extent of changes in 1,4-dioxane (Kikani et al. 2022). The production of metabolites with are structurally distinct via redox mechanisms is the consequence of 1,4-dioxane transformation by biomaterials. There have been papers on microbial systems' qualitative evaluation of 1,4-dioxane intermediates and metabolites. The intermediates produced by *Cordyceps sinensis* during the biodegradation of 1,4-dioxane are shown in Fig. 4.15 (Nakamiya et al. 2005; Mahendra et al. 2007; Kang and Doty 2014).

Shaily and colleagues (Mahendra et al. 2007) described a process for dioxane oxidation by monooxygenase-expressing cells that does not result in the buildup of hazardous intermediate compounds in the environment. In this mechanism, dioxane is first transformed to 2-hydroxy-1,4-dioxane, which is then instantaneously oxidized to 2-hydroxyethoxyacetic acid. During a second monooxygenation step, 2-hydroxy-1,4-dioxane is further hydroxylated, yielding a mixture of dihydroxyethoxyacetic acids with a hydroxyl group in the ortho or para position. After the second ether bond is broken, small organic molecules such as ethylene glycol, glycolate, glyoxylate, and oxalate are progressively formed and mineralized to CO_2 via common cellular metabolic mechanism.

4.7 Conclusion

The occurrence of 1,4-dioxane in the water, wastewater, soil, drinking water, and groundwater is globally reported. This chemical is classified as a carcinogenic compound, posing a threat to ecosystems upon its chronic exposure. Its occurrence in many consumer products as either an impurity or a solvent and its high miscibility to water lead to its widespread contamination, complicating its remediation methods. Bacteria such as *Pseudonocardia dioxanivorans* CB1190 through aerobic biotransformation, *Rhodococcus rhodochrous* ATCC 21198 through co-metabolic transformation, and *Shewanella oneidensis* through anaerobic transformation have shown a significant bioreduction of 1,4-dioxane concentration in the contaminated environments. The role of these bacteria is through either consumption of 1,4-dioxane as a source of energy, thus reducing its concentration, or transformation to different products that are harmless compared to parent molecule. In the future, relying of microbial remediation of 1,4-dioxane is expected to take a pace since nature does not leave behind unattended waste resulting in an ecological safety.

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Persistence, Toxicity, and Strategies for Remediation of Brominated Flame Retardants in Soil and Sedimentation in Aquatic Matrices Under Aerobic and Anaerobic Conditions

5

Amy Nava and Hemen Sarma

Contents

Abstract

Novel brominated flame retardants (NBFRs) and legacy BFRs have been used in industrial and home applications to reduce the risk of ignition. However, the use of flame retardants is of particular concern due to the likelihood of being found in

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high concentrations, persistence in the environment, and for bioaccumulation in the environment. BFRs are of interest due to the potential toxicity to humans and endocrine-disrupting properties. To adress toxicity and persistence of BFRs, new or novel BFRs (NFBRs) have been introduced as a replacement. However, NBFRs have similar chemical properties and environmental fates as legacy BFRs. This chapter discusses various methods of abiotic and biotic degradation of BFRs, culturing conditions, potential microorganisms, and enzymes that can biodegrade BFRs from various environmental sources. We include the proposed mechanisms of biodegradation and persistence in the environment for several congeners. Water matrices are also discussed as an environmental source since BFRs in sedimentation are not well known and pose an essential factor in assessing the amount of BFRs present in the environment. The presence of BFRs in our environment have been concerning as they have been linked by various studies to the decline of sperm counts and fertility issues of both genders as well as contribute to cognitive and developmental problems in children.

Keywords

Brominated flame retardants · Bioremediation · Halogenated · Endocrine disruptor · Polybrominated diphenyl ethers (PBDEs) · Neurotoxicity · Decabrominated diphenyl ether (BDE-209) · Decabromodiphenyl ethane (DBDPE) · New brominated flame retardants · Tetrabromobisphenol A (TBBPA) · Minimal salts media (MSM) · Hexabromocyclododecanes (HBDC)

5.1 Introduction

Epoxy resins are widely used for many products but are highly combustible. Furthermore, the amount of heat created and the toxic gases released once ignited are significant causes of deaths and property damage. For this reason, flame retardants (FRs) have been developed to mitigate this problem (Waaijers and Parsons 2016). BFRs represent various chemicals applied to many products, including plastics, polymers, textiles, wood, or other ignitable objects, to prevent combustion. During the process of combustion, free radicals are formed. Halogens, namely bromine, are good at detaining free radicals and lowering the decomposition temperature (Kodavanti et al. 2017). Approximately one-quarter of the world's flame retardants are brominated (Andersson et al. 2006). There are three main groups of BFRs used. These are decabrominated diphenyl ether (BDE-209), tetrabromobisphenol A (TBBPA), and hexabromocyclododecane (HBCD) (Andersson et al. 2006).

BFRs, also known as organohalogens, comprise a group of chemicals that use flame retardants, which is concerning due to their toxicity, bioaccumulation, and environmental accumulation. NBFRs have been cited as being neurotoxic in children who are still developing (Roze et al. 2009). Due to bioaccumulation and toxicity, BFRs have been banned in various countries, and novel BFRs are being used as an alternative to BFRs. However, novel BFRs have been shown to accumulate in aquatic matrices, air, sediment, and sludge and bioaccumulate in animals (Xiong et al. 2019). In this review, we will also focus on water matrices as sedimentation is a part of land management that is often overlooked and often harbors pollutants that are harmful to aquatic ecosystems (Bakker et al. 2008).

5.2 Toxicity of BFRS

The toxicity of BFRs has been cited in many publications. BFRs are lipophilic and are stored in adipose tissue, and have the ability to biomagnify in the food chain. This is a potential risk considering that the animals humans consume have been shown to harbor BFRs. Evidence shows that DBDPE was found to induce oxidative stress, changes in morphology, and transcriptomics in white rot fungus *P. ostreatus* (Wang et al. 2022a). This study observed a decrease in fungal biomass in concentrations from 1 to 50 mg L^{-1} DBDPE. A decrease in superoxide dismutase, catalase, and glutathione was also observed. This is significant since all three are crucial in the detoxification process. Most significant was the role in the downregulation of genes involved in metabolisms such as oxidative phosphorylation, TCA cycle, and carbon metabolism. This study highlights transcriptomics as an essential tool in molecular biology for understanding the mechanisms of toxicity after exposure to pollutants. Moreover, a multi-omics approach can accurately map the pathways in response to pollutant exposure, thus revealing the mechanisms of toxicity for organisms (Li et al. 2022).

Kidney miRNAs from grass carp were found to be significantly changed after exposure to BFR and DBDPE (Gan et al. 2016). The study found that five kidney miRNAs were significantly downregulated, while 36 kidney miRNAs were significantly upregulated. Interestingly, miR-155, miR-205, and most miR-10 family members were upregulated. miR-155 is known to regulate immune response, miR-205 is linked to nephropathy, and dysregulation of miR-10 family members is associated with various cancers (Gan et al. 2016). The study proposes using miRNAs as biomarkers for evidence of environmental toxicity. This could be a useful tool to determine the extent of toxicity in organisms.

Sun et al. (2020) found that exposure to DBDPE and BDE-209 was linked to hepatoxicity, liver pathology, and changes in the morphology of the liver. These changes also included an increase in liver weight, with an abnormal liver/body ratio. The study also found that BDE-209 and DBDPE could induce inflammation and oxidative stress, increase serum glucose levels, and interfere with metabolic pathways through the downregulation of enzymes in rats. A recent publication found similar results with DBDPE and BDE-209. Jing et al. (2019) linked BDE-209 to morphological and structural changes in the heart. The study on male rats also found that decabromodiphenyl ethane (DBDPE) and BDE-209 increased inflammatory markers, interleukin-1 beta (IL-1 b), as well as IL6 and IL10. The results of the study also indicated that BDE-209 had stronger toxic effects and could cause oxidative stress, inflammation, and heart damage. DBDPE also caused oxidative stress, lipid peroxidation, genetic toxicity, and DNA damage in the earthworm, *Eisenia fetida* (Zhao et al. 2020). Lipid peroxidation and enzyme inhibition were also found in a study by Feng et al. (2013) in *Carassius auratus*. These findings present severe implications for public health as chronic exposure and high concentrations of DBDPE lead to heart and liver disease, lipid peroxidation, and possibly DNA damage.

Ji et al. (2014) discovered gender-specific responses to TBBPA. The physiological effects on the model organism, *Mytilus galloprovincialis*, were determined using iTRAQ-based proteome analysis. TBBPA exposure may cause a variety of physiological responses, including apoptosis, signal transduction, immunological and oxidative stress, and energy disturbance. More importantly, the study revealed gender-specific responses and encouraged inclusion of both genders when investigating the effects of environmental toxicity of BFRs. Several articles highlight a cocktail of pollutants, including BFRs that may be responsible for the declining sperm counts and semen quality within the past few decades (Ingle et al. 2018; Yu et al. 2018). In addition, BFRs were cited as causing fertility problems in both genders as well as developmental problems in children (Kodavanti et al. 2022).

5.3 Persistence of BFRs in the Environment

Polybrominated diphenyl ethers (PBDEs) are ubiquitous in the environment as they are present in air, soil, and water. PBDEs, penta-PBDE, octa-PBDE, and deca-PBDEs, have been on the persistent organic pollutants (POPs) list since 2017 (Jing et al. 2019; Ezechiáš et al. 2014). Altogether, there are 209 different congeners. Since PBDEs are not bound to other chemicals, they can be easily added to furniture or textiles. In addition, they are volatile and quickly released into the air (Webster et al. 2009). For this reason, household dust and indoor air have a higher concentration of PBDEs than outdoors. Novel PBDEs have been used as a replacement for legacy PBDEs however, they are also persistent in the environment and are toxic and biomagnified in the food chain (Ezechiáš et al. 2014).

Due to various physiological properties such as low vapor pressure, low Henry's law constant, low solubility, and low octanol-water partition, legacy BFRs such as TBBPA can quickly be deposited onto the soil, sediments, and particles in the atmosphere (Dong et al. 2022; Sunday et al. 2022). The majority of BFRs are additives. They are added and mixed as the polymer is being made but are not usually bound to the polymer covalently (Yu et al. 2016). Therefore, PBDEs are considered additives, allowing them to easily volatilize away from the original product they were added to and subsequently enter the environment (Yang et al. 2018). More concerning is that little is known about the toxicity of partially degraded BFRs or lower brominated BFRs as a result of natural environmental processes. Moreover, assessing the amount of BFRs trapped in sedimentation is difficult. Figure 5.1 illustrates the broad distribution of BFRs in soil and sedimentation in Europe, Asia, and the USA. Lao et al. (2023) found that the amounts of BFRs, especially PBDEs, present in sediment were significantly correlated with the amount

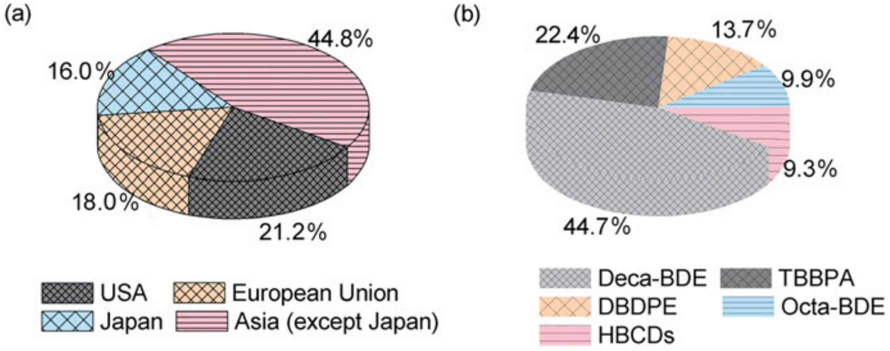

Fig. 5.1 BFR consumption and distribution in soil and sediment. [Retrieved from Yu et al. (2016)]

of industrialization and output of the surrounding geographical areas along the Pearl River Delta (Lao et al. 2023). Figure 5.1 shows the distribution of various BFRs in Asia, Europe, the USA, and Japan in soil and sediment.

5.3.1 Potential Exposure to Legacy BFRs and NBFRs in Indoor and Outdoor Settings

The persistence of legacy BFRs in indoor settings poses a health risk for humans, and the same may be expected of NBFRs. Four main routes of toxicity were identified. These are ingestion of indoor dust, absorption through the skin, inhalation of BFRs in indoor dust, and ingestion of BFRs in food (Zuiderveen et al. 2020). Reche et al. (2019) collected samples of outdoor ambient air, indoor workplace ambient air, and indoor dust across Spain to determine concentrations and trends for each. The study found that high concentrations of outdoor PBDE ranging from 1.18 to 28.6 pg m^{-3} were correlated to outdoor landfills and recycling centers. In addition, high dechlorane plus (DP) concentrations in indoor air at concentrations of 2.90–42.6 pg m^{-3} were strongly correlated to new electronic devices.

A similar study by McGrath et al. (2018) conducted in Melbourne, Australia, tested 51 dust samples from homes, offices, and vehicles to identify prominent BFRs in each setting. The BFRs tested were eight PBDEs (−28, −47, −99, −100, −153, −154, −183, and −209) and seven NBFRs (PBT, PBEB, HBB, EH-TBB, BEH-TEBP, BTBPE, and DBDP) identified using selective pressurized liquid extraction (S-PLE) and gas chromatography coupled to tandem mass spectrometry (GC-MSMS). The study also found that legacy and NBFRs were linked to specific areas, such as offices with the highest concentrations of penta-BDE. At the same time, homes and vehicles contained higher levels of EH-TBB and BDE 209. In addition, toddlers were more at risk by up to 2 orders of magnitude than adults for exposure to PBDEs and NBFRs. This is especially concerning since evidence suggests that BFRs are neurotoxic to children (Roze et al. 2009).

Ingestion of BFRs has been found to vary with different foods and locations close to e-waste recycling areas. Various studies have found the presence of PBDEs in fish and meat products in China (Shi et al. 2018). Sun et al. (2014) found that daily consumption of PBDEs in the coastal regions of South China ranged from 1.42 to 5.91 ng d^{-1}. HBCDs were ubiquitous in human milk and food products of animal origin in China despite that HBCD has been restricted since 2016 (Shi et al. 2018). The implications of this are that HBCD and relevant congeners are likely airborne, and contaminated dust is being ingested and tends to persist in the environment and biomagnify in the food chain.

5.4 Biodegradation of BFRs in Soils and Sedimentation Under Anaerobic and Aerobic Conditions

The kinetic rates for the biodegradation of BFRs in both anaerobic and aerobic soils differ. Generally, degradation kinetics are faster in aerobic soils (Nyholm et al. 2010). However, biodegradation is much more substantial and efficient under anaerobic conditions (Gerecke et al. 2006). During the anaerobic digestion of organic micropollutants, four main stages occur. These consist of methanogenesis, hydrolysis, acidogenesis, and acetogenesis (Carneiro et al. 2020). These processes are also influenced by microorganisms and cometabolite biotransformation (Arias et al. 2018).

Biodegradation of other BFRs, such as tetrabromobisphenol A (TBBPA), was found to be influenced by the complexity of the carbon source. Complex sources such as wastewater, as opposed to glucose, were biodegraded slower (Macêdo et al. 2022). This was further corroborated by Balaban et al. (2021) demonstrating that the addition of a vitamin source delayed bacterial growth and, as a result, reduced TBNPA and DBNPG biodegradation. Moreover, the study concluded that concentrations higher than 0.5 mg L^{-1} inhibited biodegradation in *Clostridium* spp. This is in agreement with Wang et al. (2022b), who stated that higher concentrations of DBDPE inhibit biodegradation. Concentrations higher than 50 mg L^{-1} were too toxic for the organisms.

Clostridium spp. has also proven to be effective in the biodegradation of HBCD (Li et al. 2020). In this study, both *Bacillus* spp. and *Clostridium* spp. were capable of biodegradation of up to 70% and 77% from cell suspensions taken from Chiang Chung soil and riverbank soil, respectively. The biodegradation was conducted under aerobic conditions. The biodegradation kinetics was slower in soil than in soil suspension for this study.

Huang et al. utilized a system of maize plants and *P. aeruginosa* strain HS9 to remove HBCD from the soil. The optimal temperature and pH reported were 30 °C at pH8, respectively, for the increased degradation rate of hexabromocyclododecane (HBCD). The study reported that the HS9 strain could remove 69% of the 1.7 mg L^{-1} of HBCDs (α-, β-, and γ-HBCD) in 14 days. The addition of HS9 was also found to stimulate plant growth by removing HBCDs from the soil. Further, adding HS9 enriched the number of microbes in rhizospheric soil. This included fungal microbes, an essential part of soil microbial ecosystems. Peng et al. (2015) reported degradation of HBCD and a-HBCD to 90% under similar culturing conditions of 30 °C and pH 7 using the bacterial strain *Achromobacter* sp. Stepwise increasing additions of HBCD were added to culturing conditions to optimize the ability to biodegrade α-, β-, and γ-HBCD in a study by Geng et al. (2019). The biodegradation of HBCD was under aerobic conditions using a *Pseudomonas* sp. strain GJY at 30 °C at pH 7. Soil samples were collected from Ziya e-waste recycling centers in Tianjin, China. The strains were derived from the soil samples using extinction-dilution techniques. The degradation of each isomer was conducted in MSM with each diastereoisomer. After 8 days, the results showed degradation efficiencies of 85.38%, 82.64%, and 75.5% for α-, β-, and γ-HBCD, respectively.

Another synergistic application for degradation was applied to degrade BDE-209. Chang et al. (2021) utilized a novel bio-slurry bioreactor (NBB), which consisted of UVA LED irradiation coupled with biodegradation by microbes in a Ca-montmorillonite clay slurry. The NBB coupled UV-resistant bacteria, *Stenotrophomonas* sp., *Pseudomonas* sp., and *Microbacterium* sp., and UV photolysis was carried out in a clay slurry under anaerobic conditions. Quantification of debromination was done by measuring Br^- using ion chromatography. Biodegradation was done by using BDE-209 as the sole source of carbon. The degradation kinetics were most efficient with the coupled system than either alone.

Yan et al. (2018) reported using soil columns under anaerobic conditions to degrade pentabromodiphenyl ether (BDE-91). The study replaced oxygen with sulfate as the final electron acceptor in columns filled with soil to remediate contaminated reclaimed water to recharge groundwater. Interestingly, this study used sulfate-reducing bacteria and archaea for the biodegradation of BDE-91. Elevated levels of sulfate were found to enhance the biodegradation of BDE-91.

Anaerobic conditions were utilized in a study by Ramaswamy et al. (2021). *Dehalococcoides mccartyi* strain CG1 debrominated tetrabromobisphenol A (TBBPA) ultimately into BPA in 10 days. *Dehalococcoides mccartyi* strain CG1 was able to utilize TBBPA as a sole source of carbon. Furthermore, a proteomic analysis revealed that the reductive dehalogenase, PcbA1, was responsible for debromination of TBBPA. Therefore, the acceleration of biodegradation of TBBPA was interpreted as metabolic utilization of TBBPA. Furthermore, a 92-fold increase in cell density of *D. mccartyi* strain CG1 demonstrated further evidence of this.

BDE-209 and other polybrominated diphenyl ethers can be broken down by coupling a Fenton system with persulfate (Wu et al. 2020). This abiotic approach can remove BDE-209 from soils or other hard surfaces. The study reported degradation efficiency ranging from 73.4 to 95.8%. The addition of persulfate resulted in the generation of SO_4. The SO_4 was believed to make a nucleophilic attack on BDE-209, resulting in debromination to lower brominated constituents and pentabromophenol (Wu et al. 2020). The mechanism was achieved through the cleavage of C–O bonds and subsequent replacement with OH groups (Wu et al. 2020). The resulting products, nona-BDEs and pentabromophenols, were vulnerable to further transformation. The study presents this data as a cost-effective solution for removing BDE-209 from soils in an aerobic environment.

Larger eukaryote organisms are potential solutions to removing BFRs from the soil. Earthworms were used in a study by Qiao et al. (2022) for the potential removal of BFRs: BDE 209, PBT, DBDPE, BTBPE, and HBB. The removal of these BFRs varied with each BFR. BFRs with similar molecular weights and chemical structures had similar enrichment and removal results. The study also demonstrated the potential for secondary pollution from worm castings that were not retained in the earthworm. The use of earthworms could remove BDE-209 and DBDPE from the soil. The removal of the other BFRs could have been more efficient.

5.5 Biodegradation of Contaminated Water and Sediment Matrices

Systematic surveillance of BFRs in wastewater treatment plants (WWTPs) is crucial for understanding efficient methods of removal and contamination. Moreover, little is known about certain BFRs, such as 1,2-dibromo-4-(1,2-bromomethyl) cyclohexane (TBECH), in aqueous environments. Anaerobic digestion is a well-studied aspect of wastewater treatment. Hydrolysis is essential in this process and facilitates the enzymatic breakdown of larger molecules into monomers (Macêdo et al. 2022). Carneiro et al. (2020) found that hydrolysis and acidogenesis were crucial steps in removing organic micropollutants from wastewater. Wastewater treatment plants could detoxify wastewater by coupling bioremediation methods with regular treatments. Ruan et al. (2019) discovered that BFRs were prevalent in influent water sampled from various WWTPs in Hong Kong. This work emphasized the need to monitor the enantiomer-specific behavior of chiral BFRs in the various treatments used in WWTPs. The study also discovered that biological treatment resulted in more efficient BFR elimination and enantiomer-specific degradation of chiral BFRs.

A novel approach of combining an upflow anaerobic sludge blanket bioreactor (UASB) and integrated fixed film/activated sludge (IFAS) system can increase the efficiency of organic micropollutant removal as was done in a study by Arias et al. (2018). This innovative approach reduced nitrogen by using methane as an electron donor. The study reported that the system consisting of methanotrophs and heterotrophic denitrifiers removed 93% of chemical oxygen demand and dissolved methane in the UASB effluent. The purpose of the system was to increase microbial diversity to achieve more efficient removal of organic micropollutants. However, different culturing conditions, which will be discussed further, are essential for achieving this goal.

In a study by Balaban et al. (2021), a four-strain consortium was used to degrade both TBNPA and DBNPG. Table 5.1 lists the genera, GenBank accession number, and species in the consortium that biodegraded both TBNPA and DBNPG. Interestingly, the study reported that both compounds were degraded at similar rates. The authors hypothesized that this might be due to similar enzymes and metabolic

Table 5.1 Table showing the genera, species, and GenBank accession numbers of the four-strain consortium with initial densities of each strain

ID	Strain (highest similarity, 99%)	GenBank accession number	OD 600 (initial density CFU mL^{-1})
DB2	*Pseudomonas citronellolis*	KY229738	0.001 (1.10×10^5)
DB3	*Gordonia sihwensis*	KY229739	0.001 (1.70×10^5)
DB4	*Shinella zoogloeoides*	KY229740	0.004 (4.90×10^5)
DB5	*Microbacterium oxydans*	KY229741	0.027 (3.00×10^6)
TB1	*Pseudomonas aeruginosa*	KY229734	
TB2	*Delftia tsuruhatensis*	KY229735	
TB3	*Pseudomonas citronellolis*	KY229736	
TB4	*Sphingobacterium siyangense*	KY229752	
TB5	*Microbacterium paraoxydans*	KY229753	

The species listed are capable of biodegradation of TBNPA and DBNPG. Retrieved from Balaban et al. (2021)

pathways of degradation for both. The study proposed a monooxygenase pathway for degradation. When both TBNPA and DBNPG were added, the degradation kinetics were almost twice as long (from 3–4 days to 7 days). Bacterial growth was determined to be the limiting factor, and a carbon source was needed for biodegradation. Yeast extract and glucose significantly enhanced biodegradation (3–7 days), while the vitamin mix slowed degradation kinetics (1–2 months).

Liang et al. (2019a) found that efficient removal of typical BFR, 2,4,6-tribromophenol (TBP), was possible using *Bacillus* sp. GZT. This study also identified genes and enzymes corresponding to the bioremediation of TBP and proposed an enzymatic pathway (pictured below in Fig. 5.2) for biodegradation. Interestingly, the study proposed the possibility of biodegradation enhancement and tolerance with recombinant strains containing the genes: tbpA, tbpB, tbpC, tbpD, and tbpE.

Lin et al. (2021) used a microbial fuel cell to bioremediate and detoxify wastewater. Microbial fuel cells (MFCs) have been used more recently to biodegrade various organic compounds and recover energy by increasing the electron transfer rate and biodegradation efficiency (Hassan et al. 2018). The efficiency of using MFCs is evident with a less toxic final product of bioremediation and energy recovery through bioelectrochemical processes (Hassan et al. 2018). Lin et al. used different genera of bacteria for dehalogenation (*Pseudomonas*), electroactive bacteria (*Desulfovibrio*), and aromatic ring-cleaving bacteria (*Geobacter*) in the MFC for further biodegradation than bisphenol A.

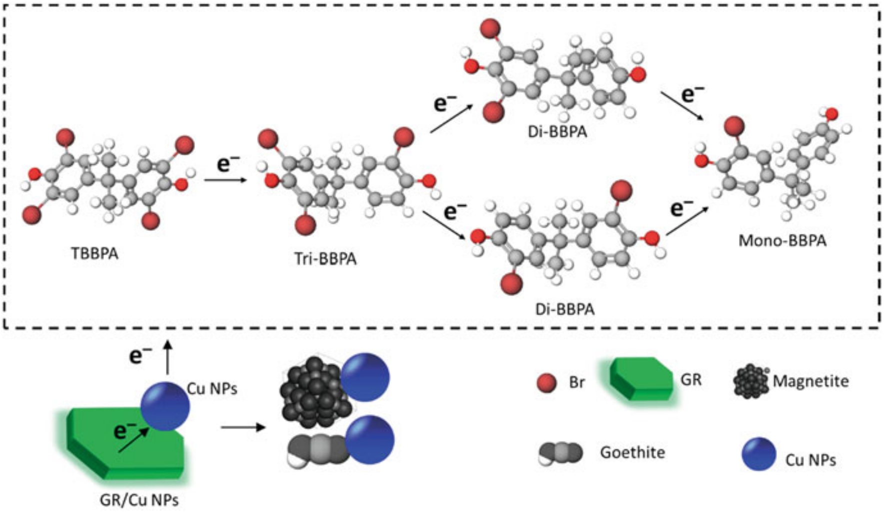

Fig. 5.2 Proposed mechanism of reduction by GR-Cu NPs. The reduction of TBBPA occurs on the surface of Cu NPs, and electrons from GR are transferred to the active sites of Cu NPs. GR(Cl) is transformed into two byproducts, goethite and magnetite, after TBBPA is reduced. [Retrieved from Fang et al. (2019)]

5.6 Catalytic Methods of Degradation and Reduction of BFRs in Wastewater, Aquatic Matrices, and Sediment

The presence of BFRs in sedimentation from a temporospatial aspect needs to be better studied and understood. In a study by Vauclin et al. (2021), sediment cores were taken along the backwater areas along the Rhône River. An age-depth model was established to find how the concentrations of BFRs and other pollutants were prevalent for each period. The findings were consistent with phasing out certain pollutants, such as polychlorinated biphenyls, which showed lower concentrations after phasing out. The study also found that novel and legacy BFRs reached peak concentrations in the early 2000s and have remained stable since the 2010s. The study highlighted the importance of sediment cores for determining spatiotemporal trends in both legacy and novel BFRs. Due to the hydrophobicity of BFRs, sedimentation often becomes a sink, and high concentrations of BFRs can be found in river sedimentation near e-waste sights (Yu et al. 2016). Xiong et al. (2017) proposed bioaugmentation with *Bacillus* sp. GZT for TBP removal from river water/sediment. This is in addition to the phyla isolated from sediments. These were Firmicutes, Actinobacteria, Proteobacteria, and Bacteroidetes. In this study, the biodegradation of TBP was enhanced by supplementation with NaCl, glucose, yeast extract, sodium propionate, and humic acids.

Catalytic methods of removing BFRs from wastewater have been explored in various studies. These methods include photocatalytic, electrocatalytic, and plasma catalytic degradation and reduction. Sedimentation can reduce and debrominate BFRs through microorganisms or reductive catalysis. Green rust (GR), which consists of layers of sedimentation with Fe(II) and high amounts of Fe^{2+}–O–Fe^{3+} in the iron hydroxide layer, is capable of reductive catalysis (O'Loughlin and Burris 2004). Figure 5.2 illustrates the proposed mechanism of reduction by GR-CuNPs, which primarily occurs on the surface of the GR. O'Loughlin and Burris (2004) demonstrated that the addition of Cu and Ag significantly enhanced the reducing capabilities of GR on halogenated organic compounds. Fang et al. (2019) also confirmed that adding Cu nanoparticles (Cu NP) to GR enhanced the reduction of TBBPA. The GR was interlayered with Cl^{-}, SO_4^{2-}, and CO_3^{2-}. The GR(Cl)-Cu NP obtained the greatest degradation efficiency at 92.11%.

Enhanced heterogeneous photo-Fenton catalytic photodegradation was utilized by Huang et al. (2020). An efficient degradation rate of 97.4% was achieved by coupling bio-template synthesized ceria with natural ferrihydrites in a novel heterogeneous photo-Fenton system. Furthermore, adding bio-template synthesized ceria with natural ferrihydrites resulted in the regeneration of Fe^{2+} and the production of photoelectrons, which is often a limiting factor.

Natural organic matter is an environmentally friendly alternative for use in photocatalytic degradation. Soluble organic matter can form active free radicals such as OH when hit with visible light that, in turn, can oxidize BFRs (Dong et al. 2022). Natural organic matter such as humic acids and carboxylate ions in the environment has proven to be a promising solution to BFRs. Humic acids can form reactive oxygen species or photochemically produced reactive intermediates capable of degrading persistent organic pollutants (Dong et al. 2022). For example, Son et al. (2019) used Aldrich humic acid to photodegrade HBCD and its three diastereoisomers in simulated solar light. Likewise, Zhang et al. (2018) found that dissolved organic matter could photodegrade novel BFR, 2,3-dibromopropyl-2,4,6-tribromophenyl ether (DPTE), in simulated light with the addition of chlorine.

5.7 Mechanisms of Biodegradation

The debromination of BFRs is the most important step in the biodegradation of BFRs since it allows for complete mineralization (Segev et al. 2009a). In general, the more bromines in a BFR, the slower the biodegradation rate. Typically, the arrangement and amount of bromines or halogens are also inversely proportional to biodegradation kinetics. Under anaerobic conditions, biodegradation of PBDEs favors reductive bromination or reduces the number of bromines (Zhao et al. 2018). In aerobic degradation, cleavage of the aromatic ring occurred first, followed by debromination and hydroxylation (Zhao et al. 2018). It is important to note that reductive removal of the halogen or debromination forming a halide anion is crucial in reducing the toxicity of the compound in question (Hug et al. 2013). This outlines the importance of organohalide respiration, which refers to the respiration process where anaerobic bacteria use halogenated hydrocarbons as a final electron acceptor (Hug et al. 2013).

The fate and intermediate lower brominated BFRs, such as in PBDEs, can often be even more environmentally toxic than the parental species (Pan et al. 2016). Therefore, it is important to understand the fate, mechanisms, and degradation kinetics of both novel and legacy BFRs undergoing natural photodegradation (Zhang et al. 2018). Pan et al. (2016) reviewed the fate of PBDEs in various environmental matrices, including aqueous, organic, solid, gas, and Ti–O_2-mediated phases, to understand the natural photodegradation of PBDE congeners.

In some instances, the method of degradation influenced the resulting congeners. For example, Wang et al. (2019) investigated the debromination of 2,2′,4,4′--tetrabromodiphenyl ether (BDE-47), which had preferential debromination at the para-bromine in the H-transfer system to generate BDE-17, while the preference was ortho-bromine in an electron transfer system to generate BDE-28. Both methods were part of a nanoscale zerovalent iron (n-ZVI) system and six n-ZVI-based bimetallic systems (Fe/Cu, Fe/Ni, Fe/Pd, Fe/Ag, Fe/Pt, and Fe/Au). Interestingly, the metals Pd, Pt, Ni, Cu, and Au use hydrogen gas to debrominated PBDEs. The study determined that bimetallic and NaBH4, Fe/Pt, Fe/Ni, and Fe/Pd preferred H-transfer mechanisms, while e-transfer mechanisms preferred Fe/Ag. Conversely, Fe/Cu and Fe/Au preferentially debrominate equally under e-transfer and H-transfer mechanisms. The mechanism for debromination of halogenated compounds has been divided into two hypotheses. The first hypothesis has been to attribute dehalogenation to electron transfer, where the difference in corrosion potential between Fe and the additive metal allowed for more current and, thus, more electron transfer (Yan et al. 2010; Wang et al. 2019). The other hypothesis is that the additive's ability to absorb hydrogen would dictate the speed of hydrogen transfer and, thus, dehalogenation (Chun et al. 2010; Wang et al. 2019). Chun et al. (2010) also concluded that the size and distribution of the metal additives on the surface of Fe were the most important variable. Hydrogen transfer in a palladized zerovalent zinc (Pd/ZVZ) system is also pH dependent, as illustrated in a study by Xu et al. (2020).

As previously mentioned, Geng et al. (2019) conducted biodegradation studies using *Pseudomonas* strain GJY. The study also proposed a mechanism of biodegradation of the three diastereoisomers of HBCD. In addition, they tracked subsequent metabolites using ultra-performance liquid chromatography-tandem mass spectrometry (UPLC-MSMS). The study proposed that the pathway for HBCD biodegradation consisted of ring opening, hydroxyl substitution, and debromination. This pathway differs from other biotransformation studies of HBCD and highlights that microorganisms influence how HBCD isomers are distributed in environmental settings. Figure 5.3 highlights a proposed pathway of debromination of HBCD-contaminated soil from Chiang Chun (Li et al. 2020).

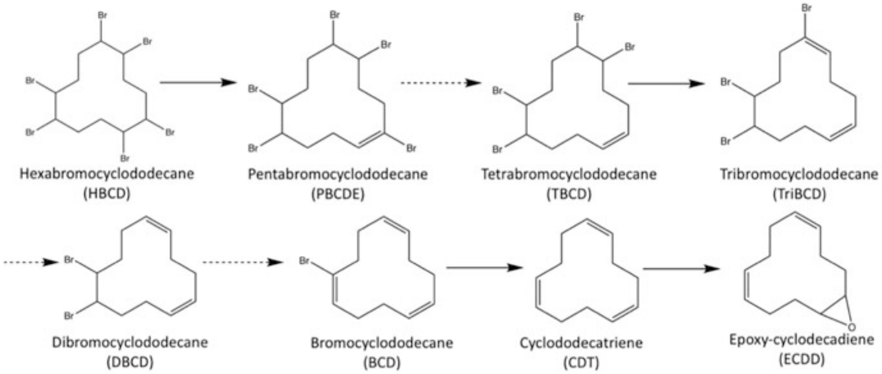

Fig. 5.3 The proposed pathway of HBCD biodegradation through the process of debromination from soils collected from Chiang Chun. The metabolites were identified via gas chromatography (GC) and gas chromatography-mass spectrometry (GC-MS). [Retrieved from Li et al. (2020)]

5.8 Genes and Enzymes Involved in the Biodegradation of BFRs

Genome annotations and identification of enzymes involved in biodegradation pathways are crucial for successful biodegradation of BFRs and other pollutants. Liu et al. (2015) overexpressed tbbpa A for biodegradation studies of TBBPA. This gene was identified due to upregulation when exposed to TBBPA. Whole-genome sequencing of *Ochrobactrum* sp. strain T was compared to the NCBI database for identification of potential TBBPA-degrading genes. Gene tbbpa A was identified and cloned into an expression vector. The constructed strain was able to degrade TBBPA and removed bromine with 78% efficiency and demineralization at 37.8% efficiency in 96 h. This was observed to be very similar to the parental strain. These results demonstrated the possibility of creating constructs for the purpose of biodegradation of POPs. Culturing conditions were aerobic in mineral medium at 37 °C at pH 7. Table 5.2 lists the genes and enzymes that have been identified as capable of degradation and mineralization of BFRs. Some enzymes may be capable of biodegradation of multiple BFRs with similar structures.

Whole-genome sequencing of microorganisms capable of debromination as well as biodegradation is another important step in deducing the molecular mechanisms involved in bioremediation of BFRs (Shah et al. 2018; Liang et al. 2019a). Genes encoding enzymes that play an important role in the biodegradation of BFRs are ideal targets for genomic analysis when considering potential candidates for biodegradation. Wang et al. (2022b) isolated extracellular enzymes, MnP, Lip, Lac, and cytochrome P450, which aided in the biodegradation of DBDPE. The most important extracellular enzyme for degradation was Lac. The study also noted that

Table 5.2 Genes and enzymes experimentally shown to biodegrade BFRs

Genes/enzymes	BFRs or congener degraded	References
C12O, C23O, C34O, Nid A, and Rf	Aromatic hydrocarbons, can facilitate oxidative cleavage of catechol and LBN PBDE congeners	Chou et al. (2016)
Dehalogenases: RdhA and Rdases Dioxygenases: C23O, RF, and ARHD	BDE-209	Chang et al. (2021)
Genes: tbpA, *tbpB*, *tbpC*, *tbpD,* and *tbpE*	TBP	Liang et al. (2019b)
Monooxygenase	TBNPA and DBNPG	Balaban et al. (2021)
Dehalogenase: PcbA1	TBBPA	Ramaswamy et al. (2021)
Gene: tbbpa A encoding for bromophenol dehalogenase	TBBPA	Liang et al. (2019a)
LinA2 and LinB: haloalkane dehalogenases	HBCD	Heeb et al. (2014)
Laccase	Bromophenols	Uhnáková et al. (2009)
Enzymes: MnP, LiP, Lac, and cytochrome P450	DBDPE	Wang et al. (2022b)
P. aeruginosa LY11 Crude enzyme extract	BDE-209	Liu et al. (2015)

antioxidant enzymes CAT and SOD were important for reducing the toxicity of *P. ostreatus.*

Enzymes have a potential to degrade BFRs more efficiently and rapidly than the organism itself. This was illustrated in a study by Liu et al. (2015). Crude enzyme extract was isolated from *P. aeruginosa* LY11. This strain is known for biodegradation of BDE-209. The crude enzyme was extracted through sonication, centrifugation, and finally filtration through a 0.22 μm filter. The resulting filtrate is what was considered crude enzyme extract. In this study, the crude enzyme was able to degrade BDE-209 in a shorter time period of 5 h and more efficiently at 92.77%. This study provides insight into the possibility of using crude enzyme extract from other microorganisms previously known to biodegrade specific BFRs. The potential to mass produce crude enzyme extract through over-expression systems may be a more efficient means of bioremediation of BFRs.

5.9 Culturing Conditions in Bioremediation Strategies

The culturing conditions for many degradation systems varied with each type of BFR. Some were cultured in aerobic or anaerobic conditions where temperature, pH, and culture supplementation varied with each organism. For some, supplementation was necessary for bioremediation, while other studies used the BFR as the sole carbon source. Table 5.3 summarizes the culturing conditions for various BFRs from optimized protocols for degradation and mineralization.

Table 5.3 Microorganisms capable of bioremediation of various BFRs and the culturing conditions for optimal mineralization

Microorganism or abiotic system	BFR degraded	Culturing aspects	References
Enterobacter and Clostridium	TBBPA	The addition of noncomplicated carbon sources such as glucose	Macêdo et al. (2022)
Bacterial consortium containing the dominant genera: *Sphingopyxis* spp.	Dibromoneopentyl glycol (DBNPG) and tribromoneopentyl alcohol (TBNPA)	Aerobic with added yeast extract for substrate and bacterial growth stimulation	Segev et al. (2009b)
P. ostreatus	DBDPE	Addition of glucose increased degradation rates	Wang et al. (2022b)
Bacterial consortium predominantly *Pseudomonas* spp.	Decabromodiphenyl ether (DBDE)	Aerobic and micro-aerobic soil slurry microcosm	Chou et al. (2016)
P. aeruginosa strain HS9	Hexabromocyclododecane (HBCD)	HBCD-contaminated soil plant/HS9 system	Huang et al. (2019)
HBCD-1 and HBCD-2 *Achromobacter* sp.	HBCD, α-HBCD	Aerobic culture with minimal salts medium (MSM) at 30 °C at pH 7	Peng et al. (2015)
R. palustris YSC3	HBCD	Modified van Niel medium at 35 °C at pH 9. Cells degraded faster at late log-phase inoculum of 1 ppm γ-HBCD	Chang et al. (2021)
Bacteria: *Thiobacillus*, *Sphingomonas*, *Geothrix*, *Paenibacillus*, *Desulforhabdus* Archaea: *Methanobrevibacter*, *Methanomethylovorans*, *Candidatus* DHVEG-6, *Candidatus, Nitrososphaera, and Methanosphaera*	Pentabromodiphenyl ether (BDE-91)	Anaerobic soil columns with microbial community of sulfate-reducing bacteria and archaea	Yan et al. (2018)
Clostridium spp. and *Bacillus* spp.	HBCD	Aerobic culturing of microbes found in the soil of Chiang Chun and riverbank soil	Li et al. (2020)
Stenotrophomonas sp., *Pseudomonas* sp., and *Microbacterium* sp.	BDE-209	Aerobic UV photolysis biodegradation in clay slurries	Chang et al. (2021)
Dehalococcoides mccartyi strain CG_1	TBBPA	Anaerobic in 100 mL of sodium bicarbonate supplemented with reductants. TBBPA was used as a sole source of carbon for screening	Ramaswamy et al. (2021)

(continued)

Table 5.3 (continued)

Microorganism or abiotic system	BFR degraded	Culturing aspects	References
Pseudomonas sp. GJY	α-, β-, γ-HBCD	Aerobic conditions in MSM with HBCD and each diastereoisomer at 30 °C and at pH 7 for 8 days	Geng et al. (2019)
Bacillus cereus JP12	BDE-209	BDE-209 was used as the sole source of carbon in MSM at 30 °C at a pH of 6	Lu et al. (2013)
Bacillus cereus HBCD-sjtu	HBCD	MSM with .5 mm HBCD at 30 °C, pH 7	Shah et al. (2018)
Sphingomonas sp. *PH-07*	PBDE selected congeners	Pre-grown with diphenyl ether as the sole source of carbon under aerobic conditions. Subsequently grown in MSM with selected PBDE congener	Kim et al. (2007)
Trametes versicolor	2-Bromophenol, 4-bromophenol, 2,4-dibromophenol, tetrabromobisphenol A, 2,6-dibromophenol, and 2,4,6-tribromophenol	Modified from Van der Merwe (2002) at 30 °C at pH 5.5	Uhnáková et al. (2009)
Bacterial genera: *Brevundimonas*, *Rummeliibacillus*, *Lysinibacillus*, and *Clostridium* *Archaea: Halalkalicoccus, Methanobacterium, Methanosarcina, and Methanocorpusculum*	BDE-209 and BDE-28	Anaerobic medium in the dark for 2 years at 30 °C, pH 7, with the reducing agent titanium citrate	Yang et al. (2017)
Geobacter, Dehalobacter, Dehalogenimonas, Desulfitobacterium, and Dehalococcoides	2,2′,4,4′-Tetrabromodiphenyl ether (BDE-47)	Sediment slurry microcosm containing MSM, spent mushroom substrate biochar, and BDE-47 incubated in an anaerobic chamber at 25 °C	Chen et al. (2018)
Bacillus sp. GZT bioaugmentation with *Firmicutes*, *Actinobacteria, Proteobacteria, Bacteroidetes*	TBP	Mineral medium and growth medium for culturing of *Bacillus* sp. GZT at pH 7. Supplementation of MSM with NaCl, glucose, yeast extract, sodium propionate, and humic acids enhanced biodegradation	Xiong et al. (2017)

Tokarz et al. (2008) reported that adding vitamin B12 enhanced the debromination kinetics. Other studies showed enhancements with the addition of glucose or other carbohydrates (Wang et al. 2022b). However, some additions for one strain may enhance degradation and inhibit others. This was evident when adding a vitamin mix slowed the degradation rate of BFRs (Balaban et al. 2021). Some bacterial strains are capable of biodegradation when the BFR is the sole source of carbon. This was observed for the *Bacillus cereus* JP12 strain (Lu et al. 2013), where BDE-209 was added to MSM at 30 °C, pH 6. Degradation efficiency was enhanced by adding other carbon sources, surfactants, and metals Cu^{2+} and Zn^{2+}. Similarly, zerovalent iron enhanced the biodegradation of BDE-209 and BDE-28 (Yang et al. 2017). Shah et al. (2018) also used *Bacillus cereus* for successful biodegradation of HBCD with another strain called HBCD-sjtu at a higher pH of 7 at 30 °C. This demonstrates that physiological conditions were as important as culturing and media for the biodegradation of certain BFRs. It also demonstrated that despite using the same genus and species of bacteria, the BFR degradation influenced the culturing conditions. Optimal temperatures ranged from 30 °C at pH 7 (Peng et al. 2015) to 35 °C at pH 9 (Chang et al. 2021), depending on the bacterial strain. Changes in pH and temperature resulted in less biodegradation efficiency and was dependent on the BFR.

5.10 Conclusion and Future Direction

The possibility of phasing out NBFRs and using bio-sustainable organobromine BFRs is a promising solution to the problem of BFR environmental contamination. Sequencing genomes of microorganisms capable of biodegradation of BFRs is essential for understanding the molecular mechanisms of biodegradation. The potential for isolating genes and enzymes that biodegrade BFRs is high when microorganisms are collected from e-waste sites or near industrial facilities where BFRs are present. There have been many different genera and species of bacteria that have demonstrated the ability to biodegrade various BFRs. However, culturing conditions vary with each species of microbes used.

Another important consideration is the possibility that microorganisms that can remove chloride from hexachlorocyclohexanes may also debrominate BFRs, especially when the chemical structures are similar. Various studies, as previously mentioned, demonstrated that bacterial strains with dehalogenases may also remove halogens from different compounds, thus implying that microorganisms can bioremediate a variety of POPs.

The strategies presented here include various methods to address emerging BFR pollutants from different environmental sources. Catalysis is a proven method for efficient mineralization and biodegradation in abiotic methods. Using natural organic matter is an environmentally friendly way to oxidize BFRs and a promising way to address environmental pollution. One example discussed is humic acids, which form free radicals when exposed to light. In biotic methods, several organisms and systems have been presented. The supplementation and culturing conditions varied with each BFR and organism. The addition of enzymes proved essential for biodegradation and highlights the possibility of engineering enzymes for the degradation of BFRs or in synergy with microorganisms.

The urgent need to remove POPs has never been more evident. Several publications have identified various pollutants including BFRs as being responsible for declining sperm counts over the past few decades. The exposure to BFRs through ingestion, inhalation, and absorption through the skin has taken their toll on the fertility of both genders as well as developmental consequences for children. This exposure to BFRs is most prevalent in indoor settings, e-waste recycling centers, and other industrial locations where BFRs are manufactured. Therefore, the best strategy moving forward is to bioremediate BFRs from wastewater treatment plants before they are released into the surrounding environment.

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Biodegradation of the Fungicide by Bacteria in Soil

6

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Abstract

Fungicides, one important class of crop protection products, are important to protect the crops from fungal attacks to meet the challenge of increased food production in the present era of increasing global population and food demand. A large amount of the applied fungicides are lost in the different environmental compartments, either directly through intentional use (such as agronomic practices) or unintentionally (e.g., spray drift, surface runoff, leaching). Moreover, the injudicious and indiscriminate use of chemical fungicides results in various human and environmental health hazards. The presence of unwanted fungicide residues and their persistence behavior in environmental matrices may not only contaminate the soil, water, and air but also possess toxicity of both acute and chronic nature towards nontarget organisms. Bioremediation is a potent decontamination technique of different xenobiotics including pesticides with the use of biological resources such as plants and microbes. Among different bioremediation techniques, biodegradation, particularly microbial degradation using bacteria and fungi, is considered as an important decontamination tool due to its cost-effective and sustainable nature. Biodegradation of xenobiotics including fungicides by using bacteria is important in this regard. Therefore, a spotlight in the form of this chapter has been shone upon the role of bacteria in the degradation of fungicides from soil, along with an address to the present limitations and future opportunities hidden underneath them.

Keywords

Xenobiotics · Pesticides · Fungicides · Biodegradation · Bioremediation · Bacteria · Soil

6.1 Introduction

The United Nations (UN) projects that the world's population will increase by medium levels during the coming decades, reaching 9.7 billion people in 2050 and 10.4 billion in 2100. The demand for food is rising quickly around the world, and yields on most farms are well below potential, and also the current track of agricultural expansion has major long-term environmental consequences. The goal of eradicating hunger worldwide by 2030 is sadly not on the right path. According to the UN, if current trends continue, by 2030, there will be more than 840 million people who will be impacted by hunger, and investments of between US$39 and US $50 billion per year until 2030 will be needed to pull about 840 and 909 million people out of hunger (Chichaibelu et al. 2021). In addition to that, there are various grounds for anticipating an increase in the disease pressure on crops. The ability of national quarantine authorities to prevent exotic infections from entering their countries will be diminished or possibly eliminated as a result of global warming and the expansion of worldwide travel and trade. Crop disease effects cannot be minimized because they are always nearby. It is alarming to learn that crop diseases can still result in up to 30% crop losses in important, intensively studied crops even when the conditions are optimum for growth and development (Oliver and Hewitt 2014). Among disease causal organisms, plant pathogenic fungi have historically been a challenge to human's ability to produce food in sufficient quantities and with acceptable quality. Nearly 20,000 of the over 1 lakh species of fungi mentioned in the world cause numerous plant diseases (Thind 2017). Currently, around four million tonnes of pesticides are used per year on a global basis, and from 1990 to 2010, it was discovered that the percentage of total pesticides coming from herbicides was 55%, while the percentages of fungicides and insecticides were 23% and 17%, respectively (Sharma et al. 2019). Gikas et al. (2022) reported that fungicide use worldwide is estimated at 4 lakh tonnes or 17.5% of total pesticide use. Geographically, Europe is regarded as the leading market for fungicides, which mostly uses fungicides on fruits, vegetables, and grains and cereals. By keeping an eye on destroying diseases in agricultural cultivars, fungicides can play a significant part in protecting crop health safety. Fungicides are treated to crops directly or to seeds. Many of the fungicides applied to seeds have systemic activity, which enables them to penetrate plant tissues and protect against infections and pests in a manner similar to that of their insecticidal counterparts (Zubrod et al. 2019). The fungicides improve food safety by preventing the growth of several fungi that can poison food and human beings. In order to feed the world's population, agriculture must develop ways to be socially, economically, and environmentally sustainable. In plant infection management strategies, fungicides are now widely accepted as the second line of defense following disease resistance. Due to this reality, crop protection management systems with fungicides as a key component must be used.

Microbial breakdown of xenobiotics in soil environments is a crucial topic to research in present days as it prevents the accumulation of these chemicals in the environment. Studies on the microbial degradation of pesticide residues first began in the 1940s (Arbeli and Fuentes 2007). Bacteria found in nature can break down xenobiotic residues cheaply, sustainably, and without causing secondary contamination. The complexity and changeability of the natural environment, however, could have an impact on the viability and effectiveness of the microbial breakdown of these chemicals. There are many different degradation processes, such as oxidation, reduction, hydrolysis, dehalogenation, dehydrogenation, condensation, and decarboxylation. Huang et al. (2018) listed several pesticide-degrading bacterial species. Bacteria have the dominant position in the study of biodegradation due to their high flexibility and ease of inducing mutations. In addition to the aforementioned, there are numerous microorganisms that break down xenobiotic compounds, including *Escherichia coli*, *Clostridium*, *Bacillus licheniformis*, *Thiobacillus*, and others. Therefore, in this chapter, we have critically analyzed the role of different types of bacteria in the biodegradation of fungicides in soil, along with addressing the constraints and future perspectives of this domain.

6.2 Risk and Environmental Fate of Chemical Fungicides

Fungicides can enter water bodies through the point (such as discharge from wastewater treatment facilities after household and agricultural usage) and nonpoint (such as drift, drainage, and surface runoff mostly from agricultural use) sources after being used (Zubrod et al. 2019). They can be harmful to a variety of nontarget organisms in aquatic systems because they affect fundamental biological functions that are not exclusive to fungus (e.g., energy production). The widespread use of chemical fungicides in agriculture also raises serious concerns about the health of the human beings. Exposure experiments on rats revealed endocrine-disrupting, histopathological, biochemical, and hematological effects (Stamati et al. 2016). Despite the widespread usage of fungicides and the related potential ecotoxicological concerns in nontarget aquatic systems, the environmental fate and consequences of fungicides have received significantly less attention than insecticides and herbicides. In contrast to insecticides and herbicides, which received 62% and 24% of the studies on pesticidal effects, between 1991 and 2013, fungicide experiments were confined to only 13% of the studies (Köhler and Triebskorn 2013).

Among inorganic fungicides, copper and sulfur fungicides are mostly used. Although they are an important element for organisms to grow, a large concentration in the environment can cause serious drawbacks. The predominant and biocidal oxidation ion when copper oxide dissolves in water is Cu^{2+}, which can accumulate in decapod crustaceans, fish, and algae and be stored in barnacles, bivalves, and aquatic insects. Cyanobacteria are the species most sensitive to copper exposure, while coccolithophores and dinoflagellates are less sensitive to copper and diatoms exhibit copper resistance (Gikas et al. 2022). Sulfur can be poisonous to bacteria and fungus that are beneficial for the environment, and toxicity in apricots, cucurbits, and raspberries has also been reported (Četkauskaitė et al. 2004). Compared to copper, there is limited information on sulfur's interaction with organisms, its threshold for toxicity, and its environmental outcome.

Organic fungicides promise a number of benefits, including increased efficacy and reduced chance of pathogens becoming resistant to fungicides. Their environmental fate depends on several physicochemical factors, such as water solubility, ionization potential, half-life in soil and water (DT_{50}), volatility, soil texture, pH, clay mineral type, cation exchange capacity, organic carbon content, and dissolved organic matter. Fungicides applied to seeds are effective against soilborne diseases, although they may persist in low quantities in the plant or rhizosphere for up to several months. Regarding direct application on crops such as trees and vine branches, drift hazard can lead to pollution of nearby natural waters from fungicide residue. An investigation regarding the presence of several pesticides in northern Italian vineyard groundwater bodies was conducted, and five fungicides (fluopicolide, metalaxyl-M, tetraconazole, penconazole, and dimethomorph) with very high concentrations surpassed the environmental quality level imposed by the European Union ($0.1\ g\ L^{-1}$) (Marsala et al. 2020). In a pesticide monitoring study of two river basins in North Greece, with cereals, cotton, and corn as the principal crops, during a period of 2 years, extremely high amounts of seven fungicides (azoxystrobin, etridiazole, diphenylamine, tebuconazole, propiconazole, and quintozene) were discovered (Papadakis et al. 2015). Cui et al. (2017) looked into the neonatal and embryonic *Daphnia magna* tissues for the acute and chronic toxicity of the strobilurins trifloxystrobin, pyraclostrobin, and kresoxim-methyl and found that, when exposed to fungicides, *Daphnia* embryos are more vulnerable than neonates.

Evaluation of chiral fungicides' half-life in crops and soils has been the principal method used to study their environmental behavior, which revealed interesting data about their possible biodegradation and persistence. In a field experiment, the half-life of penconazole enantiomers in soil and plant tissues was studied, and the findings revealed that in grapes and soil, the penconazole enantiomer (−) decomposed considerably more quickly than its (+) isomer (Zhang et al. 2019). The aquatic alga *Chlorella pyrenoidosa* was the subject of an investigation by Deng et al. (2019) on the toxicity of four stereoisomers of metconazole. The study revealed that the 1S, 5S isomer more severely triggered the disruption of photosynthesis, the production of reactive oxygen species, and the antioxidant response.

Nanofungicide has its active ingredients within the size range of 10–100 nm. Their application in the control of fungal diseases can be categorized into two groups: nanoparticles acting as protectants (on their own) and as carriers for organic fungicides (Worrall et al. 2018). The primary benefits of using nanoparticles as organic fungicide carriers are the enhancement of the active ingredient's activity and persistence, the enhanced capacity for translocation within plants, the overcoming of issues with poor water solubility, and the attainment of gradual release. However, environmental fate, toxicity towards nontarget organisms, and decontamination technologies have not been adequately studied. According to Ameen et al. (2021), different parameters, such as application rate, size, and kind of nanomaterial, might affect how a plant grows after being exposed to nanopesticides. The nanofungicide $Cu(OH)_2$ was applied to maize, and the results showed that it reduces biomass (17–20%) and the amount of chlorophyll a and b in the leaves (Zhao et al. 2017). Abd-alla et al. (2016) reported that high concentrations of silver nanoparticles reduced glomalin content, mycorrhizal colonization, and responsiveness of *Glomus aggregatum*.

Another class of fungicides with a distinctive method of action is chemical plant defense activators. Acibenzolar-*S*-methyl is a chemical that can activate plants' defense mechanism, is moderately toxic to invertebrates, is moderate to highly hazardous to fish, and is extremely harmful to aquatic flora (Guziejewski et al. 2014). Acibenzolar-*S*-methyl is also reported to be phytotoxic and has been associated with productivity losses, and under some circumstances, it may enhance other pest attacks (De Oliveira et al. 2018). Chemical plant activators' environmental destiny and toxicological effects on nontarget organisms are still unexplored and require thorough investigation. Fungicides are principally employed to protect human life by boosting agricultural productivity and reducing the spread of infectious diseases, but occasionally, their negative consequences outweigh the advantages of their use.

6.3 Biodegradation: A Potent Soil Bioremediation Strategy for Fungicides

Industrialization's rush to achieve quick economic development is having a detrimental effect on environmental management and pollution issues, causing the accumulation of potentially dangerous elements in the environment, including plastic, rubber, metal, industrial waste, etc. The contaminated ecosystem has a detrimental effect on the plants, aquatic life, soil environment, microbial activities, and metabolic functions. The biogeochemical cycle of the elements present in the environment has an impact on the ecosystem and how it functions, as well as how it affects human health. Waste management is extremely important for the creation of sustainable and livable communities, yet it is still challenging in many developing countries.

Traditional waste remediation methods, like soil washing, adsorption, flocculation, chemical oxidation, landfilling, pyrolysis, and incineration, are resource and time intensive; also, they are not environmentally friendly. Recently, as people are working to develop sustainable methods for cleaning up and restoring contaminated soil, their curiosity to learn more about the bioremediation of harmful pollutants has increased. Bioremediation can be defined as a technique used to treat contaminated sites in order to restore them to their pre-contamination state that involves the use of green plants, living organisms, primarily microorganisms, and their enzymes to degrade, transform, remove, mineralize, and detoxify environmental pollutants and hazardous elements of the environmental waste (Azubuike et al. 2016). These organisms may already exist at the contaminated site or they may be isolated and transported from elsewhere for bioremediation. Through their metabolic processes, they break down and convert these contaminants and use them for growth. Since multiple bacteria must work together to completely degrade a pollutant, it is often required to add additional microbes to the contaminated spot to speed up the degradation process. When it comes to the movement and removal of pollutants from contaminated sites, bioremediation technology can be divided into two groups: ex situ bioremediation (which involves the excavation and transportation of pollutants from the actual polluted location and transporting them to another site) and in situ bioremediation (performed at the original site of the contamination) (Saxena et al. 2021; Randika et al. 2022). However, there are several negative aspects to the bioremediation process. Some substances like chlorinated organic contaminants and radionuclides cannot be broken down by microbes. When bacteria break down pollutants, they occasionally create harmful byproducts or metabolites. Since bioremediation is a highly scientific process, it should be adapted to site-specific conditions; therefore, a small-scale treatability study should be conducted before using the approach to treat a contaminated site (Boopathy 2000). The term "biodegradation" describes the process by which harmful xenobiotics are changed into less toxic substances. The word "xenobiotic" refers to a chemical compound that is not a natural part of a living creature exposed to it (from the Greek words "xenos" and "bioticos," which mean "strange" and "life related," respectively) (Hashmi et al. 2017). They are alien to living organisms and have the propensity to accumulate in the environment. Microorganisms offer a lot of potential for biodegradation. Their sustained adaption to environments containing these substances is directly related to their capacity to lower the concentration of xenobiotics.

Persistent behavior of different pesticides exerts contamination and toxicity problems towards different environmental compartments and nontarget organisms in both the short and long terms (Cuevas et al. 2018; Shahid et al. 2020). Among different microbial remediation techniques such as bioaugmentation and biostimulation, biodegradation utilizing microbes directly or microbial enzymes is quite popular nowadays (Ortiz-Hernández et al. 2013). Biodegradation can be used as a strategy to remove different xenobiotics including fungicides from environmental compartments. Biodegradation is an economical, environmentally benign, and sustainable decontamination approach in this regard.

6.4 Bacterial Biodegradation of Synthetic Fungicides in Soil

6.4.1 Mechanism of Degradation

Pesticides are converted into breakdown products or mineralized by microorganisms during biodegradation processes, which employ the pollutant xenobiotics as nutrition for their metabolic processes (Raffa and Chiampo 2021). The microbes including bacteria or fungi that participate in the breakdown process can produce extra- or intracellular enzymes. Several enzymes like peroxidases, hydrolases, and oxygenases play a crucial part in the biotransformation mechanisms by influencing and catalyzing the biochemical reactions. There are three stages to the microbial enzyme-based breakdown of pesticides (Verma et al. 2014), which can be summed up as follows:

Phase 1: In this phase, the pesticides undergo hydrolysis, oxidation, or reduction processes to become more water-soluble and less dangerous compounds.

Phase 2: Here, the products from phase 1 are transformed into sugars and amino acids, which are more water soluble and less poisonous.

Phase 3: The secondary conjugates of the phase 2 metabolites that are less poisonous are produced.

When a bioremediation activity is proposed, the degradation time must be considered a pertinent factor. The first-order model (Khajezadeh et al. 2020), which is dependent on the pollutant concentration at the start and end of the process, is often used to interpret it. However, this strategy has some limitations since it depends on several factors, including microbial activity, water content, temperature, availability, and leaching of pesticides in the soil (Soulas and Lagacherie 2001).

6.4.2 Bacteria-Mediated Biodegradation of Fungicides in Soil

6.4.2.1 Biodegradation by Bacteria

Over time, several bacterial strains that can break down pesticides in soils have been discovered. Each bacterium has a unique characteristic that makes it especially well suited for a degradative process. The degradation is frequently easier if a bacterial consortium is used rather than an isolated pure culture (Doolotkeldieva et al. 2021). Actually, in the natural environment, bacteria cohabit and rely on one another to survive. However, the formation of metabolites during the degradation process can also result in extra-environmental issues because they might be harder to get rid of than the original component. This must be taken into account as a disadvantage.

Mineralization

Pesticides can degrade into inorganic substances such as carbon dioxide, salts, minerals, and water through the mineralization process (Bhoi et al. 2018). The pesticide may serve as a source of nourishment for the microorganisms. The concentration of the microbial community determines the pace of mineralization; hence, a decline in the microbial population does not accelerate degradation. For instance, when the soil microbial community is diminished, numerous metabolites might emerge that are more poisonous, persistent, and mobile than the original chlorothalonil (CTN), an organochlorine fungicide that is destroyed in CO_2 (de Souza et al. 2017). This is caused by a lack of actively degrading groups in the soil or a decline in soil biodiversity, which results in limited microbial diversity. Different bacteria involved in degradation of fungicides have been enlisted in Table 6.1 and briefly summarized in the following subsections.

Nitrophenols

To date, numerous pure cultures of bacteria that can break down DNOC have been identified and reported. One bacterium, *Arthrobacter simplex*, used DNOC as its sole source of carbon and energy and decomposed it by releasing nitrite (Jensen and Gundersen 1955). Via formation of the 4-amino-2-methyl-6-nitrophenol, 5-amino-3-methylcatechol, and 2,3,5-trihydroxytoluene (THT), a *Pseudomonas* sp. decomposed DNOC (Tewfik and Evans 1966). According to Lenke and Knackmuss (1996), *R. erythropolis* HL 24-1 biotransformed DNOC into 4,6-dinitro-2-methylhexanoate. Two hydride ions were added to DNOC to start the reaction, which continued by protonation to produce 4,6-dinitro-2-methylhexanone. Thereafter, 4,6-dinitro-2-methylhexanoate was produced by the subsequent hydrolysis of 4,6-dinitro-2-methylhexanone.

Dinoseb, another fungicide of this group, was transformed by bacteria under anaerobic reducing conditions by first having the nitro groups converted to amino groups and then having the amino groups replaced with hydroxyl groups (Kaake et al. 1995). Either a single anaerobic bacterium or a group of anaerobic bacteria may entirely mineralize NPs into CO_2 and methane. Complete mineralization of DNOC into CO_2 and acetate by an anaerobic consortium made up of three bacterial morphotypes was examined by Stevens et al. (1991).

Table 6.1 Bacterial biodegradation of fungicides

Chemical group	Name of fungicide	Bacteria involved in degradation	References
Benzimidazole	Carbendazim	*Bacillus subtilis*, *Paracoccus* sp., *Flavobacterium*, *Pseudomonas* sp.	Xiao et al. (2013)
		Streptomyces sp. CB1, *Bacillus subtilis* CB2, *Rhizobium leguminosarum* CB4, and *Pseudomonas aeruginosa* CB3	Singh et al. (2019)
Strobilurin	Azoxystrobin	*Rhodanobacter* sp. CCH1 and *Cupriavidus* sp. CCH2	Howell et al. (2014)
	Pyraclostrobin	*Klebsiella* strain 1805	Lopes et al. (2010)
Nitrophenol	DNOC	*Rhizobium leguminosarum*	Hamdi and Tewfik (1970)
	Dinoseb	*Clostridium bifermentans* KMR-1	Hammill and Crawford (1996)
Ethylene-bis-dithiocarbamate	Mancozeb	*Bacillus* sp.	Doneche et al. (1983)
Dicarboximide	Dimethachlon, iprodione, and procymidone	Cocultures of *Brevundimonas naejangsanensis* J3 and *Providencia stuartii* JD	Zhang et al. (2021)
Azole	Epoxiconazole and fludioxonil	Different bacterial species of Proteobacteria phylum, having most common genera of *Ochrobactrum*, *Pseudomonas*, and *Comamonas*	Alexandrino et al. (2020)
	Thiabendazole	Bacterial consortium with dominant genera of *Filimonas*, *Sinobacteriaceae*, *Bradyrhizobium*, *Sphingomonas*, and *Hydrogenophaga*	Vasileiadis et al. (2022)
	Tebuconazole	*Alcaligenes faecalis* WZ-2	Sun et al. (2020)
		Serratia marcescens B1	Wang et al. (2018)

Carbendazim

It takes around 3–6 months for carbendazim to break down on turf soil, about 6–-12 months on bare soil, and up to 25 months in water, both under aerobic and anaerobic conditions (Panda et al. 2018). Additionally, a sizable inhibitory effect on the activities of soil dehydrogenase, nitrification, and ammonification has been noted (Pattanasupong et al. 2004). A schematic representation of bacterial degradation products of carbendazim has been shown in Fig. 6.1.

In different studies, the degradation of carbendazim in different matrices was demonstrated by several species of *Rhodococcus*, including *R. erythropolis CB11*, *R. qingshe*, *R. erythropolis djl-11*, *R. jialingiae djl-6-2*, etc. (Singh et al. 2016) Another bacterium with the exceptional genetic ability to use a variety of carbon sources for survival is *Pseudomonas*, which has already been used for carbendazim

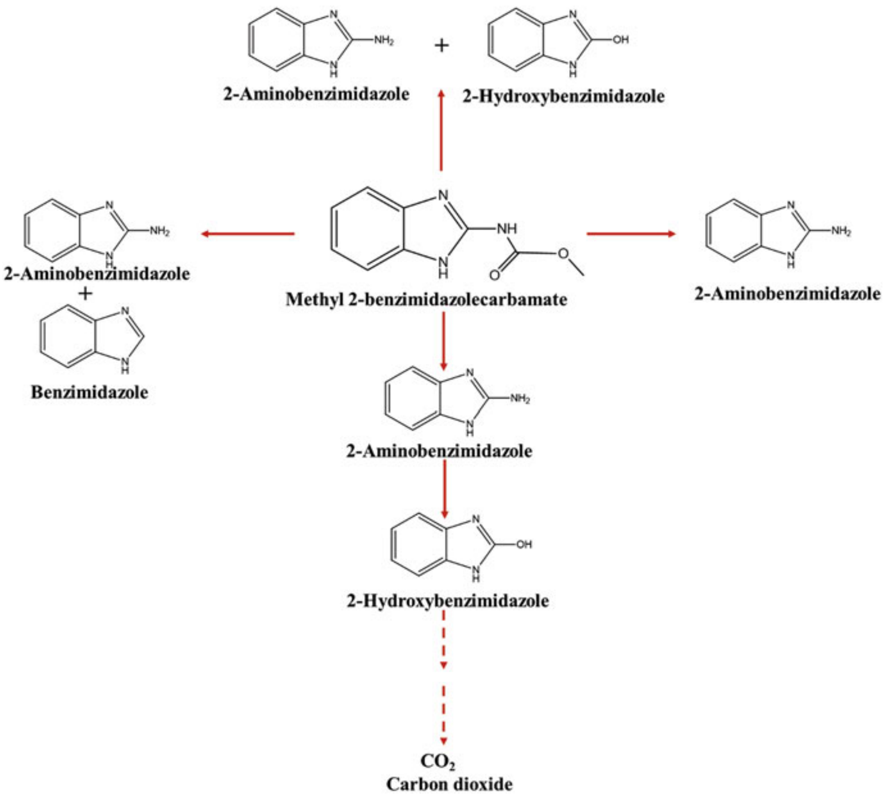

Fig. 6.1 Bacterial biodegradation of carbendazim (Modified from Singh et al. 2016)

bioremediation. One study used biological assays and 16s rRNA sequence homology to identify *Pseudomonas* sp. strain CBW, which used carbendazim as its sole source of carbon and nitrogen (Fang et al. 2010). Aside from these, *Ralstonia* sp. 1-1 (Zhang et al. 2005), *Bacillus pumilus* NY97-1 (Zhang et al. 2009), *Bacillus subtilis* (Salunkhe et al. 2014), etc. were other microorganisms obtained from soils of various countries having the degradation potential of carbendazim. According to a different study, in 24 h, *Brevibacillus borstelensis* and *Streptomyces albogriseolus* degraded carbendazim by 98% and 91%, respectively. However, the combined inoculation was considerably more successful, as evidenced by the 97% deterioration after just 12 h (Arya and Sharma 2016).

Strobilurins

According to experts, the most important method of removing strobilurin is by the microbial breakdown (Chen et al. 2018; Feng et al. 2020). *Arthrobacter*, *Bacillus*, *Cupriavidus*, *Pseudomonas*, *Klebsiella*, *Rhodanobacter*, *Stenotrophomonas*, and *Aphanoascus* are a few of the strobilurin-degrading bacteria that have so far been isolated (Feng et al. 2020). Bacteria have the most important function among the strobilurin-degrading microorganisms, including fungus and other organisms. The long-term use of strobilurins has an impact on ecosystems' microbial populations and biodiversity. By suppressing mitochondrial respiration, strobilurins may directly decrease fungal biomass and cause a switch from fungal to bacterial dominance in soil activities because of their distinct mode of action (Baćmaga et al. 2015). For instance, even in the absence of light, the parent compound azoxystrobin undergoes considerable biodegradation within 21 days, which can diminish the diversity of fungi in soil. When used in the same environment, these compounds prevented the growth and development of fungi but did not affect the diversity of bacteria (Adetutu et al. 2008).

In one study, both the fungicides pyraclostrobin and epoxiconazole were found to be degraded by a *Klebsiella* strain 1805 isolated from soil (Lopes et al. 2010). Four different species, namely, *Arthrobacter oxydans*, *Stenotrophomonas maltophilia*, *Bacillus flexus*, and *Bacillus amyloliquefaciens*, isolated from soil were able to use trifloxystrobin as a carbon source (Clinton et al. 2011). In another study, four different *Bacillus* sp. and two different *Aphanoascus* sp. also survived when exposed to a high dose of azoxystrobin (22.50 mg kg^{-1}) when isolated from polluted soil (Baćmaga et al. 2015). Additionally, Chen et al. (2018) discovered two microbial communities (HI2 and HI6) from Hawaiian soils that were capable of utilizing pyraclostrobin as their sole source of carbon and nitrogen.

Others

In a study by Mohamed and Mostafa (2018), *Planomicrobium flavidum* strain EF, a newly discovered soil isolate, was investigated to check whether it could use captan as its only source of carbon. When compared to the minimum salt medium without captan, this bacterium exhibits greater growth patterns on captan-only supplemented media. It is captan resistant up to 2000 ppm. Additionally, *Planomicrobium flavidum* used nearly 77.5% of captan after just 2 h of growth under shaking, and only 0.8% of the fungicide was left after 24 h of bacterial growth. Wang et al. (2018) isolated one tebuconazole-degrading bacterial strain, *Serratia marcescens* strain B1. The mixing of the strain (3×10^7 CFU g^{-1} dry soil) with tebuconazole (200 mg L^{-1}) in soil revealed around 96.46% degradation of the fungicide in 30 days, as compared to only 70.42% degradation in control, i.e., without bacterial strain. In another study, co-cultures of *Brevundimonas naejangsanensis* J3 and *Providencia stuartii* JD were tried to degrade three dicarboximide fungicides, namely iprodione, dimethachlon, and procymidone (Zhang et al. 2021). The degradation study revealed more than 90% degradation of the test fungicides after 7 days in field soils treated with the co-cultures immobilized in a charcoal–alginate–chitosan matrix.

Co-metabolism

It is the biotransformation process of an organic substance that is not needed to sustain microbial growth through a sequence of processes. Due to this synergistic impact, the pesticides are eventually destroyed by microbes and enzymes into valuable chemicals for various biological, chemical, and physical transformations (Van Eerd et al. 2003). The application of this strategy in bacterial biodegradation of fungicides in the soil is still limited. In one study by Katayama et al. (1991), 11 bacterial strains having the degradation potential of chlorothalonil were isolated and identified as *Flavobacterium*, *Azomonas*, *Pseudomonas*, and *Moraxella* spp. Most of the isolates except two from *Flavobacterium* strains showed the requirement of other carbon sources for chlorothalonil degradation.

6.4.2.2 Biodegradation by Enzymes

The enzymes produced by microorganisms or plants during their metabolic processes are responsible for enzymatic biodegradation. Enzymes are biological macromolecules that can speed up biochemical processes like the breakdown of pesticides (Atalah et al. 2019). By reducing the process's intrinsic activation energy, these molecules influence the reaction rate. They mostly participate in the metabolic processes of oxidation, hydrolysis, reduction, and conjugation.

The first stage of pesticide degradation, oxidation, involves the transfer of an electron from reductants to oxidants (Martín et al. 2009). Microorganisms use the heat or energy produced during the reaction for their metabolic processes. By introducing hydrogen or hydroxyl groups from water molecules, hydrolysis enables the breakage of substrate bonds (Anwar et al. 2009). Thus, the original pesticide molecules are split into smaller chain compounds. Typically, esterases, cellulases, and lipases are involved in the hydrolysis routes. The reduction process is made possible due to the action of reductive enzymes such as nitroreductase (Carles et al. 2021), whereas the conjugation reaction is carried out utilizing different enzymes (Verma et al. 2014). To speed up the mineralization of pesticides, different exogenous or endogenous natural chemicals are also added (Raffa and Chiampo 2021).

In general, esterase and other degrading enzymes play a significant role in the biodegradation of ester-containing pesticides (Zhan et al. 2020; Bhatt et al. 2020). For instance, the metabolic process of pyraclostrobin biodegradation was proposed by Chen et al. (2018), where carbamate hydrolysis allowed pyraclostrobin to be detoxified by allowing the tertiary amine group to be decarboxylated and hydrolyzed to the primary amine group. The metabolic mechanism revealed that carboxylesterase is essential for the biodegradation of pyraclostrobin. Due to the numerous active sites on their molecules, strobilurins have complex structures, but the potential chemical mechanisms involved in their biodegradation pathways are comparable (Wang et al. 2018). Additionally, Chen et al. (2018) hypothesized that carboxylesterase would help with pyraclostrobin detoxification.

6.4.3 Application of Bacterial Biodegradation in Microbial Remediation

The bioremediation processes can be used in situ, ex situ, or directly on the site (Raffa and Chiampo 2021). Different microbial remediation techniques of pesticides have been enlisted in Table 6.2. Among all the techniques, the in situ methods are mostly in practice for fungicide removal from contaminated soils. In the in situ methods, treatment is done in the contaminated area, and the procedure is usually

Table 6.2 Different microbial remediation techniques of pesticides

Technique	Description	References
In situ		
Natural attenuation	This method makes use of the microorganisms found in contaminated soil for decontamination purpose.	Mulligan and Yong (2004)
Biostimulation	It is the process of maximizing the types and amounts of nutrients used to stimulate and enhance the growth of native microorganisms.	Aldas-Vargas et al. (2021)
Bioaugmentation	It is the addition of enzymes or microbial strains to contaminated soils.	Xu et al. (2018)
Bioventing	Supplying oxygen to areas of the soil that are not yet saturated encourages the development of local microorganisms that can break down pollutants.	Hvidberg et al. (2007)
Biosparging	To raise the oxygen level and encourage the microorganisms to break down the contaminant, this strategy involves injecting air under pressure into the saturated soil zone.	Varshney (2019)
Ex situ		
Composting	The pesticide-contaminated soil is blended with nutrients to encourage the chemicals' aerobic breakdown. This method includes biopiles and land cultivation.	Lin et al. (2022)
On-site	Contaminated soil is taken and processed in a nearby location of the polluted area.	Raffa and Chiampo (2021)

aerobic. The soil must be given oxygen for this to occur. These techniques are inexpensive and incredibly efficient. The fact that the contaminated soil is not transported is their greatest benefit. In one study by Baćmaga et al. (2017), soil augmentation by bacterial consortia showed increased activity of soil enzymes, namely dehydrogenases, catalase, urease, acidic phosphatase, and alkaline phosphatase, in azoxystrobin-contaminated soil. In another study, *Pseudochrobactrum* sp. BSQ1 and *Massilia* sp. BLM18, which can hydrolytically and reductively dehalogenate chlorothalonil (TPN), respectively, were used in bioaugmentation by Xu et al. (2018). In all bioaugmentation treatments, the test fungicide (50 mg kg^{-1}) was entirely eliminated within 35 days, with half-lives for strains BSQ1 and BLM18 of 6.8 and 9.8 days, respectively.

6.5 Factors Affecting Bacterial Biodegradation of Synthetic Fungicides in Soil

6.5.1 Structure of Pesticide

The design of the chemical's stability is greatly influenced by its composition. The pesticide's biotransformation is dramatically altered by a slight alteration in its chemical makeup, which eventually has an impact on biodegradation. The rhizosphere's microorganisms may turn pesticides into compounds that crops can absorb and move around with more efficiency. In light of this, any component that increases microbial activity in the rhizospheric region should also increase the overall efficacy of the bioremediation of pesticides (Yan et al. 2020).

6.5.2 Concentration of Pesticide

The success of biodegradation depends on the pesticide concentration. The frequency of bioremediation is impacted when a pesticide approaches its biodegradation capacity.

6.5.3 Characteristics of Soil

For the diffusion and movement of pesticides within crops, soil moisture is an important element. When the soil is dry, the rate of degradation decreases, while pesticides show higher degradation as the moisture content increases (Raffa and Chiampo 2021). The pH of the soil and the charge that pesticide molecules carry both affect how quickly a pesticide degrades. It controls how pesticides are absorbed and moved throughout the plant's root and shoot.

Another critical aspect in the removal of pesticides is temperature. Pesticides easily dissolve in the aqueous phase when the temperature rises, improving their availability to bacteria. Thus, the microbial populations in the soil may either directly or indirectly aid in the bioremediation process. At higher temperatures, it has also been shown that some pesticides volatilize. However, low temperatures impede the breakdown of pesticides.

6.6 Present Limitations and Future Outlooks

1. The aforementioned information makes it clear that only a limited number of microbial strains can consume and subsequently remove fungicides from the environment. Since fungicides demonstrate long-term environmental persistence, bioremediation of the severely contaminated soil requires the use of bacteria that are highly effective, competent, and ecologically competitive. Positively, new strains are being isolated from a variety of sources that have exceptional bioremediation qualities. Future approaches to fungicide bioremediation are anticipated to include the use of activated carbon, immobilized microbial carriers, bioaugmentation, and genetically modified microorganisms (Singh et al. 2016).
2. The previous studies also showed that the fungicide metabolites may be considerably more hazardous and persistent in the environment than the parent substance (Khandelwal et al. 2014). Therefore, more in-depth knowledge of the fungicides' potential molecular pathways and their ultimate fate is critical. The research on the isolation and characterization of rhizobacteria that can increase

pollutant bioavailability is also very important in the context of bioremediation. This asset is especially concerning because some biodegradable microorganisms respond positively to contaminants through chemotaxis. Therefore, the combined effects of biosurfactant and chemotaxis can promote bacterial growth and microbial spread in contaminated areas, aiding in the removal of pesticides (Orozco et al. 2014).

3. The bioavailability of the contaminants is a problem with soil bioremediation. This lack of bioavailability frequently lowers the efficacy of pesticide extraction (Megharaj et al. 2011). The application of biosurfactants may solve this problem. Hydrophobic pollutants are dissolved in the hydrophobic layers of the micelles to speed up the transition of substances from a solid to a liquid phase, where bacteria can more easily access them. The primary source of bacterial biosurfactants is rhamnolipids, which are derived from glycolipids. Rhamnolipids have been found to speed up the biodegradation of pesticides (Bai et al. 2017). However, the application of biosurfactants in the biodegradation of fungicides in the soil is still lacking.
4. A well-known tactic is to genetically modify bacteria to increase their capacity for bioremediation (Kaur et al. 2021). It is still feasible to create recombinant species that can combine different traits, such as the capacity to produce biosurfactants while degrading contaminants, colonize healthy environments, and support plant growth. Regarding the application of genetically engineered bacteria in fungicide bioremediation, several countries have laws that prohibit the introduction of recombinant species, and these restrictions, along with some persistent environmental problems, may hinder the development and large-scale application of this strategy (Gkorezis et al. 2016). Therefore, further development of regulatory frameworks is also important in this regard.

6.7 Conclusion

The presence of unwanted fungicide residues and their long-term persistency behavior in soil possess a serious threat to the nontarget organisms and the environment. Microbial degradation of fungicides using bacteria is, therefore, an eco-friendly option to remove these unwanted xenobiotics. Different types of bacterial genera employed for the degradation of various kinds of fungicides in soil have been discussed in this chapter. The success of the biodegradation program depends mostly on three factors, i.e., genera and species of bacteria used, properties of the fungicide to be degraded, and physicochemical characteristics of the contaminated soil. Most of the studies conducted so far are limited only in isolation and characterization of fungicide-degrading bacteria, and their degradation potential in the mineral salt medium. However, bacterial biodegradation potential in soil, particularly under field conditions, is most important to generate more realistic information for the large-scale application of this technique. Therefore, future studies on biodegradation potential of bacterial consortia, combinatorial decontamination approach using bacterial degradation as one of its components, cost-effective large-scale bacterial degradation-based fungicide-contaminated soil decontamination program, and government intervention in terms of monetary support and public awareness for adoption of biodegradation-based decontamination technologies are required for the success of this sustainable and green decontamination approach to achieve environmental as well as agricultural sustainability in the long run.

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Fungal Enzymes in Bioremediation of Environmental Pollutants

7

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Contents

Abstract

The fungi grow in diverse habitats and potentially secrete an array of extracellular enzymes capable of decomposing matter. The fungal enzymes include amylases, cellulases, catalases, cytochrome P450s, dehalogenases, dehydrogenases, hydrolases, laccases, lipases, peroxidases, proteases, and xylanases; they play an essential role in the detoxification of pollutants. The potential of using extracellular fungal enzymes for detoxifying organic substances is promising, as it offers an environmentally friendly remediation approach. These enzymes effectively break down and degrade organic pollutants, making them a valuable

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tool for restoring contaminated environments in a sustainable and eco-friendly manner. The substances comprised coal, agrochemicals, paper leather tanning effects, persistent organic pollutants, pharmaceuticals and personal care products (PPCPs), polycyclic aromatic hydrocarbons (PAHs), and textile dyes. Fungal microbes give an extensive range of enzymes specified in hazardous detoxifying compounds and could be potential candidates for bioremediation of environmental toxic waste. This chapter examines fungal enzymes used in bioremediation, emphasizing their applicability, effectiveness, and role in breaking down environmental waste. It shows how these enzymes are crucial in the remediation process, aiding the removal of pollutants and restoring polluted environments.

Keywords

Fungal microbes · Extracellular enzymes · Pollutants · Mycoremediation

7.1 Introduction

Environmental pollutants are growing increasingly due to toxic compounds' arbitrary and often decisive discharge (Temporiti et al. 2022). The application of chemicals in industrial processes like nuclear experiments, agricultural practices, and various aspects of daily human activities and needs results in the discharge of toxic substances into the environment either intentionally or by accident (Vishwanath et al. 2014; Clark et al. 2022). The hazardous chemicals recognized as polluting the atmosphere include pesticides, heavy metals, hydrocarbons, drugs, halogenated solvents, and agricultural chemicals. After their release into the environment, these chemicals are transported through the water, soil, and atmosphere (Deshmukh et al. 2016).

Similarly, the environment is being polluted with a large number of pollutants and obstinate substances such as heavy metals, polyaromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), polychlorinated dibenzo-*p*-dioxins (PCDDs), and polychlorinated dibenzofurans. Various conventional chemical processes for the degradation of these toxic substances have been explored to overcome these threats. However, they are insufficient for large-scale commercial administration (Deshmukh et al. 2016; Akcil et al. 2015; Sonawane et al. 2022). Bioremediation is a biological degradation mechanism (by microbes, plants, and microbial or plant secretions) to degrade environmental pollutants. Microbe-assisted remediation uses microbial processes to treat areas polluted by harmful substances, eliminate unwanted components, and reduce the production of toxic by-products (Temporiti et al. 2022). Fungi use environmental pollutants by interacting with them physically, which results in complete degradation or accumulation of environmental pollutants as the known cosmopolitan distribution of fungal microbes can release various enzymes, making it possible candidates for the remediation of extreme pollutants. They play a crucial role in the normalization of pollutants, including agrochemicals, coal, persistent organic pollutants, paper leather tanning effects, pharmaceuticals, personal care products, polycyclic aromatic hydrocarbons, and textile dyes (Deshmukh et al. 2016). Fungal enzymes like amylases, catalases, cellulases, cytochrome P450, dehydrogenases, dehalogenases, hydrolases, laccases, lipases, peroxidases, proteases, and xylanases have shown promising potential degradation of agrochemicals, aromatic hydrocarbons, dyes, detergents, halogenated compounds, and polymers (Vishwanath et al. 2014; Anasonye et al. 2014; Deshmukh et al. 2016; Rao and Li 2017; Li et al. 2020). For instance, heavy metal tolerance has been studied in hyphae-producing fungi such as *Aspergillus*, *Acremonium, Curvularia,* and *Pythium* (Akhtar et al. 2013). Rosales et al. (2013) have studied the degradation of polycyclic aromatic hydrocarbons in solid-phase fermentation during the growth of agro-industrial wastes by *Pleurotus ostreatus* and *T. versicolor*. Fungal forms (such as *Aspergillus* sp., *Penicillium* sp., and alkalophilic white-rot fungus) possess potential application in the degradation of colored substances from bleached kraft pulp mills, sugar industry, leather tanning effluents, and textile dyes. An elimination of petroleum hydrocarbons (PHs) from soil polluted with petrol and diesel was achieved using fungi like *A. niger* and *P. chrysosporium* (Maruthi et al. 2013).

Filamentous and other mycorrhizal fungi demonstrate a remarkable potential for the degradation of lignin, a recalcitrant substance, and phenolics by oxidation mechanism (Baker et al. 2019). Morel et al. (2013) and Rudakiya et al. (2019) have reported that fungi produced these enzymes to implicate in the degradation and decomposition of toxic substances (discharge as industrial waste and organic substances). A literature survey suggested that the fungal microbes could confirm with comparative genomics to recognize the genes involved in the detoxification of hazardous substances, and currently, these fungi-secreted enzymes have been extensively modified for remediation of hazardous substances in a cost-effective and environment-friendly approach (Baker et al. 2019; Temporiti et al. 2022).

7.2 Fungal Enzymes in Bioremediation

Bioremediation is the application of living entities to remove harmful pollutants by reducing the harmfulness of pollutants and returning them to their normal environment (Mahmud et al. 2022). Microbial enzymes are known to be superior enzyme systems (primary metabolites) derived from diverse microorganisms, especially fungi, for utilization in industries on commercial levels (Clark et al. 2022). Fungal microbes are the important candidate for bioremediation as they are typical degraders of organic and inorganic matter or toxic substances from their surroundings by secreting different extracellular enzymes through the processes of immobilization, metabolism, degradation, or absorption (Deshmukh et al. 2016; Hiralal et al. 2022) (Table 7.1). The most studied fungal secreted enzymes involved in bioremediation include amylases, cellulases, catalases, cytochrome P450s, dehalogenases, dehydrogenases, hydrolases, laccases, lipases, proteases, peroxidases, and xylanases, which have exhibited potent decomposition of hazardous environmental pollutants (Table 7.2). Likewise, the polymers like cellulose, lipids, protein, starch,

Table 7.1 List of fungi involved in bioremediation

Fungi	Remediated pollutants	References
White-rot fungi	Pesticide degradation	Deshmukh et al. (2016)
Aspergillus foetidus	Nickel and chromium	Chakraborty et al. (2013)
A. niger	Refinery effluents	Sabah et al. (2016)
Penicillium sp.	Nickel and chromium	Malla et al. (2022)
Rhizopus sp.	Cu-, Fe-, and Zn-contaminated waters	Ezeilo et al. (2020)
Aspergillus niger	Petroleum-contaminated soil and water	Odili et al. (2020)
Trametes versicolor	Atrazine in soil and organic contents	Deshmukh et al. (2016)
Pleurotus ostreatus	PCBs and phenols	Shraddha et al. (2011)
Lasiodiplodia sp.	Cadmium, Pb, and zinc	Deng et al. (2014)
Pestalotiopsis sp.	Cu, Pb, Zn, and chromium	Choo et al. (2015)
Fusarium sp. *Colletotrichum* sp.	Pb, chromium, Cu, and Zn	Mahish et al. (2022)
Trichoderma, *Aspergillus* *Mortierella*, Apecilomyces	Co	Townsley and Ross (1986)
T. versicolor *Pleurotus ostreatus*	Xenobiotics and PCBs	Keum and Li (2004)
Peniophora incarnata	Xenobiotics and PAHs	Lee et al. (2016)
Coriolus versicolor	Pesticides	Yang et al. (2013)
Aspergillus foetidus	Textile dyes	Sumathi and Manju (2000)
Phanerochaete velutina, Stropharia rugosoannulata	Dibenzofurans and polychlorinated dioxins	Anasonye et al. (2014)
P. ostreatus, T. versicolor	Polychlorinated biphenyls	Rubilar et al. (2008)
Chrysosporium, Trametes versicolor	BTEX (benzene, toluene, ethylbenzene, xylene)	Godambe and Fulekar (2017)
Aspergillus oryzae	Petroleum hydrocarbons	Mahmud et al. (2022)

and xylan in the waste can be hydrolyzed by the administration of fungi-secreted extracellular enzymes produced in their developmental stage.

7.2.1 Proteases

The fungi-secreted protease enzymes potentially convert proteinaceous waste into simpler amino acids. Similarly, they play an essential role in the bioremediation of organic waste products (Table 7.2). For example, Haider et al. (2019) have reported that proteases are employed in the decomposition of polymers, such as the

Table 7.2 Fungal enzymes in bioremediation of organic and other pollutants

Enzymes	Origin	Mode of action	References
Cellulases	*Aspergillus niger, Trichoderma viride* VKF3, *Rhizopus oryzae* CCT 7560, *Trichoderma* sp.	Degradation of lignocellulosic biomass through solid fermentation	Srivastava et al. (2018)
Xylanases	*Thielavia terrestris, Talaromyces thermophiles, Paecilomyces thermophile, Achaetomium* sp., *Rhizomucor pusillus, Rasamsonia emersonii, Talaromyces leycettanus, Melanocarpus albomyces*, and *Aspergillus oryzae* LC1	In animal feed industries, agriculture wastes, breweries, food industries, juice industries, paper industries, refineries, and textile industries	Bhardwaj et al. (2019) and Rao and Li (2017)
Amylases	*Aspergillus niger, Aspergillus oryzae, Thermomyces lanuginosus*	Production of acetic and citric acids, and α-amylase enzyme (hydrolytic potential and tolerance to acidity)	de Souza and Magalhaes (2010)
Proteases	*Aspergillus, Penicillium, Trichoderma, Cladosporium Rhizopus, Mucor, Humicola, Thermoascus, Thermomyces*	Food, baking, brewing, detergents, cheese, leather and textile, biodegradation of proteinaceous waste remediates into simpler amino acids	Bhunia and Basak (2014) and Kumar and Jain (2020)
Lipases	*Aspergillus, Penicillium, Rhizopus, Candida*	Synthesis of biodegradable polymers, biodiesel production, in detergent industries, diagnostic and medical fields, fine chemicals and pharmaceuticals, food industries, and textile industries	Kanmani et al. (2015)
Laccases	*Agaricus bisporus, Ascomycetes, Basidiomycetes, Coprinus cinereus, Deuteromycetes, Phanerochaete chrysosporium, Pleurotus ostreatus, Trametes versicolor*	Bioremediation of pharmaceuticals, particularly antibiotics, and detoxification of persistent organic pollutants are essential environmental challenges that require effective solutions	Yang et al. (2017)
Peroxidases	White-rot fungi	Bioremediation of phenolic and non-phenolic substances by oxidation	Deshmukh et al. (2016)
Catalases	*Aspergillus foetidus, Aspergillus niger, Penicillium* sp., *Rhizopus* sp.	Bioremediation of heavy metals and restoration of oil-contaminated soil	Deshmukh et al. (2016)
Cytochrome P450	*P. chrysosporium, Aspergillus oryzae*	Degradation of xenobiotic compounds, pesticides, and industrial wastes	Pratiwi et al. (2022)

(continued)

Table 7.2 (continued)

Enzymes	Origin	Mode of action	References
Hydrolases	*Trametes polyzona*	Degradation of macromolecular substances	Rao et al. (2010)
Laccase, lignin-degrading systems	Ascomycetes, Deuteromycetes, Basidiomycetes, *P. chrysosporium, T. versicolor*	Polyaromatic hydrocarbons (PAHs)	Peng et al. (2008)
Cytochrome P450	*P. chrysosporium, Aspergillus oryzae*	Petroleum hydrocarbons	Mahmud et al. (2022)
Lignin peroxidase Manganese peroxidase	*C. polyzona, P. ostreatus, T. versicolor*	Polychlorinated biphenyls	Rubilar et al. (2008)
Peroxidase	*Cladophialophora* sp. strain T1, *Phanerochaete chrysosporium*, *Trametes versicolor*	BTEX (benzene, toluene, ethylbenzene, xylene)	Godambe and Fulekar (2017)
Cytochrome P450	*Aspergillus niger, Coriolus versicolor, Pleurotus sajor-caju, Trametes pubescens*	Pesticides	Kvesitadze et al. (2004) and Rudakiya et al. (2019)

decomposition of α-ester, lipase c-ω, and polyhydroxybutyrate depolymerase β-ester linkages. The proteases are also useful in deleting or deproteinizing marine crustacean wastes. Likewise, they can potentially decompose keratin proteins and could be applied in poultry discharge management. Thus, the enzyme keratinase can be useful in deleting keratinous wastes. Kumar and Jain (2020) have reported that the fungi (*Aspergillus, Cladosporium, Penicillium*, and *Trichoderma*) were screened for the synthesis of proteases and their action to degrade proteins discharged from temples. The proteases secreted by the fungi *Endothia parasitica* and *Mucor miehei* progressively replace rennin in cheese making (De Souza et al. 2015). The proteases have been secreted from different fungal forms such as *Aspergillus flavus, Candida mogii, Myceliophthora thermophila, Neurospora crassa, Phanerochaete chrysosporium, Pleurotus ostreatus, Saccharomyces pombe, Schizophyllum commune, Sporotrichum thermophile, Thermomyces lanuginosus, and T. ibadanensis*, which are employed to prepare enzyme-derived detergents to eliminate the harsh dyes from clothes for a shine cleansing effect (Naeem et al. 2022).

7.2.2 Lipases

The lipases have efficient applicability in industries as they have been isolated from microbes (bacteria and fungi), plants, and animal cells (Karigar and Rao 2011; Deshmukh et al. 2016) (Table 7.2), and they act by catalyzing various reactions like aminolysis, alcoholysis, esterification, and hydrolysis (Riffaldi et al. 2006). For instance, they influence the hydrolysis reaction of triacylglycerols, converting oils into free fatty acids and glycerol. The hydrocarbon degradation in soil was achieved through lipase activity and is considered the most beneficial indicator. The enzyme lipase was isolated from *Candida rugosa* through a biphasic oil-water system, resulting in the hydrolysis of triolein and being more efficient. Enzyme lipase can cleave the ester links of triolein and subsequently derive monoolein, diolein, and glycerol forms, and in the catalysis reaction, the synthesis of oleic acid was recorded at every subsequent step (Karigar and Rao 2011). Lipase enzymes can improve the detoxification of lubricant wastes (oils, fats, and proteins) discharged from industries (Basheer et al. 2011).

7.2.3 Laccases

Many fungi have been recognized as enzyme laccase producers, and they belong to the blue oxidase group and are copper-containing extracellular enzymes implicated in detoxifying toxic elements. The secretion of laccases from *T. versicolor* oxidizes most phenolics and non-phenolic substances (Margot et al. 2013; Deshmukh et al. 2016). The catalytic activities of enzyme laccase affect the oxidation reaction of phenolic substances like orthodiphenols and para-diphenols. The production of polymeric substances by enzyme laccase can be used for remediation processes, especially removing xenobiotic components. The laccases derived from *Coriolopsis rigida, Myceliophthora thermophila*, *Pycnoporus coccineus,* and *Trametes villosa* are used in recycled paper industries for the decolorization of flexographic inks (Fillat et al. 2012). Similarly, the marine fungi secreted laccase-mediated decolorization, decomposition, and mineralization of reactive blue 4 dye (Verma et al. 2012; Vishwanath et al. 2014). Likewise, Chhaya and Gupte (2013) studied an endocrine-disrupting chemical (bisphenol A), and its degradation was achieved with *Fusarium incarnatum*-derived enzyme laccase. Schultz et al. (2001) showed that the enzyme laccase secreted by *Pycnoporus cinnabarinus* could dechlorinate and detoxify chlorinated hydroxybiphenyls. *Agaricus bisporus, Coprinus cinereus, Phanerochaete chrysosporium*, *Pleurotus ostreatus,* and *Trametes versicolor* fungal forms are potentially involved in the remediation of pharmaceutical waste, antibiotics, and persistent organic pollutants (Yang et al. 2017).

7.2.4 Peroxidases

With the high redox potential, non-specificity, and capability to oxidize substrates (Conesa et al. 2002; Temporiti et al. 2022), peroxidases are categorized (based on origin and activity) into lignin peroxidase, manganese peroxidase, and versatile peroxidase, and white-rot fungi and basidiomycetes secrete them and are mostly accounted for the degradation of environmentally toxic substances. The most recognized group of enzyme peroxidase-secreting fungi (ligninolytic fungi) like

Bjerkandera adusta, Ceriporiopsis subvermispora, Dichomitus squalens, Phanerochaete chrysosporium, Pleurotus spp., *Phlebia radiata,* and *Trametes versicolor* (Temporiti et al. 2022; Ayuso-Fernández et al. 2017). The phenolics and non-phenolic substances are oxidized with the versatile type of peroxidases (VP) and are highly potential applications in removing environmental pollutants (Karigar and Rao 2011). They are concerned with the fabrication of biofuels and paper (Li et al. 2015), waste management, and remediation of industrial waste like synthetic dyes and PAHs (Daccò et al. 2020; Temporiti et al. 2022). Godambe and Fulekar (2017) have studied the peroxidases released by fungi such as *Cladophialophora* sp. strain T1, *Phanerochaete chrysosporium*, and *Trametes versicolor* and which are employed in the detoxification of benzene, toluene, ethylbenzene, and xylene (BTEX).

7.2.5 Catalases

Catalases are the group of oxidoreductase enzymes secreted by fungi that have the proficient potential of converting hydrogen peroxide chemicals into water and oxygen; thereby, catalases are used as oxygen molecules in the route of degradation of pollutants (Deshmukh et al. 2016). Chakraborty et al. (2013) have studied and reported good development and resistance of the fungus *Aspergillus foetidus* by increasing the level of catalase for degrading malondialdehyde (MDA) and hydrogen peroxide with exposure of Pb (200 mg/L). Swaminathan et al. (2009) have reported that catalase also has potential application in the degradation of pesticides by initial oxidation, reduction or hydrolysis, and amalgamation of pesticides, which reduces water toxicity and enhances water solubility and subsequently converts remaining metabolites into secondary nontoxic substances. Pb^{2+} and Cu^{2+} added alone or mixed with the 50 mg/L consortia of fungi (*A. niger*, *Penicillium* sp., and *Rhizopus* sp.) exhibited an increased catalase action (Thippeswamy et al. 2014). The activities of the enzyme catalase can be utilized as a tool for examining decomposition potential; on the other hand, the catalase actions are reduced along with the rising concentration of oil at the time of restoration of oil-polluted soils (Lin et al. 2009). Therefore, considering the activity of catalases in giving heavy metal resistance to fungi and fungal microbes secreting this enzyme could be effective candidates for remediation of heavy metal-polluted sites (Table 7.2).

7.2.6 Cytochrome P450

It is a heme-containing ubiquitous enzyme and very significant for the remediation of toxic substances by oxidation reaction (Li et al. 2020). It can also implicate the metabolic detoxification of xenobiotic compounds via chemical normalization such as aliphatic hydroxylation, dealkylation, dehalogenation, and epoxidation (Bancel et al. 2002). Cytochrome P450 is an extremely versatile redox enzyme that can be a beneficial tool for developing biocatalysts that can achieve reductive exclusion mechanisms for the degradation of environmental pollutants (Behrendorff 2021). For instance, Baker et al. (2019) have discussed that the *Phanerochaete chrysosporium* fungi have been exhibited to degrade PAH (anthracene) and the endocrine-cleaving alkylphenols. The degradation and detoxification of benzoate derivatives were attempted by secreting P450s from both Ascomycota and Basidiomycota group species. Furthermore, the non-ligninolytic fungi (*Scopulariopsis brevicaulis*) secreted class II P450s, which showed significant detoxification and complete transformation of anthracene.

7.2.7 Dehalogenases

The dehalogenases are frequently employed in the remediation of halogenated organic substances by cleaving C–X bonds via three processes such as hydrolysis, reduction, and oxygenolysis (Hussain et al. 2018). Allpress and Gowland (1998) have investigated that dehalogenase catalyzes dehalogenation reactions such as the alteration of halogen atoms by a hydroxyl group (OH) from hydrogen and water. For instance, Schultz et al. (2001) investigated the dehalogenation reaction of chlorinated hydroxybiphenyls catalyzed by the enzyme laccase secreted by the fungus *Pycnoporus cinnabarinus*.

7.3 Fungal Enzyme in Bioremediation of Organic Pollutants

Fungi are very versatile microorganisms to detoxify an array of pollutants by secreting various enzymes; likewise, fungi alter their metabolic pathways for the degradation of relatively new organic pollutants. Fungal enzymes play a vital role in the detoxification of organically contaminated soils like diesel, petroleum, PAHs, pesticides, fuels, polychlorinated biphenyls (PCBs), chlorophenols, and dyes (Diez 2010; Singha and Chatterjee 2022) (Table 7.2; Fig. 7.1). Fungal metabolic processes are utilized for the degradation of organic substances into nontoxic compounds in an economical, eco-friendly, and efficient way (Yair et al. 2008). The fungal enzyme oxygenase that can metabolize trichloroethylene is associated with dichloroethylene and vinyl chlorides into CO_2 and Cl, the nontoxic final products (Yoshikawa et al. 2017; Shelke et al. 2022). Various organic pollutants penetrate through the fungal cell membranes, and these can be degraded by intracellular enzymes like cytochrome P450, dehalogenases, and nitroreductases (Tripathi et al. 2017; Stella et al. 2017; Ostrem and Yu 2018), get converted into simpler organic substances by β-oxidation, and consequently enter into the TCA cycle (Varjani 2017).

The degradation of aromatic hydrocarbons by white-rot fungi (*P. chrysosporium* and *Pleurotus pulmonarius*) was attained in historically contaminated soils (naphthalene, tetrachlorobenzene, dichloroaniline, diphenyl ether, and *N*-phenyl-1-naphthylamine) (Diez 2010). Kües (2015) reported that white-rot fungi achieved lignin degradation by secreting class II peroxidases specialized for high oxidation effect. The enzyme cytochrome P450 is secreted by fungi such as *Aspergillus niger,*

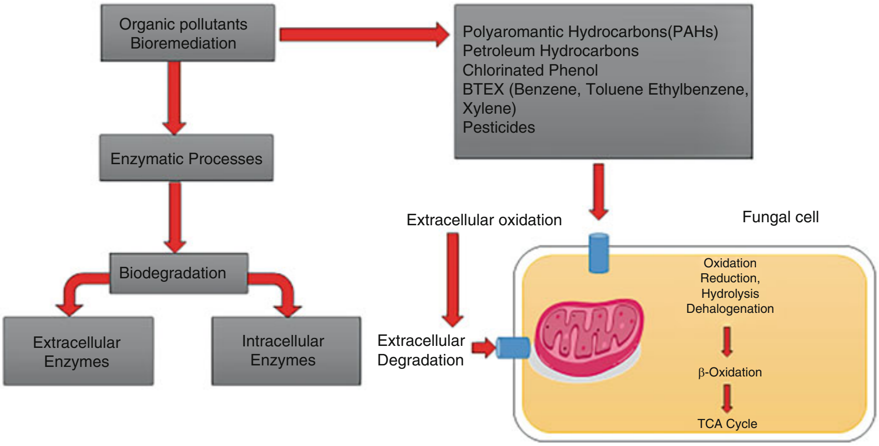

Fig. 7.1 Bioremediation of organic pollutants

Coriolus versicolor, Pleurotus sajor-caju, and *Trametes pubescens*, which are employed in the detoxification of pesticides (Kvesitadze et al. 2004; Rudakiya et al. 2019). Similarly, *P. chrysosporium* and *Aspergillus oryzae* produced cytochrome P450 enzyme, which was beneficial for the degradation of petroleum hydrocarbons (Mahmud et al. 2022), xenobiotic substances, pesticides, and industrial wastes (Pratiwi et al. 2022). Moreover, Kvesitadze et al. (2004) and Rudakiya et al. (2019) have reported that the detoxification of agrochemical waste was attained by the cytochrome P450 produced by fungi like *Aspergillus niger, Coriolus versicolor, Pleurotus sajor-caju,* and *Trametes pubescens*. Therefore, the various fungal forms secreted by various enzymes were employed in the detoxification/degradation of toxic organic pollutants, and some of the examples are explained in Table 7.2.

7.4 Conclusion

Fungal microbes are essential in decomposing environmental pollutants due to their diverse enzyme secretion capability. Fungal enzymes have the potential to make over and detoxify environmental pollutants efficiently. In this chapter, we have discussed and explored diverse aspects together, exhibiting fungi's varied and new metabolic capabilities and their significance in the remediation of toxic substances. The chapter represents extensive studies of fungal diversity, fungal actions against environmental hazards, utilization of fungal microbes for detoxification of toxic substances, and perceptions on the application of fungal microbes in bioremediation. The fungi-assisted removal of heavy metal and hazardous compounds from the environment would be studied well, and their targeted gene amplification could be a potential area of research. Further investigations would be holding out for inclusive perception of bioremediation routes, and progress in the genetic study indicates that complete genome investigations can help to recognize and exhibit the detoxification mechanisms.

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Mycoremediation of Heavy Metals and/or Metalloids in Soil

8

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Contents

Abstract

Soil and water pollution is a matter of great concern in the twenty-first century, the majority of which is caused by various organic compounds, agricultural and municipal wastes, heavy metals, and microorganisms. Due to fast industrialization, mining, and other technical breakthroughs, the soil environment is continuously poisoned by heavy metals in the modern period. As a result, heavy metal contamination has become a major concern worldwide. Mycoremediation is a

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type of bioremediation that uses fungi to remove, degrade, or reduce the toxicity of various pollutants from various substrates. Filamentous fungi have several properties that make them suitable for heavy metal (HM) bioremediation. Fungi have a high adsorption and accumulation capability for HMs; thus, they could be helpful. Bioaccumulation, bio-adsorption, biosynthesis, biomineralization, bio-oxidoreduction, extracellular or intracellular precipitation, surface sorption, and other bio-mechanisms involved in HM tolerance and removal by fungus differ from species to species. However, the major influential parameters that affect HM bioremediation include time, pH, temperature, HM concentration, dose of fungal biomass, and shaking rate, which vary depending on the fungi and composition of the HMs. Hence, mycoremediation is thought to be a more effective strategy than traditional methods for removing hazardous chemicals, including heavy metals, from soil and water bodies in a long-term and cost-efficient manner.

Keywords

Soil pollution · Heavy metals · Filamentous fungi · Mycoremediation

8.1 Introduction

Mother Nature is continuously impacted by increasing industrial and developmental activities, and as a result, foreign elements are continually being introduced to nature. These elements include heavy metals, pollutants, chemicals derived from agricultural lands, and other sources. They are the most dangerous substances and are discharged in substantial quantities that enter the ecosystem directly or indirectly. Many metals function as micronutrients when used in the wrong quantities, but when used in the right quantities, they are advantageous for the growth and development of plants and also support metabolic activity as metalloenzymes. But if used in appropriate amounts, they are not hazardous or behave like heavy metals. Heavy metals are highly soluble in water and are consumed by aquatic species that pose a significant risk to human health due to their non-biodegradability, high toxicity, and long persistence. Continuous exposure to these heavy metals is quite concerning. Thus, it is a crucial time to find a better solution. Bioremediation is an environmentally benign approach that uses fungi, bacteria, or plants to treat wastewater and other contaminated areas (Kumari et al. 2019). In intensive agricultural and horticultural systems, large amounts of fertilizers and pesticides are being routinely used on the soil and the plant to provide enough nitrogen (N), phosphorus (P), and potassium (K) as well as protection, respectively. Heavy metals are contaminants present in trace amounts in the compounds used to supply these elements, and following repeated fertilizer and pesticide applications, their presence in the soil and in the environment may dramatically increase (Jones and Jarvis 1981; Basta et al. 2005; McLaren et al. 2005; Wuana and Okieimen 2011). In addition to macronutrients, plants also need certain micronutrients in order to develop and complete their life cycle.

Some soils are deficient in the heavy metals required for healthy plant development (Lasat 1999); thus, crops can be given these by adding them to the soil or spraying them on the leaves. Occasionally, copper (Cu) and manganese (Mn) are also added to the soil to treat cereal and root crops if the soil has a deficit in the elements. When some phosphate fertilizers are applied to the soil, cadmium (Cd) and other hazardous metals such as lead (Pb), mercury (Hg), and fluoride (F) are unintentionally added to the soil (Madhavan et al. 2017). Due to the application of numerous biosolids, heavy metals like copper, arsenic, lead, cadmium, and nickel, and some other pollutants like manures from livestock, municipal sewage sludge, and composts, are unintentionally accumulated in the soil (Basta et al. 2005). Animal manures from farms, such as those from chickens, cows, and pigs, are regularly applied to pastures and crops as solids or slurries (Sumner 2000). However, copper (Cu) and zinc (Zn) are added to diets as growth promoters, and the arsenic (As) found in poultry health products in the pig and poultry sectors may have the potential to pollute the soil with metals (Sumner 2000). The manures generated by animals on such diets have high concentrations of Zn, As, and Cu. If these are often dispersed over constrained areas of land, a sizeable amount of these metals may ultimately accumulate in the soil. Most organic solid waste products that can be recycled for environmental objectives are sewage sludge or biosolids (USEPA 1994). In most of the nations that permit biosolid reuse produced by urban populations, the application of biosolid materials in the soil is a prevalent practice. The heavy metals that are most frequently discovered in biosolids include Zn, Pb, Cd, Ni, Cu, and Cr, and the concentrations of these metals are determined by the type of industrial activity, its intensity, as well as the procedure used to treat the biosolids. Under some conditions, metals added to soils during the treatment of biosolids may seep through the soil layer and possibly pollute groundwater (McLaren et al. 2005).

It has been a regular practice in many regions of the world for more than 400 years to apply municipal, industrial, and related effluents to land (Reed et al. 1995). As per the estimation, it was found that wastewater irrigates 20 million hectares of arable land globally. In practice, farmers are more focused on growing their yields and profits than on the benefits or threats associated with the environment. Even while wastewater effluents typically have low metal concentrations, they may eventually cause a significant metal accumulation in the soil if used to irrigate land over an extended period. The legacy of widespread distribution of metal pollutants in soil has been left to many nations by the mining and processing of metal ores in conjunction with industries. When dumped directly into natural depressions such as on-site wetlands, heavy and larger particles known as tailings that get deposited at the bottom of the flotation cell during mining can accumulate in high quantities (DeVolder et al. 2003). The extensive smelting and mining of zinc and lead ore have been contaminating the land and threatening human and ecological health. Most of the lengthy, expensive restoration techniques employed for these sites may not restore soil productivity. The environmental risk that heavy metals in soil pose to people is correlated with bioavailability. Another significant source of

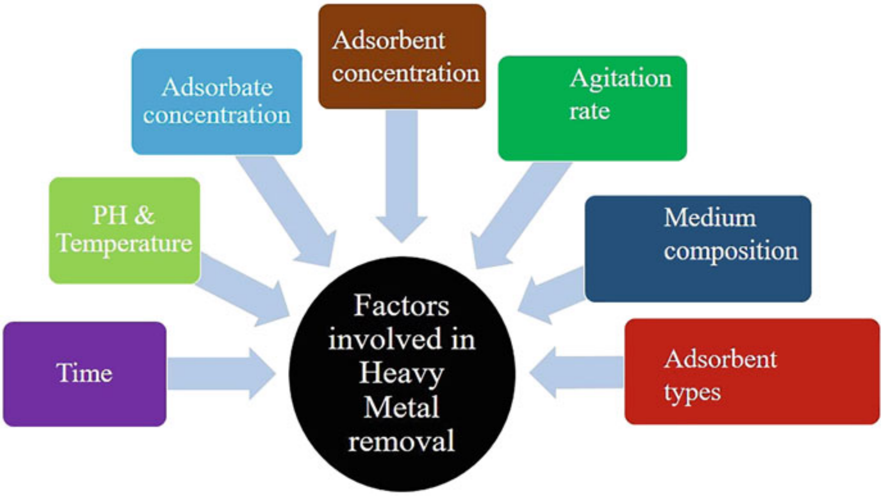

Fig. 8.1 Factors involved in heavy metal/metalloid removal

soil pollution is the airborne emission of lead from the combustion of gasoline containing tetraethyl lead; this dramatically raises the level of lead in urban soils and major roadways. Due to lubricating oils and tire treads, Zn and Cd may also be added to soils close to roads (USEPA 1994; Wuana and Okieimen 2011). The numerous factors which are involved in heavy metal removal are illustrated in Fig. 8.1. The purpose of this review is to provide information on heavy metals and different metalloids that are responsible for environmental pollution because of their persistency, toxicity, and accumulation in the biosphere, as well as to highlight the bioremediation methods like mycoremediation that have so far proven to be effective (Raffa et al. 2021).

8.2 Heavy Metals/Metalloids in Soil

All metals and metalloids having a density of more than 5 g cm^3 have been collectively referred to as “heavy metals” (Wuana and Okieimen 2011; Pendias and Pendias 2001). Generally, common transitional metals like zinc (Zn), copper (Cu), lead (Pb), cadmium (Cd), and mercury (Hg) are referred to as “heavy metals” in this context, whereas “metalloids” refer to a class of chemical elements that exhibit properties that fall somewhere between those of metals and nonmetals and naturally occur as poly-hydroxylated species. This category often includes the chemical elements arsenic (As), boron (B), silicon (Si), antimony (Sb), germanium (Ge), and tellurium (Te), as well as less frequent elements like astatine (At) and polonium (Po). These heavy metals and metalloids in the soil or water may substantially impact human and ecological health (Chan et al. 2016). Any metallic chemical element that has a high density and has the potential to be poisonous even at low doses is referred to as a heavy (or trace) metal. Although heavy metals are easily absorbed and bioaccumulated in different plant sections, they are neither essential nor play a crucial function in cells' metabolic pathways (Nas and Ali 2018). Cobalt (Co), nickel (Ni), copper (Cu), vanadium (V), zinc (Zn), and chromium (Cr) are heavy elements that, at low concentrations, are not poisonous (Nas and Ali 2018).

Heavy metals are an essential component of the planet and cannot be removed or degraded. Because of their propensity to collect in live cells, they are enormously hazardous. When a chemical compound gradually assembles within living things over time in contrast to its environmental concentration, this is referred to as bioaccumulation. Industrial and consumer waste, as well as acid rain, which causes weathering and the release of heavy metals into groundwater, rivers, lakes, and streams are all ways that trace metals can enter the water and harm aquatic life. Heavy metals and metalloids are present in the soil due to the parent materials. These materials come from lithogenic and human-made processes (Alloway 2013). Anthropogenic activities that are increasing the number of heavy metals in the environment include mining, smelters, foundries, burning of fossil fuels, using gasoline, waste incinerators, and other industrial operations. This affects the environment's ability to sustain life and provide for its basic needs. The three heavy metals that are most problematic are cadmium, mercury, and lead, according to the European Monitoring and Evaluation Programme (EMEP), because of their severely detrimental impacts on human health. According to Damodaran et al. (2013), the physiology and composition of the organism's cell wall, as well as physicochemical factors like concentration of the metal, time, temperature, pH, and ionic strength of the metal, all play a role in the intricate process by which the heavy metal removal mechanism operates. Any environmental product containing these heavy metals may be harmful to human health as well as to soil, plants, and animals. According to Singh and Kalamdhad (2011), it is highly concerning that heavy metals are absorbed by plants, subsequently accumulated, and transferred to human tissues through the food chain. Interactions between plants, fungi, bacteria, and other living and nonliving elements of the environment occur. Under stress, they often adapt metabolically to the environment by going through various mechanisms to lessen the toxicity (Abdullahi et al. 2021).

Heavy metal and metalloid soil pollution is a problem that affects every nation on the planet. Since heavy metal contamination cannot biodegrade and builds up in the soil, hurting people, animals, and the ecosystem for a very long time, it has drawn more attention recently. Exposure to heavy metals and metalloids is linked to various health issues, including kidney problems, developmental and neurobehavioral difficulties, bone problems, blood pressure issues, and tumor growth. These issues become pertinent when there are appreciable concentrations of heavy metals in the soil. An estimated five million locations worldwide have soil that is polluted with heavy metals and metalloids. The primary source of this pollution is frequent anthropogenic activities. Developed nations like the USA, China, Australia, and EU members tend to have more heavy metal-contaminated areas than developing nations (Brito et al. 2020; Yu et al. 2020). The average global amounts of these pollutants in soil vary depending on the kind of soil, the environment around it, and the distance from the source of contamination. Heavy metal/metalloid species continue to get attention worldwide due to the persistent nature of such damaging pollutants, which include static, durable, accumulative, and nonbiodegradable properties (Zhao et al. 2019). The soil near metal smelters has been contaminated by the heavy metal/metalloid species that metal smelting activities have discharged into the environment. The buildup of heavy metal/metalloid species poses a danger to the ecological environment, variety, functioning of soil microorganisms, food security, and human health. Soil microorganisms have a key role in defining the quality of the soil since they are the guardians of the ecosystem's structure and functioning (Hou et al. 2019). Although soil microorganisms can influence soil properties, the physicochemical properties of the soils can also have a large influence on them. According to research, microorganisms greatly enhance soil fertility, crop health, and nutrient circulation in the soil. It is commonly acknowledged that the toxic stress brought on by heavy metals and metalloids may significantly influence the number, variety, and ecological functions of the soil's microbial communities. For instance, heavy metal/metalloid pollutants have an impact on the ecological processes in soils that functional groups and a variety of functional genes sparked. As a result, the variety of microorganisms has diminished and the structure of soil microbial communities has changed even more. Numerous heavy metal/metalloid-tolerant bacteria may transform or eliminate heavy metals from polluted soil (Qiao et al. 2019). Bioremediation has been recognized as a promising green and sustainable method for cleaning up heavy metal pollution. Bioremediation has been recognized as a promising green and sustainable method for cleaning up heavy metal pollution. Furthermore, alterations in the chemical forms of heavy metal/metalloid species brought on by the physicochemical characteristics of soil may have a secondary effect on the makeup of microbial communities (Hu et al. 2021). Approximately 51 elements in the periodic table are considered heavy metals or metalloids. Because of their chemical properties and those of the soil, they are mobile and bioavailable in the soil. The interaction of soil components with metals and metalloids is influenced by the pH, the characteristics of the adsorbent surface, and the presence of cations and anions. Zinc (Zn), chromium (Cr), nickel (Ni), manganese (Mn), cadmium (Cd), lead (Pb), copper (Cu), and arsenic (As) are the most prevalent heavy metals and metalloids. The most hazardous substances are those with Cr, Cu, Zn, Cd, Pb, Hg, and As in them. As the underlying bedrock weathers, they are frequently discovered as ores (sulfides of Pb, Co, Fe, As, Pb, Zn, Ag, and Ni, and oxides of Se, Al, Mn, and Sb). Along with sulfides of arsenic, mercury, lead, and cadmium, chalcopyrite, CuFeS2, and pyrite, FeS2, are naturally occurring sulfides of copper and iron in the soil. In particular, ore mining and refining, using pesticides and fertilizers, and solid wastes all contribute to the environmental problem by raising the levels of heavy metals and metalloids. Heavy metals and metalloids are used in many industries, increasing market demand, and worldwide output. Many biological processes, including the nervous system, production of complex molecules, respiration systems, and control and functioning of enzymes, require trace amounts of copper, selenium, zinc, iron, vanadium, and manganese. Electronic gadgets, especially semiconductors, are made largely from metals, including iron, zinc, tin, lead, copper, and tungsten (Koller and Saleh 2018). It is clear that certain elements, particularly chromium, copper, zinc, and lead, are employed in many industries and that there is a significant annual output worldwide, wherein the United States, China, Australia, Russia, Peru, and Mexico are the major producing nations (Raffa et al. 2021). Microbial bioremediation lowers the expense of the heavy metal pollution treatment process while also being effective, economical, and ecologically benign (Mishra 2017). The primary mechanisms for microbial removal of heavy metals are biosorption, which includes ion exchange, redox reactions, adsorption of chemicals, precipitation, and formation of a complex with organic ligands; secondly, biomineralization which includes bioleaching, which involves releasing heavy metal ions from insoluble ores through dissolution or complexation; and thirdly, bio-oxidation (González Henao and Ghneim-Herrera 2021).

8.3 Mycoremediation of Soil

8.3.1 Important Fungal Species Involved in Bioremediation

Microbial bioremediation lowers the expense of the heavy metal pollution treatment process while also being effective, economical, and ecologically benign (Mishra 2017). The primary mechanisms for microbial removal of heavy metals are biosorption, biomineralization, and bio-oxidation (Jin et al. 2018; González Henao and Ghneim-Herrera 2021). Fungi are used in bioremediation because of their resistance and tolerance, which are used in some aquatic environments where they overpower heavy metals. *Aspergillus niger*, which functions as a multi-tolerant fungus, is one example of the growing fungi employed in the mycoremediation approach. Different fungi, including *Penicillium*, *Aspergillus*, *Trichoderma*, *Fusarium*, etc., use a variety of strategies within the cell wall to remove different kinds of heavy metals, including cell surface precipitation, detoxification, accumulation, efflux, and alterations. Contaminated water and soil keep the majority of metal-tolerant fungi separate. The nature of the fungal resistance is a result of the genetic makeup of the fungi, concentration of HMs, environmental conditions, nutritional availability, and various forms of heavy metals. These factors also affect how fungi react to metal and how resistant they are. *Aspergillus flavus* CR500 and *Trichoderma harzianum* are two examples of heavy metal-resistant fungi. According to Table. 8.1, most fungi belong to the class Ascomycetes and are resistant to heavy metals.

Aspergillus, Chaetomium, Coniochaeta, and *Phoma*, all Ascomycetes, have been researched for their similarities between the genomic and secrotomic to allow their presence in the breakdown of biomass and parthenogenesis in the dry environment (Hua et al. 2012; Challacombe et al. 2019). According to the investigation, it was found that all fungi can readily produce melanin because of their melanized structural makeup. Because of these qualities, they can thrive in arid environments. Some proteins have also tested positive and are found in nature and fungi. Both positive and negative interactions between heavy metals and fungi exist (Ruley et al. 2006).

Table 8.1 Fungi used to remove metals and contaminants

Metals	Fungal species	Classes
Zinc (Zn), chromium (Cr), lead (Pb) Copper (Cu) Cadmium (Cd) Aluminum (Al)	*Penicillium* sp., *Aspergillus* spp., *Fusarium* sp., *Trichoderma* sp. *Botrytis* sp. *Humicola* sp.,*Trichoderma* sp. *Trichoderma* sp.	Ascomycetes/ Basidiomycetes/ Zygomycetes
Zinc (Zn), lead (Pb), cadmium (Cd) Chromium (Cr), mercury (Hg)	*Ganoderma* sp., *Pleurotus* sp. *Pleurotus* sp.	
Chromium (Cr) Zinc (Zn)	*Mucor* sp. *Rhizopus oryzae*	

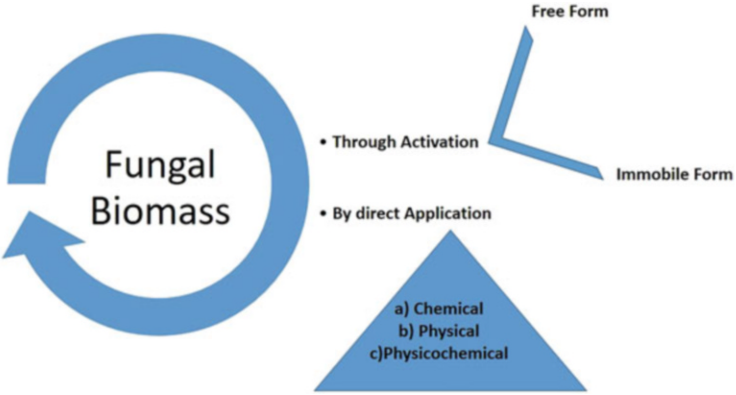

Fig. 8.2 Mycoremediation of heavy metals

In a positive interaction, the presence of HMs has no effect, but in an adverse interaction, the presence of HMs can cause fungus death or growth inhibition. A new phase in removing heavy metals from a wasteland may result from the interaction of heavy metals and fungi. Numerous experts have noted that the majority of fungi can remove various metals in a viable form. Fungi have excellent qualities that can be exploited in bioremediation, and they also function as decomposers with vigorous enzymatic activity (Baker 1987). In large plants, the fungi and microorganisms in the rhizosphere play a crucial part in the synergistic mechanism, which directly increases the tolerance capacity of heavy metals. Few researchers have studied the interactions between different species of fungi and microorganisms in the remediation of heavy metals (Kumari et al. 2019). A schematic diagram of fungal remediation is depicted in Fig. 8.2.

Trichoderma fungi are well adapted to aid in eliminating lead from the environment. Hence, *Trichoderma asperellum* may be used in mycoremediation and may play a supporting function in soil phytoremediation (Bandurska et al. 2021). The study of the interaction between the cell surface of fungi and heavy metals is essential because the composition, structure, adsorption and absorption processes, and accumulation of heavy metals in the fungus vary from fungus to fungus (Chan et al. 2016). Myco-adsorption and mycoremediation are other terms for the adsorption of heavy metals on the surface of fungi. Heavy metals like cadmium, mercury, arsenic, chromium, and lead are used for the adsorption process using fungus-like *Aspergillus* sp., *Thamnidium* sp., etc. (Kumar and Dwivedi 2019). It is safe for biological systems to use the fungus to absorb and remove heavy metals from contaminated locations. The removal of heavy metals is seen to be a very safe and environmentally beneficial method when live creatures like fungi, or mushrooms, are used (Kumari and Kumar 2019). It is widely acknowledged that mushroom farming is an important tool for restoring, replenishing, and remediating the earth's overburdened ecosphere and being a rapidly growing sector of the agricultural industry.

In comparison to microfungi, mushrooms are crucial in the buildup of heavy metals. Since mushrooms are thought to be more advantageous than plants due to their shorter life cycles and more adaptability, mycoremediation can be viewed as an advanced remediation method. An efficient biosorbent for hazardous metals is the mushroom. They expand rapidly in their natural habitat but lack the immobilization or deployment of specific reactor configurations necessary for other microbial sorbents. Instead, they evolve into sorbents because of their texture and other favorable properties (Damodaran et al. 2013). *Elekes* and *Busuioc* examined the levels of heavy metals in five different mushrooms taken from the Bucegi Massif in the Carpathian Mountains: *Collybia butyracea, Calvatia excipuliformis*, *Boletus griseus*, *Marasmius oreades*, and *Hygrophorus virgineus.* Compared to other species, *C. excipuliformis* has higher concentrations of Cu (244.864.26) and Zn (92.190.21) than other species. Additionally, compared to other mushrooms, *C. butyracea* and Zn *C. excipuliformis* have a larger bioaccumulation factor for Cu (Pihurov et al. 2019).

8.3.2 Toxic Compounds Degraded by Fungi

The intake of essential and nonessential metals is crucial for eliminating heavy metals. The internal mechanism of fungi can tolerate some metals quite easily. They have a unique level of metal tolerance (Renu and Singh 2016). Antioxidants that are both enzymatic and nonenzymatic help keep the fungus' ability to tolerate stress in check. Within a single organism, more than one antioxidant property is present for the antioxidant mechanisms (Yang et al. 2016). In the tropical plant species *Candida*, the enzyme glutathione first assembles the metal glutathione complex, which causes the cellular level of oxidized glutathione to rise and aids in detoxifying metals. By generating metallothionein, which enhances fungal tolerance to cadmium, glutathione also aids in lowering the levels of toxicity (Wu et al. 1975).

Thiol is a substance utilized to signal cells and is thought crucial. Thiol synthesis has increased in the plant species *Aspergillus flavus*. Gamma-glutathione makes up one of the two tails of glutathione, and the other tail belongs to the thiol group. Here, the reaction between the thiol group and the glutathione results in cadmium bisglutathionate. The catalase, phenol, proline, and thiol concentration in *Aspergillus flavus* increases in response to the chromium stress (Salt et al. 1998). Again, in some fungus, large amounts of particular proteins are produced that can aid in the buildup and reclamation of heavy metals. Even the overproduction of these proteins causes a stressful condition known as heat shock. Organic acids can also be used to relieve heavy metal stress. Plants are protected from the stress brought on by heavy metals by the formation of organic acids. The fungus *Penicillium* sp. contains organic acids that help detoxify and remedy metals, including zinc, copper, cadmium, chromium, arsenic, manganese, and lead. These acids include pyruvic acid, oxalic acid, citric acid, gluconic acid, and malic acid (Kumari and Kumar 2019). These acids have metabolites that are intracellular, intercellular, and extracellular. During the phytomining of metals, these extracellular organic acids facilitate the extraction process from the low-grade mining ores. Due to the organic acid present inside the cells, all of these metals precipitate (Kumari et al. 2019). Numerous kinds of inactivated fungal biomass and live fungal cells have been used in comprehensive research on heavy metal removal by sorption utilizing fungus (Chan et al. 2016).

Through various enzymatic processes, fungi may change hazardous metals and metalloids into less toxic forms, changing the concentrations of heavy metals in the environment. Using mercuric reductase, fungi may detoxify organomercury compounds, and the resulting mercury, Hg(II), can then be further reduced to the more combustible elemental mercury, Hg(0). Similarly, it happens in the conversion of As(V) to As(III) by arsenate reductases, which are a few common detoxification processes that may be involved once As(V) enters the fungal cells via the phosphate transporters (Gonzalez-Chavez et al. 2011). It is shown that three contiguous genes control *Saccharomyces cerevisiae*'s resistance to arsenic, a transcriptional regulator (ACR1), an enzyme arsenate reductase (ACR2), and a plasma membrane arsenite efflux pump (ACR3). The methylation of inorganic arsenic to create volatile derivatives is another mechanism by which fungi are resistant to metals and metalloids. Metals and metalloids can be methylated by an enzymatic process in which the metal is transferred to the methyl group. The methylated metal compounds commonly differ from their parent compounds in terms of toxicity, solubility, and volatility. Metals that can be methylated include Pb, Hg, and Sn and metalloids like Se, As, and Te. Monomethylarsonic acid and dimethylarsenic acid can be converted to volatile trimethylarsine oxide by *Candida humicola*, *Gliocladium roseum*, and *Penicillium* sp. (Cullen and Reimer 1989). The heat-resistant *Neosartorya fischeri* was found to effectively volatilize (up to 23% of total As) (Hartmann et al. 2003). Reactive oxygen species (ROS) produced by heavy metals like copper, iron, chromium, cadmium, lead, and mercury can lead to oxidative stress, affect calcium homeostasis, and cause damage to DNA (Klaunig et al. 1998). ROS generation has the potential to make fungi poisonous and harm a variety of vital macromolecules, including lipids, proteins, and nucleic acids. Metal/metalloid tolerance in fungi has been linked to their capacity to remove ROS (Fujs et al. 2005). Due to their high thiolate sulfur content, small proteins (between 2 and 7 kDa), such as metallothioneins, can bind metal ions for storage and detoxification in both eukaryotes and prokaryotes. In addition to glutathione (GSH), glutathione disulfide or oxidized glutathione (GSSG), non-protein sulfhydryl groups (NP-SH), and protein-bound sulfhydryl groups (PB-SH), it has been shown that cysteine-rich peptides, such as phytochelatins, and other thiol substances can bind metal ions and scavenge ROS. Additionally, the response of fungi to metal/metalloid exposure or their detoxification is significantly influenced by antioxidant enzymes. Numerous antioxidant enzymes have been found in fungi, and they may neutralize ROS and its byproducts or repair the harm they cause. The ability to shield cells against metal/metalloid-induced stress has been demonstrated for superoxide dismutase (SOD), glutathione peroxidase (POD), glutathione reductase (GR), glutathione S-transferases (GSTs), and catalase (CAT) (Shen et al. 2015). Jiang et al. (2015) demonstrated that the synthesis of NP-SH, GSH, PB-SH, and GSSG, as well as the induction of antioxidant enzymes, greatly altered *Oudemansiella radicata*'s responses to Cu exposure or Cu detoxification.

8.3.3 Enzyme Involved in the Biodegradation of Toxic Compounds

The best tools for bioremediation are enzymes since they hasten all chemical reactions that take place on pollutants. Enzymes frequently have broad enough specificities to work on several substances with structural similarities. Additionally, it is possible to alter enzymes to enhance both their stability and function in specific situations or with particular substrates (Theerachat et al. 2012). For the bioremediation of pollutants, many distinct enzymes, such as mono- or dioxygenases, peroxidases, hydrolases, halogenases, transferases, oxidoreductases, and phosphotriesterases, are derived from a wide variety of microorganisms and plant sources as well. Every time, the soil, in addition to the air and water, is polluted by significant quantities of organic pollutants. These pollutants include pesticides and herbicides, plastics, dyes, medicines, and heavy metals. Most organic substances that need to be cleaned up on a global scale include aromatic molecules, chlorinated hydrocarbons, polymers, polycyclic aromatic hydrocarbons (PAHs), organocyanides, steroids, etc. The primary contributor to their lethality is the sturdy structure they possess. The following is an example of an enzyme that plays an essential role in bioremediation.

Hydrolases (EC3): Hydrolase enzymes such as nitrilases, aminohydrolases, and organophosphorus hydrolases are among the most helpful in the bioremediation of numerous chemicals, including pesticides and herbicides and nitrile, polymers, and organophosphorus compounds. Some other hydrolase enzymes include lipases and cutinases (Ufarté et al. 2015). **Nitrilases (EC 3.5.5.1)** can hydrolyze the triple bonds present between the carbon and nitrogen (known as the nitrile group) in polymers, herbicides, and plastics in a stereo-, regio-, or chemoselective manner, resulting in the production of carboxylic acid and ammonia. Many species, such as *Streptomyces* sp., *Fusarium solani, Rhodococcus rhodochrous, Aspergillus niger*, and others, can express these enzymes (Martinkova et al. 2017). **Organophosphorus hydrolases (EC 3.1.8.2)** are organophosphate chemicals that were produced and utilized not just as pesticides but also in warfare and the pharmaceutical industry. The enzyme known as organophosphorus hydrolase, which also goes by the name phosphotriesterase, is one of the enzymes that may be used for the bioremediation of organophosphorus chemicals. *Aspergillus niger* and *Penicillium lilacinum* are two examples of well-known fungus species that are responsible for the synthesis of this enzyme (Martinkova et al. 2017). **Ligninolytic peroxidases**: White-rot fungus (WRF) and other groups of fungi generate enzymes that break down lignin, and these enzymes have a wide range of uses in bioremediation. Because of the strong nonspecificity and high non-stereoselectivity of these enzymes, they are able to digest a wide variety of molecules that are resistant to degradation. These four varieties include things like laccase (LAC), lignin peroxidase (LiP), manganese peroxidase (MnP), and versatile peroxidase (VP) (Kaur et al. 2016).

Fungi can lower the toxicity of metals and metalloids through their enzymatic activity, which can affect the amounts of these compounds in the environment. The enzyme fungal organomercury lyase is responsible for the conversion of organomercury compounds to Hg(II), which may then be further reduced by mercuric dehydrogenase into the more volatile element Hg(0) (Gadd 1993). After phosphate transporters move As(V) into fungal cells, many common detoxification mechanisms may be engaged, including arsenate reductases reducing it to As(III) and AMF sequestering it (Sharples et al. 2000; Gonzalez-Chavez et al. 2011). *S. cerevisiae*'s resistance is caused by three contiguous genes: ACR1 (a transcriptional regulator), ACR2 (arsenate reductase), and ACR3 (plasma membrane arsenite efflux pump). Fungi may also resist metals and metalloids by methylating inorganic arsenic to form volatile derivatives. An enzymatic process transfers metals like Hg, Sn, and Pb to the methyl group, resulting in molecules with varied solubility, volatility, and toxicity (Barkay and Wagner-Döbler 2005). Trimethylarsine oxide is produced when the nonvolatile monomethylarsonic acid and dimethylarsenic acid are fermented by the microorganisms *Candida humicola* (Cullen and Reimer 1989), *Gliocladium roseum,* and *Penicillium* sp. (Cox and Alexander 1973). Heat-resistant *Neosartorya fischeri* was shown to biovolatalize (up to 23% of total As) (Cernansky et al. 2007) effectively. *Scopulariopsis brevicaulis* (Andrewes et al. 2000) and *Cryptococcus humicola* (McDougall and Blanchette 1996) have both been found to biomethylate As and Sb (Hartmann et al. 2003). Both investigations found that these fungi methylate As and Sb similarly. Iron, copper, cadmium, chromium, lead, and mercury produced reactive oxygen species (ROS), causing oxidative stress, calcium homeostasis changes, and DNA damage (Klaunig et al. 1998). ROS may destroy proteins, nucleic acids, and lipids, making fungus poisonous. Fungi with metal/metalloid tolerance can reduce ROS (Fujs et al. 2005). Metal ions may be stored and detoxified in tiny proteins like metallothioneins (2–7 kDa) in both pro- and eukaryotes because of their high thiolate sulfur content. Phytochelatins, cysteine-rich peptides, and other thiol compounds, including nonprotein sulfhydryl groups (NP-SH), protein-bound SH, GSH, and GSSG, are known to connect metal ions and scavenge reactive oxygen species (Cobbett and Goldsbrough 2002). In addition, antioxidant enzymes contribute significantly to the reactions of fungi to the presence of metals and metalloids, as well as to the detoxification of these substances (Raab et al. 2004). Antioxidant enzymes have been isolated thanks to the work done by fungi. These antioxidant enzymes have the potential to either get rid of reactive oxygen species (ROS) and their derivatives or repair the harm caused by these substances. It has been shown that the enzymes superoxide dismutase (SOD), catalase (CAT), glutathione peroxidase (POD), glutathione reductase (GR), and glutathione *S*-transferases (GSTs) are all capable of protecting cells from the damage that is caused by metals and metalloids (Shen et al. 2015). Jiang et al. (2015) discovered in their research that the production of NP-SH, PB-SH, GSH, and GSSG, as well as the activation of antioxidant enzymes (including SOD, POD, CAT, and GR), played a significant role in *Oudemansiella radicata*'s reactions to copper toxicity or copper detoxification. These enzymes were found to be involved in the production of NP-SH, PB-SH, GSH, and GS.

8.3.4 Bioaugmentation and Biostimulation

8.3.4.1 Bioaugmentation

Autochthonous or allochthonous wild-type or genetically modified microorganisms are applied to contaminated hazardous waste sites through bioaugmentation to speed up the removal of unwanted substances. Oil-contaminated settings are typically the focus of bioaugmentation efforts as bioremediation (Mrozik and Piotrowska-Seget 2010).

Factors Affecting Bioaugmentation

Bioaugmentation relies on microbial consortia adapting to the location to be decontaminated. To succeed, the newly imported microbial consortia must compete with indigenous microbes, predators, and abiotic influences. According to research, it increases the biodegradation of polluted soil by enhancing remediation efficiency. Bioaugmentation is mainly done in soils with fewer pollutant-degrading microorganisms and chemicals that require multi-process treatment. Several more criteria govern soil bioaugmentation. pH, temperature, moisture, organic matter, aeration, and nutrient concentration affect bioaugmentation. Remediation is ineffective if specific soil properties are missing in nature (Yuniati 2018). According to literature, *Burkholderia* sp. FDS-1 degrades nitrophenolic pesticides best at 30 °C and slightly alkaline pH. Catabolic genes and enzymes are responsible for the varied catabolic actions of microbial organisms (Rivelli et al. 2013).

Selection of Microbes

Bioaugmenting microorganisms played different roles in polluted site augmentation in the literature. Soil augmentation uses several microbial strains or consortia. Soil contaminants influence soil quality and soil microbial populations, which perform many vital tasks. Selecting the right microbial strains or consortiums is crucial for successful soil augmentation. Fast growth, easy culturing, high pollutant concentration resistance, and tolerance of a wide variety of environmental conditions are just a few characteristics of microorganisms that must be considered when choosing a strain or microbial consortia. Soil contamination can also be remedied by harvesting beneficial microorganisms from other polluted areas that have been exposed to the same or comparable chemicals and then reintroducing them to the target area (Adams et al. 2020).

8.3.4.2 Biostimulation

Biostimulation is a low-cost and efficient green remediation strategy. Rate-limiting nutrients, including phosphorus, nitrogen, oxygen, and electron donors, are added to highly polluted areas to stimulate the local bacteria into degrading the harmful and toxic pollutants (Elektorowicz 1994).

Mechanism of Stimulation

Hydrocarbon bioremediation is more effective than biostimulation (Adams et al. 2020). Biostimulation is an effective hydrocarbon-degrading technique, notably for petroleum compounds and derivatives. Rate-limiting nutrients increase decontamination and boost microbial degradation capacity. In particular, biostimulation or rate-limiting nutrient input can considerably repair petroleum-contaminated locations with less efficient and metabolically deficient microbial populations. Most of the credit for this goes to the low price of carbon (C), one of the rate-limiting resources needed by native bacteria for metabolic activities involving petroleum contaminants. Thus, adding a few rate-limiting nutrients besides carbon to the soil dramatically increases petroleum breakdown. Besides rate-limiting minerals, additional nutrient-rich organic materials can accelerate restoration. Organic waste from household sewage treatment (biosolids) with nitrogen- and phosphorus-rich inorganic fertilizers accelerates petroleum hydrocarbon breakdown by 96%.

Factors Affecting Stimulation

Environmental factors, including pH, moisture, temperature, and others, affect biostimulation-based contaminated site bioremediation (Abdulsalam et al. 2011). The biostimulation rate is also affected by environmental physiology. In this situation, marine bioremediation might be considered. The marine ecosystem's bioremediation rate could be better because microorganisms cannot target the polymer for destruction since wave motion dilutes or washes it out. There are examples of the harmful impacts of excessive fertilizer input to soil. An increased quantity of N and P sources can promote eutrophication, which increases algae growth and lowers water dissolved oxygen, killing aquatic life (Nikolopoulou and Kalogerakis 2009). Thus, biostimulation's environmental dependence can restrict the method's development or efficiency. By balancing the soil's rate-limiting nutrient additions, biostimulation efficiently removes complex pollutants from the ecosystem (Zawierucha and Malina 2011).

Biostimulation has the potential to remediate several contaminants, including polyester polyurethanes, sulfate, and petroleum hydrocarbons. Sulfate contamination of groundwater is harmful to ecosystems and human health. They are being fixed using biostimulation. Electron-donor alteration can enhance sulfate reduction (Miao et al. 2012). Soil degradation of polyester polyurethanes is hastened by biostimulation. Foams, fibers, textiles, and synthetic leather are just a few of the many applications for polyester polyurethanes (PU), a synthetic polymer (Cosgrove et al. 2010). Like macromolecules in living organisms, these polymers form connections within themselves (such as ester and urethane linkages). The disintegration of microbes is accelerated by intramolecular interactions, which serve as attack sites for the microbes (Zheng et al. 2005). The best strategy for acclimating microbial communities in petroleum-polluted environments is called biostimulation. Consequently, the pace of cleanup was higher in adapted populations than in uncontaminated ones.

8.3.5 Agricultural Effluents and Their Mycoremediation

Modern farming techniques wholly depend on agricultural chemicals, including herbicides, pesticides, weedicides, insecticides, and fertilizers, to increase crop output; this trend has developed throughout the past century (Carvalho 2017). Agrochemicals and residues remain in the environment because agricultural effluents create pollutants. The soil ecosystem's biota, which contains many fungal species, helps biological processes. These activities include mineralization, elemental cycling, biodegradation of organic molecules, and enhanced agricultural production due to the bioavailability of insoluble components. Agrochemicals in excessive quantities can harm the biological processes they were meant to boost. Here is a list of the fungi used in the mycoremediation process in Table 8.2.

8.4 Factors Affecting Mycoremediation

Mycoremediation is intimately linked to several crucial elements. Heavy metal remediation can be affected by pH, temperature, duration, pollutant concentration, and adsorbent dosage. Mycoremediation can be performed by either cultivating fungus or using fungal biomass, although in both circumstances, the most influential parameter is the pH of the solution. Fungal cell viability in the context of mycelial growth, metallic solubility, available active sites (functional groups) on the adsorbent, and interaction like attraction and repulsion between the adsorbent and metal ions due to the hydrogen ion (H^+) isoionic effect all play a role in the removal capacity. Acidic or basic pH reduces HM sorption and fungi growth. Fungi biologically collect metal. Therefore, medium pH impacts clearance rate. Aspergillus is affected at pH 4. It was observed that biosorption was inhibited below pH 3.0 (Pundir et al. 2018). Metal cations repelled positively charged fungal biomass metal-binding active sites or ligands, limiting biosorption. Pundir et al. (2018) found that metal hydroxide formation reduces metal removal above pH 5. Fungi with more outstanding negative charges bind strongly with metal ions at higher pH. Surface functional group separation impacts it (Mohsenzadeh and Shahrokhi

Table 8.2 List of some fungi used for the mycoremediation process

S. no.	Fungi used	Agriculture effluents	Mode of action	References
1	*Trametes versicolor*	Oxytetracycline, imiprothrin, carbofuran, and cypermethrin	Degradation occurs via the respiratory pathway when the enzymes laccase and cytochrome P450 reductase are active	Mir-Tutusaus et al. (2014)
2	*Acremonium* sp. (GFRC-1), *Cladosporium, Cladosporioides*, and *Verticillium* sp.	Chlorpyrifos	In a short time, chlorpyrifos is hydrolyzed, with a km of 6.7974 M and a maximum rate of 2.6473 mol/min	Gao et al. (2012)
3	*Tylospora fibrilosa*	4-Fluorobiphenyl	Both 4-fluorobiphenyl-4-ol and 4-fluorobiphenyl-3′-ol were generated after breakdown and biotransformation.	Green et al. (1999)
4	*Phanerochaete, Chrysosporium,* and *Trametes hirsutus*	Lindane	Tetrachlorocyclohexane and tetrachlorocyclohexanol are produced as a result of lindane degradation within cells	Singh and Kuhad (1999)
5	*Pisolithus tinctorius*	Monofluorophenols	At 1 mM and 3-fluorophenols, the degradation efficiency increased to 92% from 79% at the highest concentration	Franco et al. (2014)
6	*Fusarium moniliforme*, *Aspergillus flavipes*, and *Fusarium roseum*	Atrazine	By co-cultivating fungi, atrazine is bioremediated and mineralized; as a result, deethylatrazine, deisopropylatrazine, and de-ethylisopropylatrazine are all created as intermediates	Sene et al. (2010)
7	*Irpex lacteus* and *Bjerkandera adusta*	PAHs, phenanthrene, pyrene, benzopyrene, and fluoranthene	The breakdown of PAHs involved fungus in a cometabolism process	Mao and Guan (2016)
8	*Mucor racemosus*	Carbonyl furan and 2,3-dihydrobenzofuran	Carboxyfuran phenol is formed when the furanyl ring is hydrolyzed during decomposition	Seo et al. (2007)
9	*Pleurotus* ECS-0190	Chlorothalonil	Several ligninolytic enzymes were detected during the biodegradation, including laccase, phenol oxidase, and MN 10 peroxidase	Camacho and Sánchez (2015)

10	*Aspergillus terreus JAS1*	Chlorpyrifos	Chlorpyrifos can be employed as a carbon and nitrogen source in agricultural chemicals because it has entirely broken down	Silambarasan and Abraham (2012)
11	*A. fumigatus*, *T. harzianum*, and *P. melanoconidium*	Diuron, chlorfenvinphos, and isoproturon	*Cis*- and *trans*-isomers of intermediate molecules were created during the degradation process. Three different compounds are 2-chloro-4-chlorobenzoic acid, 2-chloro-4-chloro-alcohol, and 2-chloro-2-chlorobenzoic acid	Oliveira et al. (2015)
12	DSE; *Alternaria, Alternata,* and *Cochliobolus* sp.	Glyphosate, cypermethrin, and carbendazim	The shape and hydraulic conductivity of the medium change, and the intracellular enzyme activity increases	Spagnoletti and Chiocchio (2020)
13	*Lentinula edodes*	Pendimethalin and diflufenican	To prevent the stability and absorption of genotoxic elements, chlorinated substrates are removed using an aerobic process	Pinto et al. (2016)
14	*Gomphidius viscidus*, *Leccinum scabrum*, and *Boletus edulis*	DDT, endrin, and chlordane	The participation of lignin peroxidase and manganese peroxidase as well as conjugated oxidation-reduction reactions were demonstrated to be crucial steps in the breakdown of the organophosphorus molecule	Bhandari (2017)
15	*Aspergillus flavus* and *Aspergillus sydowii*	Malathion	Cutinase and laccase enzymes were implicated in the biodegradation process, with mercaptosuccinate playing the role of an intermediate	Ramadevi et al. (2012)
16	*Phlebia acanthocystis*, *Phlebia aurea*, and *Phlebia brevispora*	Dieldrin and aldrin	Aldrin and dieldrin's methylene moiety underwent an oxidation–reduction reaction with carboxylic acid esters and hydroxylation	Xiao et al. (2011)
17	*Coriolus versicolor*, *Stereum hirsutum*, and *Hypholoma fasciculare*	Metalaxyl	The ligninolytic peroxidase system and the cytochrome P450 monooxygenase system carried out the detoxification process	Bending et al. (2002)

(continued)

Table 8.2 (continued)

S. no.	Fungi used	Agriculture effluents	Mode of action	References
18	*Ganoderma australe*	Lindane	Approximately 61% of lindane was broken down by ligninolytic enzymes at a rate of 3.11 mg lindane per gram of biomass	Dritsa et al. (2009)
19	*Phanerochaete sordida*	Acetamiprid	The presence of Na^+ ions stimulated the detoxification of 45% of the total insecticide by lignin peroxidase and ligninolytic enzymes	Wang et al. (2012)
20	*P. chrysosporium*	Terbufos	Several enzymes, such as glyoxal oxidase, superoxide dismutase, disaccharide oxidase, and glycerol trinitrate biofilm, were essential for the biodegradation of terbufos	Pointing (2001)
21	*Trichoderma viride* and *T. harzianum*	Vydate	The respiratory system's alcohol dehydrogenase enzyme and continuous gamma radiation both destroy Vydate by 83%	Helal and Abo-El-Seoud (2014)
22	*G. trabeum*	Endosulfan and lindane	With the help of peroxidase and laccase enzymes, degradation proceeded via oxidation, biosorption, and biomineralization	Spina et al. (2018)
23	*Mucor racemosus*	Aldrin and dieldrin	Two ring alterations include the hydroxylation of the epoxide ring and the creation of an intermediate from aldrin-*trans*-7 endophosphate and aldrin-*trans*-diol	Singh (2017)

2014; Rawat et al. 2020). The adsorption of fungal biomass is prevented by pH changes (Li et al. 2018). When the pH of the solution drops, the dead biomass of *Auricularia polytricha, Flammulina velutipes, Pleurotus eryngii*, and *P. ostreatus* binds Cu(II), Zn(II), and Hg(II) at quantities ranging from 5.64 to 77.39%. At pH – 2 (Pourkarim et al. 2017), dead biomass from the artist's bracket fungus is an effective source for Cr(VI) adsorption.

Temperature affects adsorption differently. The fungal (*Penicillium fellutanum*) endothermic process in Ni and Zn removal is from deceased cellulose hybrid with bentonite (FBC) (Rashid et al. 2016). Endothermic or exothermic adsorption reactions occur (Pourkarim et al. 2017). Active fungus clears well at 25–35 °C (Kumar and Dwivedi 2019). Elevated temperatures distort and damage biosorbent surface functional groups (active sites) and affect cell membrane integrity, microbial cell wall configuration, metal microbe complex stability, and ionization characteristics, decreasing metal bioabsorption using fungal biomass. The clearance rate drops with adsorbing species' thermal energy (Pourkarim et al. 2017). A fungal (*Penicillium fellutanum*) mixture of bentonite and decomposing biomass (FBC) eliminates Ni and Zn better at 30–51 °C than at 51 °C (Rashid et al. 2016). Fungal cell wall component reorientation and chemical moiety ionization may explain the active site's high affinity for metal ions at moderate temperatures.

Fungal biomass absorbed heavy metals faster than by mycoremediation (Salvadori et al. 2015). While fungal biomass adsorption takes minutes to hours, growing fungi can remove HM in a matter of hours to days. At 100 min, Cai et al. (2016) noticed that the combination of polyvinyl alcohol (PVA) and sodium alginate (SA) more efficiently removed Cu, Pb, and Cd from immobilized live conidia of *Penicillium janthinellum* strain GXCR. Dried artist's bracket and *Lepiota hystrix* biomass removed Cr, Cu, and Hg(II) in 30 and 5 min, respectively (Pourkarim et al. 2017). Adsorption occurs after pollutant interaction; with the process being functional group dependent, the adsorbent surface's active site is quickly saturated. As a result, pollutant removal will either be constant or reduce because of desorption phenomena (Hajahmadi et al. 2019). Adsorption processes have two phases: an initial quick phase that lasts a short while and an additional slower phase that lasts a long period until equilibrium.

After equilibrium, ions had trouble filling the adsorbent's vacant active sites; hence, increasing time duration lowered the adsorption potential. Periodic intraparticle diffusion may reduce fungal biomass adsorption potential. Gupta and Balomajumder (2015) discussed dual-phase adsorption; the adsorbent's active sites are free to bind metal ions in the first phase. The second phase removes leftover active sites and may reject pollutants and bulk phase. Because they share charges, some of the dissolved solutes may have a repulsion toward the small adsorption inorganic on the adsorbent surface, reducing adsorption and rate of interaction between the active substituent and solute particles following the second phase. Solute concentration directly impacts the adsorption rate. Growing fungus and fungal biomass remediation require it.

In developing fungus, heavy metal concentration initially increases the clearance rate, but it declines after reaching its optimal concentration. The first phenomena may be related to active locations on growing fungus, and increased interaction between HMs and developing cell fungi that encourages maximal clearance. However, time, growth, and metabolic rate regulated metal buildup and promoted metal elimination. However, greater HM concentrations are hazardous to developing fungi, slowing sorption and removal by inhibiting their metabolism and development. Lead enhances fungal biomass, predominantly filamentous, in the culture's beginning and end phases (Samadi et al. 2017). Fungal biomass (dead and treated) affected removal rate similarly to growing fungus, initially increasing HM concentration to saturate the active site and then decreasing after equilibrium. The concentration differential between the fluid and fungal biomass allows metal ions to saturate active sites as the removal rate increases (Zang et al. 2017). Due to increased diffusion, the lower metal concentration gradient decreases transport (Chen et al. 2012). At the point of equilibrium concentration, the removal rate may decrease due to adsorbent inactivity and HM repulsion.

According to Uzunoğlu et al. (2014), *Sargassum acinarum* can remove 100 mg L^{-1} of Cu(II) at its maximum rate (seaweed). While Saravanan et al. (2016) used a mixed biosorbent of custard apple seeds and *A. niger* to remove Cr (VI) and Ni(II), they discovered that the specific removal rate decreases with metal concentration. Zang discovered that *Auricularia auricula* has its maximum adsorption capacity at 200 mg L^{-1} Cr(VI) in effluent. Adsorption tests rely on the amount of fungal adsorbent used. Adsorbent concentrations that are higher enhance HM interaction and active site availability. When mycelial pellets were raised from 2 to 10 g L^{-1}, rates of Cr(VI) ion elimination improved from 20.1 to 88.5%. Biosorbent also increased the number of active sites. In other investigations, the correlation between fungal adsorbent dosage and pollutant removal rate was maintained despite differences in pollutant and adsorbent (Mondal et al. 2017). Figure 8.3 shows the general process of mycoremediation of heavy metals.

8.5 Recent Advancements in Mycoremediation

Humans contaminate the environment by introducing heavy metals, radionuclides, hydrocarbons, and pollutants. The urban and industrial expansion has polluted surface and groundwater, harming persons and the ecosystem (Kour et al. 2021). Thus, the need for environmental ethics pollution-reduction methods is growing. Pesticides and herbicides protect crops from pests and weeds, enhancing productivity and yield. Agriculture has increased pesticide use. These poison ecosystems and are intransigent. Pesticides cause cancer, mutagenesis, immunosuppression, hormone imbalance, and other health problems (Gupta 2004). To use and abuse pesticides as a means of generating power, microorganisms have evolved various enzymes, activation mechanisms, and metabolic pathways (Goel et al. 2008; Kumar et al. 2021). Many different pollutants can be degraded by fungus via two different processes called mycodegradation and mycodeterioration. "Mycoremediation" describes the process of using fungus in nature to break down pollutants and garbage. Fungal species, including *Phanerochaete velutina, Coriolus versicolor,*

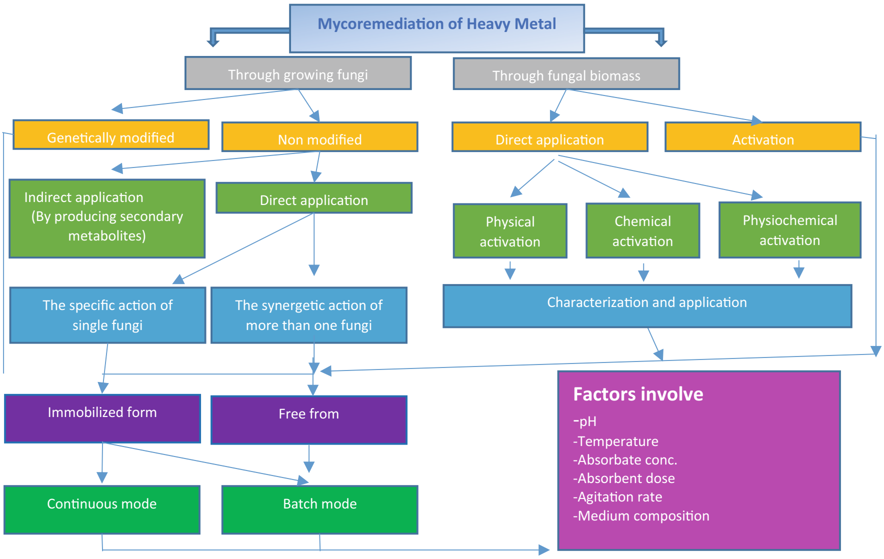

Fig. 8.3 The overall process of mycoremediation of heavy metal

and *Pleurotus ostreatus*, have exhibited the capacity to degrade a variety of herbicides, including atrazine (Castillo et al. 2001). Biodegradation of Granstar (tribenuron methyl) to various metabolites was shown to be most effective when performed by *Aspergillus versicolor* over 5 weeks (Ai-jawhari and Ai-seadi 2016). Exploring endophytic fungus aids heavy metal biosorption. *Penicillium* sp. and *A. niger* have a better biosorption capability in metal contaminant settings by binding metals present in various pollution sources. Polluted environments can absorb heavy metals through biosorption utilizing metabolically driven or physico-chemical adsorption processes. Aromatic hydrocarbons are more environmentally harmful than aliphatic ones. Endophytes help their hosts degrade organic contaminants and reduce phytotoxicity by using relevant degradation pathways and metabolic capacity (Soleimani et al. 2010). Many microbes extract hydrocarbons from air, water, and soil. Biodegradation is slow. Thus, instead of depending on a specific organism, microbes from diverse genera can act together to extend degradation. Petroleum-contaminated soil, water, and surfaces include many microorganisms. Microorganisms may attach heavy metal ions to their cell walls, rendering them immobile. In addition, they may transform certain contaminants into water-soluble molecules and utilize them as food and fuel. Bioremediation is a method that can be used to speed up by the presence of microorganisms that stimulate plant growth or promote decomposition by rhizobia (Kavamura and Esposito 2010). Because of their high biomass content, fungi are helpful in the biodegradation of heavy metal-polluted areas. Because they break down so easily, convert, and cycle nutrients, fungi play a crucial role on Earth. In their groundbreaking research, Wunch et al. (1999) documented for the first time the fungi's ability to degrade anthropogenic chemicals.

8.6 Conclusion and Future Prospectus

It is possible to increase the resistance of metal/metalloid-resistant fungus to environmental toxins using various genetic engineering techniques. Pocsi (2011), using *S. cerevisiae* as a model system, has suggested increasing synthesis of extracellular and intracellular metal chelators as a possible target for genetic modifications, taking off the metal scavengers to slow the metal flow, increasing the production of components of the antioxidative defense system, altering the network of regulators, and interfering with programmed cell death (apoptosis). Scientists have developed fungal strains from the endophytic fungi *Mucor* sp. CBRF59 by fusing protoplasts (Deng et al. 2013). Rape plants were injected with the mutant strain CBRF59T3 to increase the stress tolerance of an unidentified fungus utilized in heavy metal-polluted soil phytoremediation. Rape sprouts cultivated on Cd(II)- and Pb(II)-contaminated soils had 35–189% higher Cd(II) levels (Deng et al. 2013). Qiu et al. (2015) discovered that a modified BY-G strain was more resistant to oxidative stress, heat, furfural, hydroxymethylfurfural, and Cd than a reference strain of *S. cerevisiae* (II). Public opinion on bioremediation using GM microorganisms is crucial. Using genetically modified fungus to treat metals and metalloids seems promising. The intricacy of the toxic effects of metals and metalloids on cells has long escaped comprehension. Still, sequence information on their genomes has enabled postgenomic techniques to gain abundant data on the roles of their genes and the mechanisms that regulate them. Immobilization of metals by their reduction has uses in bioremediation and in creating new biomaterials and catalysts (Gadd et al. 2012). Subtracting heavy metals from wastewater and soils using a biosorption-based biosynthesis of nanoparticles can also help in the production of heavy metal nanoparticles that may be used in the technology industry (Karman et al. 2015). One innovative strategy for creating metal nanoparticles (NPs) involves using the highly organized physical and metabolic activity of microbial cells (Gericke and Pinches 2006). Compared to other microorganisms, fungi are preferable for synthesizing NPs due to their manageability, simplicity of food requirements, strong cell wall-binding capability, and high intracellular metal absorption capabilities (Sanghi and Verma 2009). Several research has examined whether fungus can detoxify polluted surroundings by producing nanomaterials and removing harmful metals. Velmurugan et al. (2010) found that *Fusarium* sp. from a South Korean zinc-contaminated mine could absorb up to 320 mg L^{-1} and produce ZnO NPs. In an aqueous solution, *Hypocrea lixii* dead biomass may produce CuO and NiO NPs by reducing Cu and Ni ions (Marcia Regina Salvadori et al. 2015). *Rhodotorula mucilaginosa* and *Trichoderma koningiopsis* biosynthesize Cu NPs (Salvadori et al. 2014). Nanoparticles improve fungal bioremediation. It was found that adding 1 mg L^{-1} Ag-NPs to *Phanerochaete chrysosporium* increased its Cd(II) removal by tenfold (Zuo et al. 2015). When used to remove Cd and break down

2,4-dichlorophenol, *P. chrysosporium* immobilized on TiO_2 nanoparticles (PTNs) is a one-of-a-kind, high-value bioremediation material due to their antioxidative defense mechanism and physiological fluxes (Tan et al. 2015). Suspiciously, fungi can efficiently remove NPs from aqueous mediums. It was found that *Pleurotus eryngii* and *Trametes versicolor* can remove 86% and 61% of Al_2O_3 NPs, respectively. Although less effective against Co NPs, *P. eryngii* can eliminate 58% of Pt NPs (Jakubiak et al. 2014).

Tripathi et al. (2013) proposed many essential sustainability metrics as a means to evaluate the potential for the durable success of corrected systems. The decrease in pollutant levels and residual concentrations after the remediation are major factors illustrating the enhancement of soil physicochemical qualities, the growth of microbial biomass, the diversity of their functions in soil, and the improvement in the biodiversity component, which includes sensitive and key species. The traditional physicochemical techniques, including evaporation, electrochemical treatment, membrane technology, filtration, ion exchange, reverse osmosis, chemical precipitation, oxidation, and reduction, are desirable and potential substitutes. This is true notwithstanding the difficulties involved in applying molecular methods to increase the likelihood of remediation. Because it is capable of meeting a number of the aforementioned characteristics, fungal bioremediation is an alternative that is both successful and durable in terms of removing heavy metals and metalloids from polluted areas. The metal-resistant fungus has arisen as a possible solution to the pollution from metals and metalloids in light of recent developments in nanotechnology and our growing understanding of the life cycles of nanoparticles.

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Bio-removal of Analgesics and Antibiotics by Soil Worm

9

Ramzan Ahmed, Jayabrata Saha, Kaustuvmoni Patowary, and Shiela Chetri

Contents

Abstract

The consequences of pharmaceuticals in the environment are still uncharted. Earthworms and soil insects have a positive significant role in the improvement of soil health and organic matter contents. They are an important part of most ecosystems particularly soil fauna, which makes a significant portion of macrofauna biomass. Because of the high rate of antibiotic and analgesic consumption in animal husbandry as well as human medicine, it has become a worldwide menace which induces antibiotic resistance in bacteria and causes toxicological damage to organisms as well as environment. Earthworm plays a major role in reducing the toxicity of the soil as well as degradation of analgesics and antibiotics. The chapter highlights the degradation of analgesics and antibiotics by soil worm.

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Keywords

Analgesics · Antibiotics · Soil biotransformation · Biodegradation · Soil worm

9.1 Introduction

Antibiotics are powerful, bioactive chemicals that are employed to treat bacterial infections. Following ingestion, these compounds are eventually excreted and reach the soil and environment, increasing the residual concentrations in soils, which can vary from a few μg to g kg^{-1} and are comparable to those found in soil that has been poisoned by pesticides. Many antibiotic compounds combine polar functional molecules with nonpolar cores. Amphiphilic or amphoteric properties are common in antibiotics. However, molecules from different structural classes exhibit an extensive variety of physicochemical properties (Thiele-Bruhn 2003). Ibuprofen and monocyclic paracetamol, which are frequently used to treat mild-to-moderate pain, are two examples of analgesics and nonsteroidal anti-inflammatory medications (NSAIDs), which are currently regarded as one of the most developing groups of xenobiotics. Degradation of such pollutants has grown to be a significant issue due to the improved understanding of the long-term negative consequences of these xenobiotics as well as their biological and pharmacokinetic activities, particularly at environmentally significant concentrations. Additionally, traditional wastewater treatment plants (WWTPs) are still not completely capable of removing these specific types of micropollutants (Żur et al. 2018). Earthworms are macroinvertebrate oligochaete worms that live in dirt and are reddish to dark brown, tubular, and segmented. As they dig their holes, these worms increase the soil's nutrition and efficiency; they are known as "farmer's friends" (Bhorgin and Uma 2014). The addition of substantial amounts of organic and inorganic matter in the form of nitrogenous waste by worm casting and air and water penetration through holes both contribute to improved soil fertility (Katsvairo et al. 2007). Antibiotics are degraded and rendered inactive more efficiently as a result of biotransformation. However, some metabolites retain antibiotic activity, and attachment to the soil matrix prevents the degradation of these antibiotics. Although all antibiotics are extremely bioactive, their effects on soil organisms are significantly distinct. Pharmaceutical residues from antibiotics have the potential to cause resistance to diseases in either a direct or an indirect way through the transmission of plasmids from nonpathogenic to pathogenic microbes (Wegener et al. 1998). Antibiotics in soil may be degraded by microbes in addition to being degraded by abiotic processes. It has been found that specific bacteria that break down pharmaceuticals exist in soils that have been contaminated with antibiotics, for instance, in liquid cultures, strains from the genera *Microbacterium* (Topp et al. 2013), *Stenotrophomonas* (Leng et al. 2016), *Burkholderia* (Zhang and Dick 2014), *Labrys* (Mulla et al. 2018), *Escherichia* (Wen et al. 2018; Mulla et al. 2018), and *Ochrobactrum* (Mulla et al. 2018; Zhang et al. 2017). Other bacteria associated with the genera *Microbacterium* (Kim et al. 2011), *Klebsiella* (Xin et al. 2012), *Labrys*

(Amorim et al. 2014), *Acinetobacter*, *Escherichia* (Zhang et al. 2012), and *Bacillus* (Erickson et al. 2014), which are able to begin degrading sulfapyridine, chloramphenicol, ciprofloxacin, sulfamethazine, ceftiofur, and norfloxacin, have been isolated from sediments, seawater, sludge, patients, animal, and feces. In particular, *Microbacterium* sp. demonstrated sulfamethazine breakdown in soil and sped up the process of minerals forming from that antibiotic by 44–57% when added to agricultural soil (Hirth et al. 2016).

9.2 Pharmaceutical Sources in the Environment

Pharmaceuticals and over-the-counter (OTC) medications have been found in trace amounts in the environment, with concentrations less than one part per billion (i.e., 1 $\mu g\ L^{-1}$). The active pharmaceutical ingredients (APIs) that are released into the environment might do so via three basic routes. Because of regular patient and consumer usage and excretion into sewage and wastewater treatment systems, the great majority of APIs are found in water systems. The inappropriate flushing or pouring of unnecessary or expired medications through drains by consumers is a second route for their inadvertent disposal. The third route uses wastewater that has been released from API manufacturing facilities. They ultimately enter the environment through several additional smaller channels, including landfill leachate and hospital discharges (Caldwell 2016).

9.3 Ecological Toxicological Effect of Analgesics

Any natural or artificial substance that reduces pain (produces analgesia) without leading to unconsciousness, paralysis, or other severe impairments of sensory function or nerve impulse conduction is an analgesic, also referred to as a painkiller. It differs from anesthetics, which result in anesthesia, or the remission of pain by inducing unconsciousness. The Greek words an- (“without”) and -algia (“pain”) are the origins of the word analgesic. Analgesia describes the lack of pain perception when a person is still conscious. Currently used analgesic medications are either narcotics or non-narcotics with known harmful and adverse effects (Table 9.1). Concern over environmental pollution has grown in recent years as a result of mixed contaminants that have been released into the environment as a result of greater living standards. The removal of toxins from a location is necessary, but is frequently impractical due to technological, environmental, geographical, social, or financial limitations.

With the progress of medicine in recent years, the demand and supply of medicinal products have both quickly expanded. About 3000 chemicals are needed to make medications, and hundreds of tons are produced annually (Carvalho and Santos 2016; Grenni et al. 2018). The most widely used drugs in the world are analgesics, antibiotics, and anti-inflammatory medications. As a result, the advancement of water-soluble and pharmacologically active organic micropollutants, also known

Table 9.1 The effects of drugs on the environment and humans

Analgesics	Effects	References
Acetaminophen	Cardiovascular abnormalities, hatch and motor behavior, and interruption of oocyte maturation/ovulation in *Danio rerio*	David and Pancharatna (2009), Lister and Van Der Kraak (2009) and Xia et al. (2017)
Ibuprofen	Inhibits CYP2M in *Cyprinus carpio*	Thibaut et al. (2006)
Diclofenac	Population declines of *Gyps* vultures	Cuthbert et al. (2007)
Ketoprofen	Inhibits CYP2M in *Cyprinus carpio*	Thibaut et al. (2006)
Diclofenac	Prostate gland synthesis and damage to the gills, liver, and kidneys of *Salmo trutta f. fario*	Hoeger et al. (2005)
Naproxen	*Pisum sativum*	Svobodníková et al. (2020)
Diclofenac	Histological alterations of the kidneys and gills; cytological alterations of the liver, kidneys, and gills; and deterioration of ionic regulation in *Oncorhynchus mykiss*	Schwaiger et al. (2004), Triebskorn et al. (2004) and Gravel et al. (2009)
Naproxen	Inhibits CYP2M in *Cyprinus carpio*	Thibaut et al. (2006)
Diclofenac	Inhibits CYP2M in *Cyprinus carpio*	Thibaut et al. (2006)
Ibuprofen	Change breeding pattern of *Oryzias latipes*	Flippin et al. (2007)
Carbamazepine	Inhibition of basal EROD activity in cultures of rainbow trout hepatocytes Inhibition of emergence of *Chironomus riparius*	Laville et al. (2004) and Nentwig et al. (2004)
Diclofenac	Alteration of estrogenic activity, response of specific tissue biomarkers, decreased superoxide dismutase and glutathione reductase activities in gills, and high catalase activity and levels of lipid peroxidation in the digestive gland in *Mytilus galloprovincialis*	Gonzalez-Rey and Bebianno (2014)
Diclofenac	Inhibition of basal EROD activity in cultures of rainbow trout hepatocytes	Laville et al. (2004)
Ibuprofen	Reduces the shoot and root lengths, fresh and dry weights, leaf area, chlorophyll a and b, carotenoid, total chlorophyll, mineral (K and Mg), glutathione reductase, and soluble protein contents of *Vigna unguiculata*	Wijaya et al. (2020)

as pharmaceutical active ingredient, has gained considerable attention globally, in contrary of being used extensively as veterinary medicine in farms worldwide to prevent and treat animal diseases so as to boost economic benefits in intensive livestock, as a variety of these pharmaceuticals are used regularly by humans for their health (Blanco et al. 2017; Ekpeghere et al. 2017; Gros et al. 2019; Ramírez-Morales et al. 2021).

The pharmaceutical's/toxicant's contact with the receptors causes functional and anatomical alterations in the organism that lead to fatal or nonlethal consequences (Vischetti et al. 2020). A few parameters, including bioavailability, toxicokinetics, biological transformation, and toxicodynamics, must be taken into account for a toxicant to have a significant impact. Pharmaceuticals are excreted from the body after ingestion as active components or metabolites in the urine and feces (Sui et al. 2015; aus der Beek et al. 2016). However, due to effluent leach-outs produced during discharge conditions, these medicines can also be traced in water bodies, including freshwater, marine settings, as well as groundwater (Furlong et al. 2017; Ojemaye and Petrik 2018; Reis-Santos et al. 2018; Fekadu et al. 2019; Letsinger et al. 2019; Zainab et al. 2020). The fundamental issue is that some of these emerging contaminants (ECs) cannot be completely eliminated out by traditional treatment plants. The tremendous increase in pharmaceutical usage globally and the resulting environmental effects, especially their hindrance in aquatic and terrestrial ecosystems, make the study of medicines extremely important. Pharmaceutical compounds are regarded as ECs in the settings of wastewater and bioremediation due to the lack of regulations for their environmental disposal and the lack of knowledge on their long-term impacts on the environment (Dhangar and Kumar 2020; Valdez-Carrillo et al. 2020; Chaturvedi et al. 2021; Rathi et al. 2021), which are yet unclear (Ahmed et al. 2017). This rising issue has been aggravated as some medications are counter sold without a prescription, which has created havoc environmentally (Gil et al. 2017).

Anthropogenic activities are the main source of the majority of new contaminants, most of which find their way into the environment. All potential emerging contaminants are put through a variety of degradation procedures prior to discharge into the environment in order to be eliminated (Khan et al. 2020). The population of xenobiotic organisms and the production of new contaminants can both be decreased by the degradation of specific synthetic compounds. The environment (soil, groundwater, drinking water, surface water, wastewater, treatment plants, or sediments) in which they are present will try to shift into a transformation product when other chemicals and emerging pollutants are stressed by biological processes (Biswas et al. 2022; K'oreje et al. 2021). When compared to their parent chemical, these altered products show increased persistence and considerable increased toxicity. When they transform, they could also acquire new characteristics. The process of biotic or abiotic transformation is followed by this chemical transition. By making the compounds more polar, the biotic process transforms the molecules (Reymann et al. 2020).

9.4 Ecological Toxicological Effect of Antibiotics

Pharmaceuticals play a vivacious role in the maintenance of human health along with the quality of life, and the extensive utilization of these compounds as a treatment option against various human and animal diseases for the last 20 years has already been reported as microcontaminants of water and soil ecosystems

(Boxall 2004; Carvalho and Santos 2016). Antibiotics are among the most imperative and lifesaving discoveries of the past era prominently contributing to the treatment of life-threatening bacterial infections and have changed our traditional way of treatment significantly. Among various pharmaceutical products available commercially, antibiotics have caught extreme attention because of (1) their availability in huge concentration in soil and water ecosystems and (2) the emergence of multidrug resistance in bacteria which has posed severe health concern in humans and animals (Thiele-Bruhn 2003; Kümmerer 2009; Pawlowski et al. 2016). In addition, gradually as a consequence of irrational or overuse of different varieties of antibiotics against various bacterial infections and in livestock production, the rapid emergence of antimicrobial residues in the environment has grown into a global concern (Ben et al. 2019).

Antimicrobial is a vast term, which refers to a compound having the ability to fight against a variety of microorganisms including bacteria, viruses, fungi, protozoa, etc. Among antimicrobials, antibiotics are the one capable of fighting definitely against bacterial infections in animals and human host, which separates them from other antimicrobials or from disinfectants available (Brandt et al. 2015). There are few antibiotics known for their anticancer activities such as mitosanes, enediynes, bleomycin, actinomycin D, anthracyclines, anthracenones, and epothilones or as pesticides like streptomycin (Demain and Sanchez 2009; Cars et al. 2001). Antibiotics available commercially are either natural, synthetic, or semisynthetic and are derived from bacteria and fungi, which helps in inhibiting or killing other opponent microorganisms with bactericidal or bacteriostatic activity. Semisynthetic antibiotics are actually natural chemicals with an alteration by introducing an additive in their formulation, which helps in increasing its effectiveness, thus making it extra stable and less biodegradable. There are different classes of antibiotics based on their chemical structure and different groups attached, and they are classified on the basis of their mode of actions like cell wall inhibitors, protein synthesis inhibitors, inhibitors of nucleic acids, and metabolic pathway inhibitors (Kümmerer 2009).

Antibiotics upon administration inside the body get partly metabolized followed by excretion of a large amount of unaltered antibiotics or active metabolites through feces or urine (European Centre for Disease Prevention and Control (ECDC), European Food Safety Authority (EFSA), and European Medicines Agency (EMA) 2017; Kemper 2008), which consequently reaches the sewage treatment plant (Louvet et al. 2010). As per the previous literature available, 70% of the consumed antibiotics are excreted via urine and feces because of their poor metabolism and absorption within human or animal body (Jutkina et al. 2018). An efficient removal of antibiotics and antibiotic-resistant genes (ARGs) from sludge or sewage waste treatment facility is not possible because of the utilization of our poor traditional method, which allows their entry into the natural environment (Berendonk et al. 2015; Cacace et al. 2019). Frequently, antibiotics and ARGs are observed in groundwater, surface water, and water supply systems, as water acts as an essential sink of antibiotic and pollution of resistance gene and their presence in the system is the greatest threat for both human health and the ecosystem (Table 9.2)

Table 9.2 The effects of antibiotics on the environment and humans

Antibiotics	Effects	References
Antibiotics	Algae and aquatic plants are severely affected	Brain et al. (2008) and Brausch et al. (2012)
Antibiotics	Block the electron chain of photosystem II and increase oxidative stress (photosynthesis inhibitors)	Nie et al. (2013)
Antibiotics	Bacteria seem to be developing resistance to antibacterial substances due to exposure to low concentrations over several generations	Kollef et al. (2017), Willyard (2017), García et al. (2020) and Wang et al. (2020b)
Antibiotics	Crustaceans such as *Artemia salina*, *Daphnia magna*, and *Ceriodaphnia dubia* show relatively low acute toxicity	Wollenberger et al. (2000), Kołodziejska et al. (2013) and Minguez et al. (2016)
Antibiotics	Invertebrates such as *Hydra attenuata* and crustaceans such as *Artemia salina*, *Daphnia magna*, and *Ceriodaphnia dubia* show relatively low acute toxicity in the presence of antibiotics	Wollenberger et al. (2000), Kołodziejska et al. (2013) and Minguez et al. 2016
Tetracyclines, macrolides, and streptomycin	Antibacterial resistance measured in soil bacteria obtained from sites treated with pig slurry	Sengelov et al. (2003)
Tylosin	Impacts on the structure of soil microbial communities	Westergaard et al. (2001)
Erythromycin	Inhibition of growth cyanobacteria and aquatic plants	Pomati et al. (2004)
Tetracycline	Inhibition of growth cyanobacteria and aquatic plants	Pomati et al. (2004)
Sulfamethoxazole	Inhibition of basal EROD activity in cultures of rainbow trout hepatocytes	Laville et al. (2004)

(Ma et al. 2017; Wang et al. 2020a; Zhang et al. 2022). Moreover, evidences regarding circulation of antibiotics and antibiotic-resistant genes in the environment, understanding on different pathways of pollution, various risks related to human health and the environment, and mechanisms of degradation and elimination of antibiotics and ARGs have always evoked a challenge for research in this area because of the intricacy of the natural and artificial systems, which makes the situation even more critical.

Human healthcare practices depend on antibiotic efficacy in treating and preventing bacterial infections (Livermore 2009). In addition, bacteria are evolving various mechanisms to combat these drugs (developing antibiotic resistance), which can increase the morbidity and mortality rate of bacterial infections by reducing their effectiveness (O’Neill 2014). The term antimicrobial resistance (AMR) refers to resistance capability developed in microorganisms, which may be bacterial, viral, fungal, or parasitic towards all the chemicals with antimicrobial action. However, now the terms antimicrobials and antibiotics are frequently used synonymously in the existing literature. Over the past years, the consequence of AMR, particularly antibiotic resistance, has accomplished AMR to be placed along with the topmost global issues like pandemic influenza, terrorism, and climate change on the UK Risk Register (UK Cabinet Office 2015; Cabinet Office 2017). It has been opined by the World Health Organization (WHO) that in a post-antibiotic era, common infections and minor injuries can kill, far from being an apocalyptic fantasy, which instead has real possibility for the twenty-first century (World Health Organization 2014).

The increasing prevalence of the drug-resistant infection globally (Livermore 2009; Finley et al. 2013; Wellington et al. 2013) has already triggered the irrational use of frequently used commercially available antibiotics and further compelled us to rely on the usage of costlier last-resort antibiotics as treatment options, which has ultimately resulted into the development of multidrug-resistant variety (e.g., colistin resistance) (Nhu et al. 2016). Development of a novel antibiotic is really a tedious effort, which involves huge investments by the pharmaceutical industries to improve a product having the potential of a small profit and limited life span before resistance develops (O'Neill 2015). If we consider the updates of the past three decades, cyclic lipopeptides and oxazolidinones were the only novel antimicrobials available commercially (Gupta and Nayak 2014), and if similar pattern continues, then it will become definitely really hard to treat the common infections which are easy to treat at present and ultimately will lead us towards pre-antimicrobial era. Furthermore, the consequence of the situation will be inability to treat and prevent any bacterial infection from common to severe, and it will gradually elevate the risk of acute morbidity and mortality linked with repetitive medical processes (O'Dowd 2018). According to a report expressly prepared by the UK Government in 2014, it is expected that by 2050, antimicrobial resistance will be the chief source of death worldwide with an increase in the death rate from 700,000 in 2014 to ten million. Additionally, as a consequence of AMR on the entire economy, a loss of up to 100 trillion USD of world's GDP has been predicted by 2050 according to this report (O'Dowd 2018). Furthermore, it is assessed that NHS has already expended £180 million each year on AMR management (O'Dowd 2018). In 2017, a frontier report published by the UN Environment Programme registered AMR as the most severe environmental pollution concern worldwide (Gaze and Depledge 2017).

The release of excreted antimicrobials into the environment via anthropogenetic sources has highly influenced the competency of microorganism to evolve and develop novel defense mechanisms. According to the previous literature available, these unique resistance mechanisms were found to be mobile genetic elements mediated and are capable of facilitating the propagation of resistance components among microbial communities (Holmes et al. 2016). Antimicrobials even after excretion (can occur via both urine and feces) from animals and humans remain in active form as high as 90% (Levison and Levison 2009). As a result of the waste ejection via accomplished sewage water discharges and agricultural effluence into the environment (Singer et al. 2016), detection of antibiotic-resistant bacteria from the polluted environment has become very frequent along with a quantifiable concentration of antibiotics ranging from ng L^{-1} to μg L^{-1} (Andersson and Hughes

2012). According to the previous reports available, even the lowest concentrations of antibiotics are capable of generating a selective pressure environment for ARB/ARGs (Gullberg et al. 2011, 2014; Murray et al. 2018, 2020, 2021, Lundström et al. 2016; Kraupner et al. 2018, 2020, Stanton et al. 2020).

As we know that antibiotics are a major pollutant of the environment which cannot be degraded via physical adsorption, photodegradation is a very costly approach, while the chemical oxidation may lead to secondary pollution. However, biodegradation of antibiotics is gathering more attention due to several advantages like being less expensive and easy to operate, with no risk of secondary pollution. Despite degradation by microbes and by activated sludge procedure, in both the cases, the dissemination of ARGs will definitely arise. Hence, the utilization of antibiotic-degrading enzymes after purification for antibiotic degradation is a noble approach, and constructing genetically engineered bacteria with useful features (like degrading enzyme-producing capability) or in vitro synthesis of associated enzymes will help in reducing the cost of our approach and will make it far more attractive. However, the problem regarding the toxicity profile of the antibiotic degradation product is the biggest concern of the hour. As health care and regulatory system differs in different countries, the changes to improve the system should be initiated with the local practices followed by their global implementation (Kuppusamy et al. 2018). Different parameters like usage of antibiotics, their availability, quality, and manufacture need to be organized in underdeveloped and developing countries, and additionally, the regulation of interventions associated with hospitals and antibiotic practice in animals (food producing) should be given the supreme priority (Chokshi et al. 2019).

9.5 Antibiotic Effects on Earthworms in Their Natural Habitat

Earthworms are the recognized predominant members of soil microfauna, which affects microbial communities of soil along with the biological processes by altering soil properties and structures (Babu Ojha and Devkota 2014) and accessibility and cycling of nutrients (Orozco et al. 1996), and further, it has been proposed that the gut of earthworm plays a vital role in influencing the microbial composition (Medina-Sauza et al. 2019) and function (Zhu et al. 2021) in soil. As already reported, the soil moisture, bacterial populations, and organic matter can be significantly improved by earthworm activities (Kim et al. 2017), and additionally it affects bacterial driven biochemical processes as well (Araujo et al. 2004; Chapuis-Lardy et al. 2010). However, few studies have demonstrated a diverse reaction upon changed soil conditions because of different cell structure, community structures, physiological traits, and interaction between divergent species when the effect of earthworms on fungi present in the soil was explored and compared with bacteria (James et al. 1995; Koide et al. 2005; Kooijman et al. 2016). Studies investigating the single properties of the microbial communities such as α-diversity and β-diversity as well as linkage among microbial taxa (for example, co-occurrence patterns) help in establishing the niche stability (Chaffron et al. 2010) and the role of microbes in several ecosystems (Ruan et al. 2006). Further, to determine the co-occurrence patterns in microbes belonging to the most complex and wide-ranging communities, network analysis has been efficaciously employed and enabling a comprehensive analysis of microbial communities within numerous samples (Banerjee et al. 2016; Qiu et al. 2021) due to the advancement in high-throughput sequencing technology. Additionally, network analysis provides a new vision to understand the structure of microbial communities (de Vries et al. 2018) and, simultaneously, may help us to recognize the complexity within microbiomes (Banerjee et al. 2019) and the association between microbes and ecosystem functioning (Qiu et al. 2021). By assessing network typology parameters, co-occurrence networks can be analyzed for their complexity and connectivity within microbial species and lineages. As reported in previous literature, earthworms play an imperative role in changing soil microbial communities and biogeochemical cycles (Araujo et al. 2004; Kim et al. 2017). However, whether earthworms change the soil microbial interactions, as indicated by network connectivity upon addition of earthworms, is still not clearly understood. Network connectivity might be implicated in the composition of the microbiome, which is particularly important (Wagg et al. 2019).

It is an established fact that antibiotic resistance genes (ARGs) are emerging as microbial contaminants of various ecosystems like water, animal gut (Chen et al. 2013; Zheng et al. 2018; Ding et al. 2019), soil, and activity sludge (Su et al. 2017; Zhu et al. 2021), which can have harmful effects on humans and animals, as they have been noticed in soil, water, activity sludge, and animal guts. It was demonstrated by Zhu and co-workers in 2021 that earthworms play an important role in decreasing risks linked with antibiotic-resistant genes (ARGs) in soils. Additionally, it is indicated that the earthworm gut facilitates reduction of bacterial hosts and mobile genetic elements (MGEs) and further contributes towards reduction of ARGs in soils of varied ecosystems (Zhu et al. 2021). Furthermore, microcosm studies and field experiments showed that earthworms have the capability to change bacterial communities and decrease the number and ARG abundance in soils. ARG patterns can be altered and disseminated across microbes (Gaze et al. 2011) in diverse ecosystems, facilitated by horizontal gene transfer (HGT), affluence of microbes, and community arrangement mediated by MGEs (Pallares-Vega et al. 2019; Rodriguez-Mozaz et al. 2015). Tang and colleagues in 2020 found that MGEs function as a major limitation for the ARG removal from an industrial scale composting system (Tang et al. 2020), as these MGEs work as an efficient vehicle for carrying ARGs and often positively associate with ARGs (McCann et al. 2019; Yan et al. 2019). Moreover, as a result of interactions between microbes, microbial abundance would be affected, changing the composition of the microbiome (Qiu et al. 2021). In a particular ecosystem, bacteria can discharge antibiotics which either inhibit or kill other microbes that are not resistant to antibiotics. Alternatively, the transfer of genes (e.g., ARGs) between bacterial cells is facilitated by microbial interactions (e.g., direct contact between bacteria) (Koonin et al. 2001). Consequently, ARG abundance may be altered as a result of the interactions between microbes affecting microbiota communities and horizontal gene transfer (HGT) between them. As already reported, the transfer of antibiotic-resistant genes among diverse microbes requires the involvement of mobile genetic elements (MGEs) (Chen et al. 2016; Zhu et al. 2017), and comparative studies of earthworm soil with normal soil (considered as control) after incubation of 30 days to analyze absolute abundance and lower relative abundance were done (Li et al. 2022).

Evidences suggest that the reduction of MGEs due to the presence of earthworms in the soil can potentially be able to reduce the transmission of ARGs within microbes. Further, one of the potential reasons for this significant alteration in the shifts of MGEs upon addition of earthworms might be variations in bacterial communities. Additionally, previous studies indicated towards a strong positive correlation establishment in various ecosystems between MGEs and bacteria (Han et al. 2018; Liu et al. 2020) and suggested the role of earthworm in altering bacterial communities in the soil, ultimately decreasing the ARG and MGE array (Zhu et al. 2021). Besides bacterial community, microbial interactions can also affect the function of the ecosystem (de Menezes et al. 2017; Wagg et al. 2019), and according to a study, the decrease in the microbial interaction between different bacteria might have a role in the decrease of MGE abundance in soil comprising earthworms. In a similar study, MGE abundance and Zi (within-module connectivity) showed a substantial and positive association, which suggests that bacterial interaction which is facilitated by earthworms would affect the MGE abundance in soil (Li et al. 2022). The bacterial conjugation frequency through plasmid or transposable elements (TEs) that carry genetic material via direct cell-to-cell contact (Sheth et al. 2016) may be decreased as a result of reduced bacterial connectivity, an imperative process of horizontal gene transfer (Heß et al. 2018). From various studies, it has been observed that for the shifting of ARGs within the microbiota of earthworms, multiple major factors are involved such as mobile genetic elements (MGEs), microbial communities, and soil properties. Therefore, it is of great importance to explore different sources and factors controlling the destiny of ARGs in the gut microbiota of our friend earthworm.

9.6 Conclusion

Earthworms are well known for their contribution to ecological processes such as soil structure, nitrogen cycling, and plant growth. There is evidence that earthworms shape soil microbial communities, either directly through their eating or indirectly through a priming effect brought on by an increase in the amount of labile chemicals available. According to studies, earthworms might encourage the removal of analgesics and antibiotics and reduce the prevalence of antibiotic resistance genes in the microbial community. This suggests that the earthworm stomach is the focal point for analgesic-antibiotic removal in analgesic-antibiotic-amended soil. The abundance of antibiotic resistance genes in the microbial community decreased as a result of lower analgesic-antibiotic concentrations and a change in the structure of the microbial community. These chapters emphasize the possible contributions of earthworms to the removal of analgesics and antibiotics as well as to further reducing the emergence of analgesic-antibiotic resistance in contaminated soil.

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Vermiremediation of Pesticides

10

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Aparajita Bagchi, and Muskan Nama

Contents

Abstract

Due to the advent of rapid urbanization and the introduction of modern techniques into the farming sector, nature witnessed the greener lands getting burdened by the chemicals day by day. Rampant usage of the pesticides has led to a major menace to the ecosystem and mankind. Organochlorine pesticides such as DDT, dicofol, and organophosphorus pesticides like malathion and parathion have been related to health concerns and environmental hazards and have polluted agricultural lands throughout the world. To bioremediate contaminated soil, an economically feasible and sustainable technology has been employed, time and again. Vermiremediation is one such technique and is a sustainable

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developing technology that involves the utilization of earthworms to eliminate the toxins from the contaminated soil. Earthworms have the potential to either absorb the chemicals present in the soil through their body wall or release poison to lower the concentration of pesticides. Earthworms are capable of either biotransformation or degradation of the pesticides leaving them innocuous in their bodies. Earthworm helps in the conditioning of the soil through biodegradation, biotransformation, and physical action. As a result, the contaminated soil gets converted into an environmentally friendly usable form. Thus, the chapter deliberates the strategic management of vermiremediation to remediate the pesticide-intoxicated soil and to restore its normal physiological ecology and functioning.

Keywords

Pesticides · Bioremediation · Vermiremediation · Biodegradation · Bioaugmentation

10.1 Introduction

With increasing colonization, the undeniable need for food supply has increased. Pertaining to the agriculture sector worldwide each year, tonnes of pesticides are used to scale up production. However, it has been predicted that up to 3.5 million tonnes of pesticides will be used globally by the year 2020. A pesticide is any substance that is used for destroying, preventing, repelling and mitigating any inflicting pest (Zhang et al. 2007). The major outcome of utilizing pesticides is that it affects the environment very ghastly. The prime elements in the negative impact of current industrial agriculture on nature are the fortuitous outcomes of the pesticides (Shi et al. 2020). By means of runoff and pesticide flow, the agricultural fields, zone of grazing, human habitation, primitive regions, and remote habitats of aquatic lives can be acquired by pesticides. Inferior methods for storing, conveying, as well as discarding pesticides also result in other problems (Gupta and Garg 2008). Repeated pesticide use builds up pest resistance over time, and its effects on other species may contribute to the pest's reappearance. Sustainable agriculture practices like polyculture and integrated pest control, which use fewer pesticides, lessen these effects without using toxic chemicals that are hazardous to humans and the environment (Shi et al. 2020). Numerous industrial and agricultural operations result in a steady release of chemicals into the environment. Without a question, the use of agrochemicals in modern agriculture has increased the output, which is crucial for fulfilling the demands of the expanding population and guaranteeing the safety and security of food (Fawole et al. 2020). However, this has also had a large detrimental influence on the human health by increasing the concentration of pesticides and other related substances in the environment and on food. Pesticide poisoning instances have been linked to an array of cases globally (Shi et al. 2020). It is now well accepted that pesticides have long-term negative effects on human health, including respiratory illnesses, diabetes, congenital problems, genetic issues, and cancer.

These health effects could change according to the type and intensity of exposure (Almutairi 2019). A sustainable method for treating agrochemicals, cleaning up chemically contaminated soils, boosting soil fertility, and producing food crops is vermiculture technology, which involves the usage of earthworms in the production of essential drugs and industrial raw materials, which is advantageous (Lacalle et al. 2020).

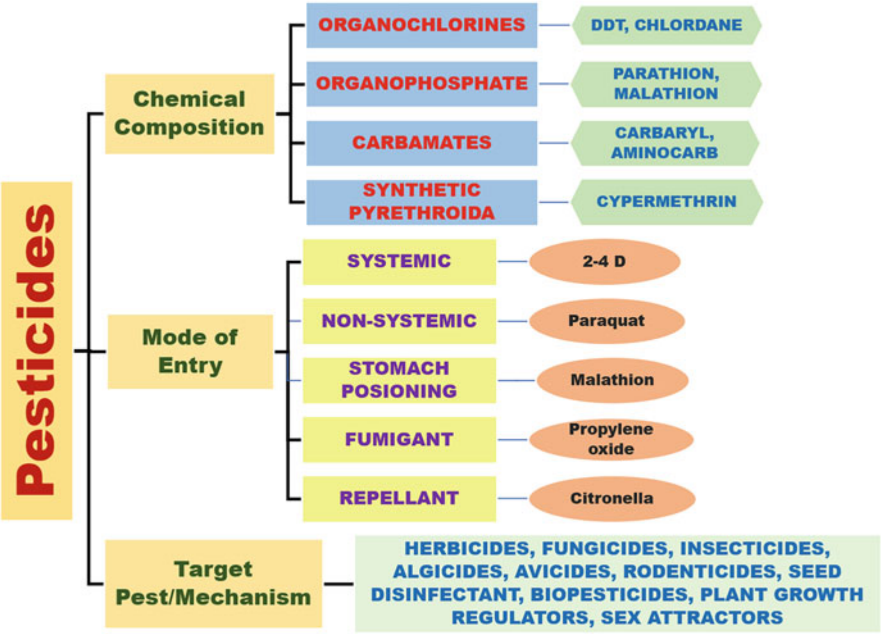
The composting of the solid debris of municipality, the vermifiltration of sewer water generated by the municipality and industries, the reintegration of soil which is chemically mutilated, and the harvesting of fruits and vegetables are some of the victorious implementations of vermicomposting (Martinkosky et al. 2015). Vermicomposting results in a 75% breakdown of waste, a 95% reduction in wastewater's total dissolved solids (TDSs) and biological oxygen demand (BOD), and a 30–40% increase in crop plant growth over agrochemicals due to earthworm castings. Technology used in vermiculture is socially acceptable, economically viable, and environmentally sustainable (Javed and Hashmi 2021). Over a period of 600 million years, earthworms have been referred to as "environmental engineers." Scientists have long recognized earthworms' function as "waste and soil engineers." The study of vermiculture, however, has been completely transformed by recent discoveries about their role in the rehabilitation of polluted soil and the presence of significant bioactive compounds for the creation of contemporary medications (Azarpira et al. 2014). Earthworms mediate all biodegradation, bioconversion, and bioproduction processes because they can consume organic materials that other organisms cannot use. They outperform all other biological treatment techniques because they obtain higher usage compared to the destruction rate reached by other techniques. They achieve value accretion that is between 100 and 1000 times greater than other biological approaches (Javed and Hashmi 2021). Earthworms have also been discovered to be beneficial for bioremediation, the process of removing toxins from soil, which increases soil fertility and crop output. Organic wastes have received the majority of attention in vermiremediation such as organophosphates and chlorates, with inorganic pollutants receiving relatively less attention (Baloochi et al. 2018). The development and productivity of the plant are enhanced by the earthworms by means of intricate mechanical and biochemical interactions with the biotic and abiotic constituents of soil. When earthworm burrows, some soil is consumed by them, which results in the mechanical disintegration of the soil particles and expands the surface area for the mechanical deed (Gupta and Garg 2008). For the transport of water, particles, nutrients, and air, earthworm burrows serve as conduits. Millions of enzymes and microorganisms found in earthworm guts speed up the biochemical conversion and mineralization of soil organic materials, enriching the soil. Increased plant growth and crop output are made possible by all of these processes working together with additional factors (Njoku et al. 2016). In order to alter, degrade, or eliminate pollutants from the soil environment, vermiremediation makes use of the biotic and abiotic interactions, life cycle, burrowing, and feeding activity of earthworms (Baloochi et al. 2018). In the second stage of metabolism, four enzyme systems—hydrolases, esterases (also hydrolases), mixed function oxidases (MFOs), and glutathione S-transferases

(GST)—are principally involved in the breakdown of pesticides (Dada et al. 2021). Enzymes are responsible for catalyzing the following metabolic processes: hydrolysis (chemical breakdown of substances by water), oxidation (addition of oxygen), epoxidation (addition of oxygen to a double bond), addition of oxygen to an amino group (NH_2) of a nitro group, addition of a hydroxyl group to a benzene ring, dehalogenation (cleavage of carbon-halogen bonds), reduction of an amino group (NO_2) to an amino group, substitution of an oxygen atom for a sulfur atom, metabolism of side chains, and aromatic ring cleavage (Baloochi et al. 2018).

10.1.1 Pesticide and Its Classification

Pesticides are organochemicals used in agriculture or in public health programs to protect functional feed from pestilence, and mankind from vector-borne ailments, such as dengue, malaria, chikungunya, African sleeping sickness, kala-azar, and others (Haddi et al. 2020; Nicolopoulou-Stamati et al. 2016). Pesticides may be classified according to their (1) chemical composition, (2) mode of entry, and (3) target pest/mechanism as described in Fig. 10.1 (Akashe et al. 2018; Kaur et al. 2019).

The mechanism of action of any chemical substance that acts as a pesticide is mainly based on three principles:



Pesticides
Chemical Composition
ORGANOCHLORINES
DDT, CHLORDANE
ORGANOPHOSPHATE
PARATHION, MALATHION
CARBAMATES
CARBARYL, AMINOCARB
SYNTHETIC PYRETHROIDA
CYPERMETHRIN
Mode of Entry
SYSTEMIC
2-4 D
NON-SYSTEMIC
Paraquat
STOMACH POSIONING
Malathion
FUMIGANT
Propylene oxide
REPELLANT
Citronella
Target Pest/Mechanism
HERBICIDES, FUNGICIDES, INSECTICIDES, ALGICIDES, AVICIDES, RODENTICIDES, SEED DISINFECTANT, BIOPESTICIDES, PLANT GROWTH REGULATORS, SEX ATTRACTORS

Fig. 10.1 Classification of pesticides

- Normal biological pathways are disrupted when molecules of pesticides react with biomolecules.
- The higher the concentration of the pesticide, the greater the symptoms.
- The greater the dose of the pesticide, the higher the concentration.

There are at least seven different types of chemical reactions by which the majority of pesticides act on their target.

10.1.1.1 Enzyme Inhibition

The pesticide may be similar in structure to the substrate or coenzyme and block the function of the target enzyme in a vital pathway. Their action may be very selective and depends upon how important the enzyme it is inhibiting; for example, carbamates and organophosphorus insecticides inhibit the enzyme acetylcholinesterase, a neurotransmitter. Glyphosate and glufosinate inhibit amino acid production in plants (Casida 2009; Lushchak et al. 2018).

10.1.1.2 Disturbing Chemical Signaling Pathways

Some pesticides imitate the signaling substances in a biological pathway and may modify the signal by making it stronger, longer lasting, or signaling at the wrong time. These are called agonists. Some pesticides act by blocking the receptor site of the real signaling agents. These are called antagonists, e.g., 2,4-dichlorophenoxyacetic acid (2,4-D) that mimics the plant hormone auxin (Casida 2009; Lushchak et al. 2018).

10.1.1.3 Reactive Molecules that Destroy Cellular Components

Radical oxygen, superoxide, or hydroxyl ions may be formed as a reaction between the pesticide and any target biomolecule. These reactive ions degrade important cellular components. These are selective toxins; for example, paraquat, a herbicide, acts by producing reactive oxygen species disrupting the membrane of mitochondria or chloroplasts (Casida 2009; Lushchak et al. 2018).

10.1.1.4 By Changing the pH

Pesticide molecules may change the pH gradient across cell membranes or walls and thereby disrupt structural integrity and functioning of the same. These molecules are usually weak organic acid or base, e.g., ammonia (Casida 2009; Lushchak et al. 2018).

10.1.1.5 By Changing Structural Integrity

Some pesticide molecules which are lipophilic substances may dissolve into the membrane and alter their structures. Some specific molecules are metabolized into potentially toxic substances; for example, hexane, when metabolized to 2,5-hexanedione, is a toxic nerve poison (Casida 2009; Lushchak et al. 2018).

10.1.1.6 By Altering Osmotic Balance

Toxic substances can act by disturbing the electrolyte balance or osmotic pressure so that the cells may rupture, thereby killing the organism; for example, NaCl in higher concentrations is toxic to aquatic animals (Casida 2009; Lushchak et al. 2018).

10.1.1.7 By Destroying Proteins

Strong alkalis, acids, oxidants, or reductants can destroy tissue, DNA, or proteins (Casida 2009; Lushchak et al. 2018).

10.1.2 Effects of Pesticide on Human Health and Environment

The effect of pesticide to improve agricultural yield and quality of food cannot be overlooked. But the safe storage, disposal, and remediation of pesticides are major environmental challenges.

There has been an approximately 11% increase per year in pesticide production globally. This has increased production from 0.2 million tonnes [in 1950] to more than five million tonnes [in 2000]. Around three billion kilograms of pesticides are used, but only 1% of this huge mass is used to control pests. 80% of all pesticides used are intended to kill insects, 15% are herbicides, 1.46% are used to treat plant fungal diseases, and 3% are other types of pesticides. Insecticides account for around 29.5% of consumption, fungicides account for about 17.5%, and the remaining 5.5% is made up of consumption. Compared to the global usage of 44% of pesticides, India accounts for 76% of the total consumption. The discharge of chemicals used in agricultural soils accounts for 50% of water pollution in rivers and streams (Rajmohan et al. 2020).

The duration for which the pesticides are retained in the environment depends on certain factors, viz.:

- Type of soil
- Method of pesticide application
- Capacity of soil to absorb pesticides
- Organic matter content of the soil

The distribution of some pesticides in major river bodies is summarized in Table 10.1.

The aquatic microbiota [zooplankton, phytoplankton] take up the various un-degradable metabolites of pesticides and unchanged pesticides from the water and store them within their cells. Over time, there is a storage pool of these toxic molecules in the ecosystem, which is referred to as bioaccumulation. The higher up we go on the food chain, the higher the concentration of these toxic end products that are stored in the body fat of the organism. This phenomenon is biomagnification.

Most of the used pesticides are carried away by rainwater and irrigation to the nearby waterbody. Some of the pesticides can percolate into the soil and contaminate the groundwater table. The remnant on the surface of the soil is carried by runoff

Table 10.1 Pesticide occurrence in river bodies

Country	Water body studied	Concentration of pesticide	References
India	Yamuna river	DDT—66.17–722.94 ng/L, hexachlorocyclohexane—12.76–593.49 ng/L	Pradhan et al. (2022); Rajmohan et al. (2020)
Japan	Chikuma River, Shinano River	Isoprothiolane—8200 ng/L, bromobutide—3 ng/L	
Bangladesh	Fishponds, tube wells	Malathion—42.58–922.8 μg/L, diazinon—31.5 μg/L	
Malaysia	Tengi River	Imidacloprid—57.7 ng/L, propiconazole—4493.1 ng/L Difenoconazole—1620.3 ng/L, buprofezin—729.1 ng/L	

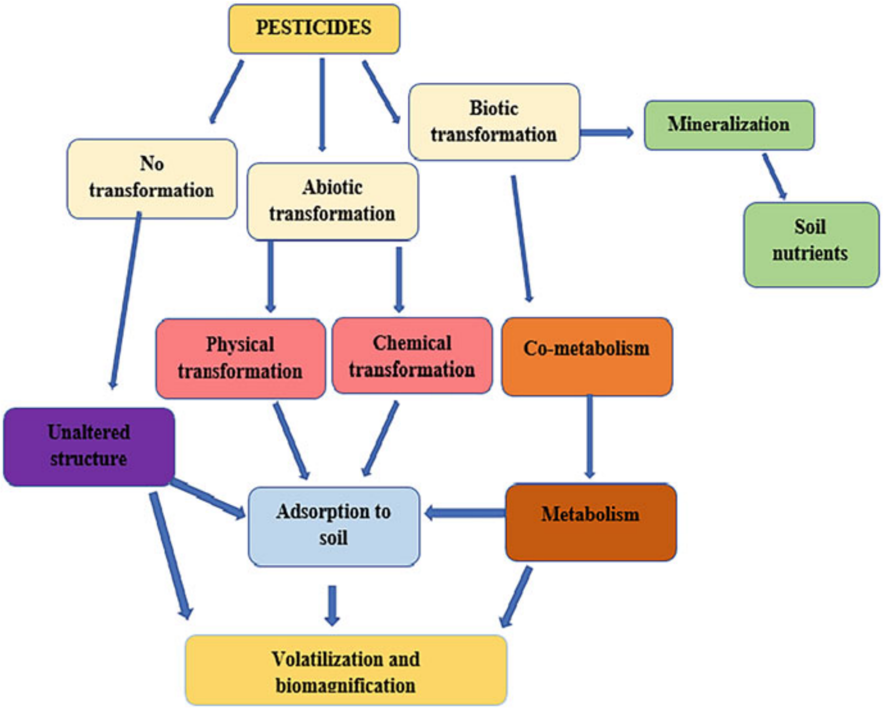


Fig. 10.2 Fate of pesticides in nature

water to the nearby water source, thus contaminating it further (Gupta and Gupta 2020). The fate of pesticides is depicted in Fig. 10.2.

On considering the effects of chemical pesticides on human health and the ecosystem (as mentioned in Table 10.2), it is clear that we need newer

Table 10.2 Effect of pesticides on human health

Pesticide	Class	Effect on human body	References
Lindane	Insecticide	Human carcinogen	IARC Working Group on the Evaluation of Carcinogenic Risks to Humans (2018)
DDT	Insecticide	Stimulates human colon cancer cells and liver cancer cell proliferation	IARC Working Group on the Evaluation of Carcinogenic Risks to Humans (2018)
Malathion	Organophosphates	Induces DNA and chromosomal damage in humans	*IARC publications website—some organophosphate insecticides and herbicides* (n.d.)
Diazinon	Organophosphates	Chromosomal damage in human cells	Pandir (2018)
Pendimethalin	Herbicide of the dinitroaniline class	Risk of acute myocardial infarction	Zago et al. (2020)
Arsenic, trimethylarsine	Organic arsenicals	Atherosclerosis and systemic arterial hypertension	Zago et al. (2020)
Carbofuran	Carbamate	Myocardial infarction	Sekhotha et al. (2016)

eco-friendly alternatives. On the one hand, various bioremediation strategies need to be implemented to clear the ecological pollutants. Vermiremediation with bio-mixtures is the next step in making the ecosystem free of these toxic pesticides.

10.1.3 Vermiremediation

The term vermiremediation was derived from the Latin terms vermis (meaning worm) and remedium (meaning to solve), respectively. Vermiremediation refers to the utilization of earthworms' life cycle (i.e., feeding, burrowing, metabolism, and secretion) for effectively removing contaminants from the soil and degrading nonrecyclable chemicals. In order to enhance vermiremediation biosurfactants, nutrient additions, management techniques, and combinations with other remediation technologies are used (Shi et al. 2020).

The earthworms while moving through the drilosphere lead to formation of burrows, which act as regions of input of oxygen and nutrients and aid in the movement of water and other particles in compacted soil. During this process, the earthworms take in and digest the soil in the region, leading to a positive impact on the soil, which enhances the process of vermiremediation (Shi et al. 2014).

The earthworms maintain a stable temperature, which fastens the biodegradation and other bioprocesses. According to several research conducted, earthworms are used in bioremediation and other bioprocess techniques to speed up the removal of agrochemicals from the soil such as a wide variety of contaminants, including crude oils, pesticides, and PCBs. Earthworms can enhance various biotic and abiotic conditions of soil, which improves the activity of indigenous soil microbes and aids in the process of biodegradation. Earthworms have played fundamental roles in various sectors from restoring the fertility of land to improving the constituents of soil.

The behavior and characteristics of various earthworm species to break down organic agrochemicals were observed and studied thoroughly. Most frequently and extensively used species, namely *Eisenia fetida*, play a significant role in the bioremediation of pesticides. To understand the ability of earthworms to bioremediate and the destiny and persistence of pesticides in the environment, numerous studies have been conducted worldwide (Usmani et al. 2020). Research shows that species like *E. fetida, Pheretima hawayana, Eisenia andrei, E. tetrahedra, Perionyx excavatus, Allolobophora caliginosa, Lumbricus rubellus, Lumbricus terrestris,* and *Pontoscolex corethrurus* show commendable result in the elimination of pollutants and pesticides from the soil. Researchers have assessed how various forces inside the intestine of earthworms remold and disintegrate the pesticides present in the soil and decrease its concentration up to 57–97%. In certain cases, the earthworms lead to reduction of size of the particles by 25–30% (Chaudhary et al. 2004). Expanding agriculture and uncontrolled use of pesticides frequently have a negative impact on the soil environment, producing severe population loss, toxicity, and soil contamination. Therefore, as we proceed towards the greener and sustainable approach of agriculture, farmers must be made aware of the utilization of earthworms and how to use pesticides more sparingly or not at all in order to protect the ecosystem and biodiversity.

10.2 Enzymes Involved in Vermiremediation of Pesticides

The assessment of biomarkers in earthworms is an essential tool to understand the vermiremediation of pesticides. It has gained importance and is considered a major key to understanding soil pollution worldwide. Owagboriaye et al. (2020) stated that activities of glutathione S-transferase (GST) and lactate dehydrogenase (LDH) in *Alma millsoni, Eudrilus eugeniae, and Libyodrilus violaceus* increased when exposed to herbicides and pesticides like glyphosate herbicides. In vermiremediation of pesticides, glutathione S-transferase plays an essential role in the detoxification, biotransformation, and elimination processes. Another vital enzyme is lactate dehydrogenase, which is a glycolytic enzyme present in the tissues of earthworms.

Lactate dehydrogenase acts as an indicator of stress when earthworms are subjected to stress, and therefore this indicator provides energy to the organism within a short interval of time. Thus, the increase in the levels of glutathione S-transferase and lactate dehydrogenase can be correlated with the physiological capability of the earthworm to cope with stressful conditions like oxidative stress induced by pesticides. A study conducted by Rodríguez-Seijo et al. (2018) showed similar results of an increase in glutathione S-transferase and lactate dehydrogenase during stress, and he correlated these with lipid peroxidation, energy consumption, and oxidative stress.

Gamma-aminobutyric acid (GABA) aminotransferase is a neuromuscular transmitter in invertebrates and regulates the chloride channels. In the presence of cypermethrin, GABA-dependent uptake of chloride ions gets inhibited and leads to neurotoxicity in the brains of earthworms. Thus, GABA aminotransferase is a sensitive biomarker for the cypermethrin contamination of soils (Ch et al. 2015).

Acetylcholinesterase is a cholinergic enzyme belonging to the class cholinesterase and plays an essential role in the breakdown of acetylcholine to choline and acetic acid. In the presence of organophosphate pesticides, the activity of acetylcholinesterase gets inhibited due to phosphorylation with serine residue, but there is no significant effect when earthworms are exposed to such stressed conditions. Moreover, the biocidal effects of pesticides via inhibition of acetylcholinesterase result in neurotransmission abnormality, paralysis, and finally death of the organism. Thus, the survival of the earthworm can be correlated with the non-effect (Tiwari et al. 2016).

Malate dehydrogenase (MDH) catalyzes the conversion of oxaloacetate to malate in the tricarboxylic acid cycle. Ch et al. (2015) state that when earthworms are exposed to high levels of pesticides such as cypermethrin, there is an increase in the levels of malate. This is due to the increased energy demand of the earthworm when exposed to such pesticides.

Recent studies suggest that the gut microbiota of the earthworms produce enzymes such as cellulose-degrading cellulase, amylose-degrading amylase, pectin-degrading pectinase, acid phosphatase, alkaline phosphatase, and nitrate reductase, which have the ability to break down the organic components of the pesticides to simpler forms. When exposed to deltamethrin, cellulase activity gets reduced, and when exposed to lindane, the activity gets increased. Exposure to these two pesticides has been found lethal to earthworms as well (Tiwari et al. 2016). The presence of fipronil leads to a decrease in the levels of cellulase, invertase, and pectinase in *E. eugeniae*. These enzymes are responsible for the degradation of complex carbohydrates and the generation of energy. Exposure to chlorpyrifos leads to a reduction in the levels of carboxylesterases, which detoxifies pesticides in the soil in *Lumbricus terrestris* (Martínez Morcillo et al. 2013). Thus, the impact of pesticides on earthworms induced variations in the different functions of the enzymes. These enzymes, therefore, serve as potential biomarkers of pesticide contamination of soil, but more research needs to be carried out in this field to manage farming practices and avoid pesticide contamination of soil. Some of these important enzymes are mentioned in Table 10.3.

10.3 Mechanism of Pesticide Remediation

Through intricate biophysical and physicochemical interactivity with soil abiotic and biotic components, earthworms increase plant growth and productivity. Earthworms consume the soil as they burrow, which causes the soil's particles to break down

Table 10.3 Enzymes as biomarkers of pesticide toxicity in earthworms

Enzyme name	EC number	Class of enzyme	Earthworm species	Biomarker	Function	References
Glutathione S-transferase	2.5.1.18	Isozymes	*Lumbricus rubellus*	Catalase LP and LPI Total GSH % GSSG	Detoxification and biotransformation of electrophilic compounds	Saint-Denis et al. (2001)
Lactate dehydrogenase	1.1.1.27	Oxidoreductases	*Eisenia fetida*	LDH	Indicator of exposure to stress	Tiwari et al. (2016)
Gamma-aminobutyric acid (GABA) aminotransferase	2.6.1.19	Transferases	*Eisenia fetida*	GABA	Regulates chloride channels	Tiwari et al. (2016)
Acetylcholinesterase	3.1.1.7	Carboxylesterase type B	*Drawida willsi*	AChE	Breakdown of acetylcholine to choline and acetic acid	Tiwari et al. (2016)
Malate dehydrogenase	1.1.1.37	Oxidoreductases	*Eisenia fetida*	Malate	Converts oxaloacetate to malate	Ch et al. (2015)
Cellulase	3.2.1.4	Hydrolase	*Eisenia fetida*	Cellulase	Breakdown of organic components	Martínez Morcillo et al. (2013)

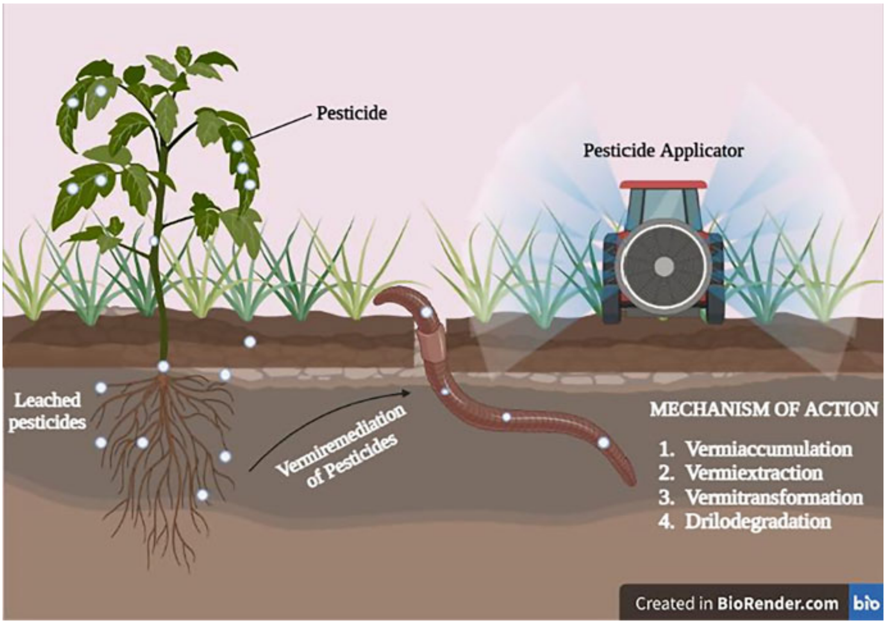


Fig. 10.3 Schematic representation of vermiremediation of pesticides at a glance (Created with BioRender.com)

mechanically and increases the surface area available for biotic activity. Earthworm species have many characteristics like the ability to estivate, and environmental physical properties, as productive survivors in soil. These options result in the increased survival rate of earthworms and accentuate adaptability to exist in adverse physiological conditions pertaining to terribly low or high temperatures (−4° to 40 °C) and pH (4.3–9.2) (Contreras-Ramos et al. 2006). For the transport of water, particles, nutrients, and air, earthworm burrows serve as conduits. Millions of enzymes and microorganisms found in earthworm guts speed up the biochemical conversion and mineralization of soil organic materials, enriching the soil. Increased plant growth and crop output are made possible by all of these processes working together with additional factors. It is acknowledged that earthworms can help with a variety of environmental issues. Vermitechnology is the study of using earthworms to increase food production and address other environmental and human problems.

The four mechanisms involved in vermiremediation are vermiextraction, vermiaccumulation, vermitransformation, and drilodegradation (Shi et al. 2020). Figure 10.3 illustrates and demonstrates a detailed schematic representation of these mechanisms at a glance and depicts the efficacy of such processes employed by the earthworm species.

Vermiaccumulation and vermiextraction are processes where the earthworm takes up pesticides from the soil, thereby leading to a reduction of the pesticides in the soil. Studies show that vermiaccumulation in the previous decades majorly focused on these aspects: pathways of intake of pesticides, its bioaccumulation, and distribution. Earthworms take up pesticides from the soil using two mechanisms: passive epidermal uptake and epidermal uptake. Passive epidermal uptake involves the uptake of pesticides in the direction of decreasing chemical potential, which later gets absorbed by the body walls of the earthworm and translocated throughout the body. On the contrary, dietary uptake pathway involves the earthworm feeding directly on soil with organic compounds, which can further be grounded, digested, and processed resulting in the absorption of pesticides by the intestinal tract of the earthworms (Shi et al. 2014). Vermiaccumulation has further been associated with physiological characteristics such as lipid content of tissues, concentration of pesticides present in the soil, and physicochemical traits of the pesticides. Recent studies show that the distribution of pesticides is heterogeneous in the earthworms, where the distribution of pesticides was fractionated into three different sections of the earthworm: sub-organism (spanning throughout the clitellum encompassing sections above and below it), tissue (body wall, gut, and body fluids), and subcellular (intracellular and extracellular fractions) (Miao et al. 2018).

Vermiaccumulation and vermiextraction are followed by vermitransformation and vermidegradation. These processes involve the degradation of the pesticides using enzymes such as CYP450 and peroxidase or gut microbiota or both. These two pathways are further associated with vermiconversion and vermicomposting. Vermiconversion involves the conversion of solid wastes into biofertilizer materials via a combined action of earthworms and microbiota, whereas vermicomposting involves the conversion of solid organic waste into compost. The major difference between these processes is that vermiconversion and vermicomposting focus on biodegradable organic wastes, and vermitransformation and vermidegradation focus on the treatment of chemicals. Currently, there are studies on vermitransformation, which are majorly focused on only the ecotoxicological impact of the contaminant on the earthworms (Bhat et al. 2018).

Earthworms also possess the attribute of accumulating pesticides and detoxifying them using their metabolic activities. The earthworm species, majorly *Eisenia fetida*, can metabolize organic pollutants such as herbicides, pesticides, trinitrotoluene, and many more. Recent studies also state the degradation of enantiomer pesticides by earthworms (Qu et al. 2014). This study suggested that the enantioselectivity of fipronil resulted from the metabolism of the earthworm and the organism's presence accentuated the degradation of fipronil in soil. The biochemical processing of organic pesticides takes place in two phases: phase I, transformation, and phase II, conjugation. Phase I involves the transformation of hydrophobic pesticides into chemically active, polarized, and water-soluble compounds via the introduction of hydroxyl or sulfonyl groups. Phase II involves the conjugation of metabolites with glutathiones, amino acids, or sugars from phase I reactions, thereby producing hydrophilic conjugates (Shi et al. 2020).

The final mechanism of vermiremediation is drilodegradation, which takes place in the drilosphere which is 2 mm thick soil around the earthworm burrow. It is based on the principle of the drilosphere effect, whereby the excreta of the earthworm supplement energy and nutrients to the indigenous microorganisms, leading to increased degradation of pesticides. Channelization by earthworms in the drilosphere leads to the growth of aerobic microorganisms, and the organic carbon supply from the earthworm mucus acts both as a source of energy and as electron donors. Thus, this multitude of processes such as breakdown, elimination, and degradation of organic pesticides collectively define what is known as drilodegradation or drilostimulation (Hoang et al. 2016). Therefore, these distinguishable characteristics make vermiremediation an essential process in the bioremediation of polluted soil with pesticides and organic contaminants.

10.4 Challenges Involved in Vermiremediation of Pesticides

Like all bioremediation techniques, the vermiremediation method has several limitations. Only weakly or moderately contaminated soils that enable earthworm survival are suitable for vermiremediation. The survival of earthworms may be impacted by the toxicity of the contaminants in soil that has been severely contaminated (Shi et al. 2019).

Additionally, depending on the biological groupings of earthworm species utilized, the only way to study the activity of earthworm is vermiremediation. Earthworms are divided into three groups based on how they like their habitats: surface dwellers (epigeic), deep burrowing (anecic), and surface feeder (endogeic). The most common example of epigeic earthworms is *Eisenia fetida*, which are categorized as detritivores based on their eating habits and are found as soil feeders where they mostly consume plant litter and other organic materials (Bhattacharya and Kim 2016).

For earthworms to exist in soil, there must be specific circumstances, like enough food. Earthworms typically avoid unfavorable soil conditions that could reduce their metabolism and chances of survival by altering their structure and function, like increased H^+ ions, increased ionic strength, and enhanced concentrations of heavy metals and pesticides (Eijsackers 2010; Kooijman and Cammeraat 2010; Lapied et al. 2009). Due to the fact that many birds eat earthworms, vermiremediation may contaminate the food chain.

Additionally, the soil's climate needs to be suitable for earthworm activity. Extreme temperatures may restrict their activities. To enable the earthworms to live by burrowing the tunnel in the soil, there needs to be a lot of water in the soil. At several organizational levels, such as the individual, population, and community levels, pesticides have an impact on earthworms. Individual pesticides may build up in the tissues of the earthworm, changing the activity of antioxidant enzymes, gene expression, and DNA structure. Pesticides can have an impact on earthworm reproduction, growth, and survival at the discrete and community levels (Brulle et al. 2011; Dittbrenner et al. 2012).

The longevity of earthworms and the dispersion and bioavailability of high-order components also limit vermiremediation. The growth of earthworms can be significantly impacted by low-grade soil and increased proportion of soil pollutants (Sinha et al. 2008). Surfactants are used to increase pollutant mobility and bioavailability, substantially increasing earthworm growth, which would increase their ability to absorb nutrients through nutrient management techniques or by combining them with other methods. Thus, it can improve the vermiremediation of organic-contaminated soils (Megharaj et al. 2011).

Since vermiremediation mostly relies upon the bias eating of the earthworm, food availability may also have an impact on its potential. Vermiremediation might also be used under tight guidelines. Due to their sensitivity, earthworms may not survive in certain climates, seasons, or other environmental circumstances, which could impede vermiremediation procedures (Butt and Lowe 2011).

10.5 Recent Advancements and Future Prospects

The amalgamation of earthworms and plants is a positive approach for potential toxic element-polluted soil remediation. According to the findings from numerous recently published articles, using plants and microbes in addition to earthworms alone or in combination with them could be an alternate method for cleaning up potentially toxic agrochemical-contaminated soils. Additionally, *Eisenia fetida* can improve the uptake and translocation of potentially toxic contaminants like cadmium in plants such as *Brassica juncea* (Kaur et al. 2017).

According to Nneji et al. (2016), vermiremediation can be augmented by utilizing the interactions between microbes and earthworms. Earthworms and drilospheric microorganisms are paired in microbe-assisted vermiremediation, which facilitates the cleanup of biotics by speeding up detoxification and degradation rates of pesticides and influencing pesticide motility and isolation, along with the absorption of pesticide (Nneji et al. 2016).

Phytoremediation can be coupled with vermiremediation. Deng and Zeng (2017) asserted that the rate of elimination of phenanthrene following the treatment of alfalfa, earthworms, and white rot fungus in soil was 93%, a level significantly greater than the control variables.

As a final "polishing" phase, vermiremediation can also be utilized to eliminate any remaining toxins after the first remedial treatment has been administered. After physical and chemical treatment as well as residual pollution cleanup, it can help to restore the soil structure and texture by supplying organic nutrients and promoting the growth of microorganisms in the drilosphere (Sinha et al. 2008).

According to Li et al. (2015), inoculating soil with both *Australopithecus robustus* Perrier and *Eisenia fetida* Savigny earthworm species substantially increases the level of pentachlorophenol in soil and deduces the basal metabolic rate (BMR). This finding raises the possibility of development of good bacteria in the soil and boosts the bacterial community that breaks down pentachlorophenol and speeds up the process.

According to Bonkowski et al. (2000) and Curry and Schmidt (2007), by employing food and improving inoculation conditions, one may increase the earthworm biomass and improve the productivity and absorption capacity of vermiremediation systems. Because of their dietary preferences, earthworms may have better growth if the quality of their feed is upgraded. According to Butt and Lowe (2011), due to the drilosphere effect, higher earthworm development results in higher rates of absorption and organic pollutant decomposition in the soil. Additionally, earthworms need an appropriate habitat to survive, and thus, it is important to maintain ideal inoculation conditions during vermiremediation operations, like heat, humidity, grade of food, and H^+ concentration, to ensure the growth of earthworm.

To promote the widespread usage of vermiremediation, a lot more basic research measures will be needed in the future given the number of unresolved issues. It is important to fully understand the capability, contribution, and mechanism of each step involved in phytoremediation. It is also important to comprehend how organic contaminants behave inside the drilosphere. Verifying the vermiremediation sweetening measures is important, and considering their possible side effects is also important. Peripheral concerns including the effectiveness of red worm collection techniques from contaminated soil and secure postharvest disposal should be taken seriously (Shi et al. 2019).

10.5.1 Conclusion

Due to the advent of rapid expansion in the agricultural sector, there is a substantial accumulation of agrochemicals and pesticides in the soil, deteriorating its normal ecological conditions. Though agrochemicals and predominantly pesticides are meant to enhance the lifestyle and shelf lives of food sources, their prolonged utilization ultimately leads to detrimental effects on human health. An average of two million tonnes of pesticide is utilized around the globe. The presence of a higher concentration of pesticides in the soil leads to various health issues concerning humans and the natural ecological niche. Pertaining to the aforementioned reasons, there is a need for risk management and toxicity assessment for the percolating agrochemicals and other organochemical compounds. Thus, it is of immense importance to biodegrade and remove such contaminants from soil. Vermiremediation is one such advanced and eco-friendly technique that has paved a path for sustainable management and degradation of organic and inorganic organophosphorus compounds present in the soil. It improves the efficiency of various biological methods related to bioremediation and bio-removal of toxic compounds. In due course of time, an array of screening methodologies have been adopted for the selection of viable species of earthworms to reach the highest sustainable efficiency. Physico-mechanical activities of earthworms play an imperative role in the optimization of contaminated soil conditions and enhancing the efficacious sorption of toxic compounds. Predominantly, the species of earthworms used in the process of vermiremediation not only aid in the bio-removal of pesticides but also improve the nutritional status of the soil. The next step is to test whether vermiremediation can be applied to fine soils because these trials could not tell us whether earthworms can reduce pollutant sorption or boost bioavailability. However, a pilot project is necessary to scale up and use the treatment procedure in uncontrolled environments where earthworm interactions may be more beneficial. Considering the immense biotechnological potential of earthworms pertaining to the agricultural sector, there is a need for scientific expeditions on the issues of sustainable remediation management techniques and toxicity assays.

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Biochar-Assisted Remediation of Contaminated Land: Prospects and Challenges

11

Tanushree Basumatary and Hemen Sarma

Contents

Abstract

The pyrolysis of organic waste produces a carbon-rich substance known as biochar. This organic waste might include biomass crops, home waste, manures, industrial waste generated in cities, agricultural forestry leftovers, nontraditional materials, and sludge wastes. Biochar is currently being utilized on a widespread scale by several stakeholders for the removal of organic and inorganic contaminants from soil. The properties of biochar are directly affected by production methods, feedstock, and operating parameters, which significantly impact their use in various applications. Furthermore, the porosity, composition,

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pyrolysis temperature, feedstock, and pyrolysis time of biochar formation determine its quality and efficacy in remediation.

Keywords

Biochar · Heavy metal · Remediation · Soil

11.1 Introduction

Biochar is a carbon-rich substance generated by the pyrolysis of organic leftovers. Biochar can be made from ordinary wastes such as biomass crops, domestic trash, manures, urban industrial waste, agricultural forestry residues, nontraditional materials, and sludge waste. However, the productivity of biochar is modified by feedstock type and pyrolysis conditions (Oni et al. 2019; Han et al. 2020).

As the economy and living conditions improve, more biowaste resources, such as organic, agricultural, and woody wastes, are generated regularly (Zhou et al. 2021). As a result, land contamination has become a major global issue, with the influence of human activities apparent in food security and safety concerns. Polluted soils serve as a repository for poisons that can be consumed by plants and other species, leached into water sources, or transported to other sites. The ecology is being devastated due to heavy metals entering the food chain. Organic pollutants (OPs) and inorganic pollutants (IPs) are the two major types of pollutants (IPs) detrimental for all living organisms. The OPs may travel long distances and are toxic, persistent, and bioaccumulative. Inorganic pollutants, such as heavy metals As, Cr, Cu, Pb, Cd, Hg, Ni, and Zn, have a deleterious impact on the health of people, plants, animals, and soil fertility. These metals, which are present in the soil, pose risks to the entire biosphere and are accumulated directly by plants, which can be dangerous for the plant and the food chain that consumes it; they also change the soil's properties, such as pH, natural chemistry, color, and porosity, which has an impact on the soil's quality and contaminates the water (Akram et al. 2018; Duarte et al. 2018; Sarma et al. 2019; Briffa et al. 2020).

Biochar has a saturation adsorption capacity to adsorb a pollutant. It has been widely utilized in environmental remediation due to its wide range of raw ingredients, low cost, and large specific surface area (Lyu et al. 2020). Biochar's distinguishing characteristics, such as its high carbon content, cation exchange capacity, and higher specific surface area, have recently been presented as an economically viable approach for remediating heavy metal-contaminated soils (Lahori et al. 2017; Sakhiya et al. 2020). Several favorable immobilization properties of biochar, such as its microporous structure, active surface functional groups, high pH, and cation exchange capacity (CEC), make it simpler for heavy metals to undergo chemical modification (Xie et al. 2015). There are numerous applications for biochar, including pollution remediation due to high CEC and specific surface area, soil fertility improvement via liming action, enrichment in the volatile matter, increase in pore volume, carbon sequestration due to carbon and ash content, and so on (Tomczyk et al. 2020). Furthermore, biochar carbon sequestration in soil significantly reduces greenhouse gas emissions, and biochar's stability is the most critical driver of its ability to absorb carbon (Leng et al. 2019). Biochar made from various agricultural biomass can boost the growth of native plants and improve the efficacy of phytoremediation in polluted soil containing metalloids (van Nguyen et al. 2022). Although biochar can absorb metals from water, its capacity is often lower than other common biosorbents, such as activated carbon. As a result, recent studies have changed biochar to improve its metal sorption capacity (Li et al. 2017) (Li et al. 2017). This chapter describes the history of biochar application and its importance in land remediation. Further, we discuss the fundamental properties of biochar, its mechanism for cleaning up contaminated soil, and various biochar feedstocks for sustainable remediation of contaminated land.

11.2 History of Biochar

Evidence shows that biochar has been utilized for at least 2000 years. However, the oldest beginnings of biochar can be traced back to American Indian cultures in the Amazon basin. The incredibly fertile Terra Preta (black soil of India) soils, which were created by ancient indigenous cultures, contain evidence of the successful usage of biochar. Biochar can be detected in these soils, indicating that biochar has been extensively used (Weber and Quicker 2018). Compared to the soils of the surrounding area, the soils in Terra Preta have a higher cation exchange capacity, pH, and base saturation, as well as a high phosphorus content ranging from 200 to 400 mg P/kg (Fraser et al. 2011). The locals would make charcoal, mix it with organic waste, and plant shattered pottery and broken glass in small patches of the soil before utilizing the concoction as fertilizer. Even though tropical rains speed up soil erosion and loss of water-soluble nutrients, many of the earth's soils are hundreds or even thousands of years old. They have retained a surprisingly high level of fertility (Sonoki et al. 2013). It is possible that the biochar is responsible for this action.

Biochar should be distinguished from Terra Preta in terms of carbon concentration and structure. Human modifications to the Terra Preta soil horizon in the Amazon rainforest have significantly increased the tropical region's potential to store carbon. Char is a soil additive that was inspired by Terra Preta and was one of the reasons that helped boost soil fertility. According to Bezerra et al. (2016), the first wave of research on Terra Preta de Indio happened throughout the 1980s. Biochar research began in 2006, making it the third field to be opened, whereas Terra Preta Nova research began in 2002. Terra Preta became less popular as biochar research got more common (Bezerra et al. 2016; Kamarudin et al. 2022). It is projected that combining biochar with manures, minerals, and clays and then heating the mixture at low temperatures will result in enriched biochar with long-term stability comparable to Terra Preta (Chia et al. 2014). However, additional in-depth studies on the carbon levels and characteristics of the Terra Preta soil were published near the turn of the century. Studies into the properties of biochar as a soil supplement began around the same time. As a result, there has been a resurgence of interest in incorporating biochar into the soil (Aller 2016).

11.3 Fate of Land Pollution

Human activities are the principal sources of soil contamination, resulting in the accumulation of contaminants in soils that can reach dangerous levels. People's and the environment's health may be jeopardized as a result of the rise in soil contamination during the last few decades (Cachada et al. 2018). Heavy metal pollution in soil has increased dramatically as a result of urbanization, industrialization, and recent agricultural advancements. Mining and smelting, combustion of fossil fuels for energy, municipal trash disposal, pesticides, sewage irrigation, and fertilizer application are all examples of anthropogenic activity. Furthermore, heavy metals may enter the food chain after being absorbed by plants, exposing people to them and having serious consequences for human and environmental health (Li et al. 2019a, 2019b; Zwolak et al. 2019; Hou et al. 2020; Sarma and Prasad 2015).

Persistent organic pollutants (POPs) can enter the environment via soil transport and landfills; household furnaces; agricultural sprays; incinerations; putrefaction; various combustions; chemical facilities; waste from various operations such as building destruction; use of outdated oil; evaporation; medical waste; organochlorine pesticide storage; industries such as pulp and paper, leather, pharmaceutical, oil and gas, and oil refineries; sites that produce produced gas; and mechanical facilities (Gaur et al. 2018; Khan et al. 2018; Bhattacharyya et al. 2022). Heavy metal pollution is caused by both natural and man-made mechanisms. Heavy metals can be inherited by soils from metal-rich parent rocks such as serpentine and black shale. Natural causes include volcanoes, soil erosion, rock breakup, and so on. Mining, smelting, incomplete fossil combustion, waste disposal, electronic product production, corrosion, car emissions, and agricultural activities, on the other hand, are examples of anthropogenic sources of heavy metal pollution (He et al. 2015; Kanwar et al. 2020) (Sarma et al. 2021).

Pollutants include oil hydrocarbons such as alkanes, alkenes, and cycloalkanes; chlorinated substances such as polychlorinated biphenyls (PCBs), polychlorinated dibenzodioxins (PCDDs), and polychlorinated dibenzofurans (PCDFs); monomeric aromatic hydrocarbons such as benzene, toluene, ethylbenzene, and xylene, collectively known as BTEX; polycyclic aromatic hydrocarbons (PAHs) such as chrysene and fluoranthene; and many pesticides (Duarte et al. 2018).

These pollutants were able to persist in the soil for extended periods due to the inability of soil microbes to break down heavy metals. Even in the soil, organic compounds have the potential to be transformed into more harmful forms. These more toxic forms can subsequently accumulate in animals and humans via the food chain and significantly affect human health (Guan and Sun 2014). Pb, Cd, As, and Cr are extremely dangerous metals that are mutagenic, carcinogenic, and genotoxic. If the concentration of the harmful heavy metals Hg, Cr, As, Zn, Cd, Ur, Se, Ag, Au, and Ni surpasses the maximum allowable values, they contaminate the environment and affect crop productivity, soil quality, and public health (Mishra et al. 2019; Ojuederie and Babalola 2017).

The types and effects of organic and inorganic pollutant are described in Table 11.1.

11.4 Synthesis of Biochar

Ordinary waste conversion is feasible for environmental sustainability and productivity (Weber and Quicker 2018). The biochar produced from various sources demonstrates a variety of performances and attributes due to the varied ratios of the components contained in the feedstock. For example, wood biochar had a lower potassium concentration and pH (Vaughn et al. 2013; Wang and Wang 2019). Biochar can be produced in traditional earthen charcoal kilns, where the pyrolysis, gasification, and combustion processes run parallel beneath the earthen kiln layer. In addition, there are other low-cost mobile biochar production systems, such as the drum method (Das et al. 2020). Microwave-assisted pyrolysis (MAP) technology, on the other hand, provides faster processing times, lower energy requirements, more effective heat transmission, and better selective heating than current methods. Therefore, microwave-assisted pyrolysis (MAP) was also used to produce biochar, bio-oil, and bio-gas, which is deemed sustainable (Xiang et al. 2020). Although biochar can be produced through pyrolysis, hydrothermal carbonization, gasification, flash carbonization, and torrefaction, pyrolysis is the most often utilized process (Yaashikaa et al. 2020).

11.4.1 Pyrolysis Procedure

Pyrolysis is one of the most practical and successful ways of getting biomass energy from char (Tripathi et al. 2016). Typically, pyrolysis yields a solid, structured carbonaceous substance with a large surface area, lower oxygen and hydrogen content, and a higher nutritional concentration than the feedstock (Ennis et al. 2012). In addition, a large quantity of carbon is successfully fixed in a more stable form due to pyrolysis (Toková et al. 2020). The chemical and physical properties of biochar are primarily determined by feedstock type and pyrolysis circumstances, such as residence time, temperature, heating rate, and reactor type. The main thermochemical techniques utilized for biochar production include traditional carbonization (slow pyrolysis), fast pyrolysis, flash carbonization, and gasification (Manyà 2012). In anaerobic settings, biomass typically undergoes pyrolysis at temperatures ranging from 300 to 900 °C (Liang et al. 2021).

Pyrolysis is classified as fast or slow based on the heating rate and reaction time; fast pyrolysis is processed at a very high heating rate (10–200 °C/s) to produce primarily bio-oil, whereas slow pyrolysis has a low heating rate (1–100 °C/min), the pyrolysis temperature is often between 300 and 700 °C, and it usually takes a long residence time (lasting minutes to hours or even days) to produce biochar. The

Table 11.1 Types and effects of organic and inorganic pollutant

Types of pollutants	Examples	Effects
Organic pollutants	Endocrine-disrupting chemicals	Perfluoroalkyl compounds (PFAS) have been linked to several conditions, including breast cancer, polycystic ovary syndrome, endometriosis, impaired glucose tolerance in children and adults, low birth weight, poor semen quality, polycystic ovary syndrome, and endometriosis (Kahn et al. 2020)
	Chlorinated phenols	Chlorinated phenols cause health issues in humans and animals, including histopathological changes (Oluwasanu 2018)
	Azo dyes	Azo dyes produce toxic metabolites, which can cause toxic effects like allergic reactions, tumor formation, and endocrine disruption (Deng et al. 2020)
	Petroleum hydrocarbons	Petroleum hydrocarbons cause neurological conditions such as fatigue, neurasthenia, and pneumonitis from aspiration into the lungs, which is accompanied by choking, coughing, wheezing, shortness of breath, cyanosis, and fever (Ahmed et al. 2018)
	Pesticides	Pesticides' effects on the spectrum of oncological (cancer) and hematological morbidity, and pulmonary dysfunction, in addition to immune system inadequacies and inborn abnormalities (Hassaan and el Nemr 2020)
	Persistent organic pollutants (POPs)	Exposure to persistent organic pollutants causes serious health problems, including hormone disruption, cancer, cardiovascular disease, obesity, reproductive and neurological diseases, learning difficulties, and diabetes (POPs). Furthermore, these pollutants induce defects in female embryos (Alharbi et al. 2018)
Inorganic pollutants	Cadmium	Cadmium-induced oxidative stress brought on by the formation of reactive oxygen species and bioaccumulation of Cd in the human system affects the antioxidant defense system, leading to various diseases (Suhani et al. 2021)
	Chromium	People can get seriously harmed, such as developing lung cancer, due to the conversion of Cr(VI) to Cr(III). Occupational exposure to Cr(VI) may also result in respiratory issues. In addition, skin rashes, reduced immune systems, kidney and liver failure, genetic material alteration, and other health hazards are connected to Cr exposure. Humans who consume Cr(VI) may also have cardiovascular collapse (Raj and Maiti 2020)
	Arsenic	Acute toxic arsenic exposure causes symptoms such as dry mouth, Mees' lines in fingernails, diffuse skin rashes, breathing garlicky odor, weakness, muscle cramps, vomiting, diarrhea, nausea, abdominal pain, abdominal pain, psychosis, cardiovascular collapse, pulmonary edema, and kidney failure. The incidence and severity of pulmonary, cardiovascular, and cancer problems later in life have also been linked to exposure to arsenic during

(continued)

Table 11.1 (continued)

Types of pollutants	Examples	Effects
		pregnancy and youth, with some findings indicating a 10-year latency period for these conditions (Bjørklund et al. 2019)
	Lead	Due to immune modulation, oxidative, and inflammatory mechanisms, Pb exposure can cause neurological, respiratory, urinary, and cardiovascular disorders. Furthermore, Pb may disrupt the oxidant-antioxidant system's balance and cause inflammatory responses in various organs. Pb exposure can cause changes in the body's physiological functions and is linked to various diseases (Balali-Mood et al. 2021)
	Mercury	The presence of mercury in the environment is becoming an increasing health problem. Mercury has been associated with several neurological disorders, including amyotrophic lateral sclerosis, Alzheimer's disease, and Parkinson's. In addition, elemental and inorganic mercury compounds have been associated with the immune system and renal damage, respectively, while MeHg has been linked to cardiovascular and nervous system harm (Wang et al. 2012)

overall pore volume and surface area hardly change at pyrolysis temperatures below 400 °C, i.e., at low temperatures. Low temperatures may not give the best conditions for completely devolatilizing volatile compounds. As a result, they may cause specific pores to become blocked and impede the creation of new pores. On the other hand, slow pyrolysis usually results in higher biochar production and better homogeneity. However, it takes a long time, making it unsuitable for the mass production of biochar. Biochar produced at lower temperatures (300–400 °C) has more diversified organic properties, such as aliphatic and cellulose-type structures, and contains more C-H functional groups and C-double bond-type bonds. The rapid temperature rise begins at 400–500 °C; as the temperature rises, amorphous carbons condense to become crystalline carbons; more volatiles are also eliminated, resulting in sparse areas that cause fissures in the material, which subsequently produces more pores. Because of the biomass's dehydration and oxygenation, biochar produced at high temperatures (600–700 °C) has a highly fragrant character, a rise in surface area, formed micropores, and well-organized carbon (C) layers. The number of oxygen-containing H and O functional groups on the biochar surface decreases as temperature rises, while its surface area increases. The latter reduces the capacity of dangerous metals to bind to aqueous media (Leng et al. 2021; Li et al. 2019a, 2019b; Ambaye et al. 2020). For example, in 2013, an experiment was carried out to make biochar from eucalyptus wood (heated to 450 °C and 850 °C, greater pyrolysis temperatures). When this biochar was applied to soils, it enhanced adsorption and decreased the desorption of pesticides such as diuron, chlorpyrifos, and carbofuran (Zhang et al. 2013).

During pyrolysis, lignin, cellulose, hemicellulose, fat, and starch are thermally broken down into three primary products: biochar (a solid fraction), bio-oil (partially condensed volatile matter), and non-condensable gases (e.g., CO, CO_2, CH_4, and H_2). Furthermore, the selective removal of particular elements (C, H, and O) into gases and other volatile molecules produces fluctuations in biochar's O/C and H/C ratios. The ratio of O/C and H/C in biochar is significantly connected to aromaticity, biodegradability, and polarity, all of which are highly desirable qualities for organic pollutant removal (Oliveira et al. 2017).

11.4.2 Biochar Characteristics

Biochar contains nutrients such as P, K, Ca, and Mg, which are concentrated from the pyrolysis feedstock (Sun et al. 2018). The qualities of biochar are strongly dependent on pyrolysis temperature and process parameters such as residence duration and furnace temperature, as well as feedstock type. The pyrolysis temperature affects biochar's physicochemical properties and structure, such as elemental components, pore structure, surface area, and functional groups. The impact of pyrolysis temperature on such features can be related to the inflow of volatiles at high temperatures. Biochar comprises aromatic, aliphatic, and stable organic carbon. Biochar's most essential qualities are their chemical composition, stability, specific surface area, and porosity (Ding et al. 2016; Saletnik et al. 2019).

Furthermore, density and porosity are crucial physical qualities that determine how biochar flows through the environment and interacts with water to affect soil hydrologic processes, particularly plant-available water-holding capacity (Brewer et al. 2014). The pore structure of biochar, which defines the specific surface area, influences its adsorption ability for heavy metals. Generally, the greater the surface area of biochar, the greater its adsorption capacity (Qiu et al. 2021). In addition, a large proportion of carbon is fixed in a more stable form during pyrolysis and efficiently stored after being applied to the soil (Toková et al. 2020).

The physicochemical properties of biochar, such as composition, surface area, water-holding capacity, pH, electrical conductivity, particle, pore size distribution, and a variety of functional groups (such as –OH, –COOH, and $–NH_2$ groups), make biochar more effective and have special significance in soil remediation as well as improving soil properties. For example, biochar's properties can aid in adsorption and immobilization by complexing, electrostatic contact, and ion exchange between contaminants. In addition, biochar's physicochemical properties allow it to be used to sequester carbon in the soil, improve composting, create organic fertilizers based on biochar, clean up polluted soils, improve soil qualities, reduce groundwater and surface water contamination, and remove pollution (Mandal et al. 2021, El-Naggar et al. 2019, Gałwa-Widera 2021). However, because modified biochar offers a wide range of practical applications, considerably more research has been put on biochar modification to increase its qualities (Zhang et al. 2018).

11.5 Adsorption Mechanism of Biochar

The ability of biochar to adsorb heavy metals is mainly determined by its specific surface area, the quantity of surface-active functional groups it contains, and its cation exchange capacity. The efficacy of biochar in removing heavy metals is highly dependent on its properties, its sources, and the surroundings (Ke et al. 2021; Qiu et al. 2021). Both the Langmuir and Freundlich isotherms are examples of adsorption isotherms and are handy tools for defining the relationship between an adsorbent and an adsorbate in any given system. The parameters produced from the various models provide essential information regarding the adsorbent's sorption mechanisms, surface properties, and affinities. The Langmuir isotherm is the one that sees the most application in the process of removing a solute from a liquid solution. The Langmuir isotherm makes the presumption that the surfacing site is at a constant temperature. When there are no sorption limitations, and the adsorption process involves heterogeneous surface energy systems, the Freundlich isotherm can model the process. This is the case when the adsorption does not include homogeneous site energies (Park et al. 2013; Azlina Wan Ab Karim Ghani et al. 2013).

11.5.1 Adsorption of Toxic Inorganic Metals

The potential adsorption mechanism for inorganic materials like heavy metals often involves the combined effects of several different interactions. These interactions include electrostatic interaction, surface sorption, ion exchange, precipitation, and complexation as shown in Fig. 11.1 (Poissant et al. 2008).

11.5.1.1 Electrostatic Interaction

In interaction with electrostatic fields, biochar is usually zwitterionic, which indicates that it possesses both positively and negatively charged atoms. Therefore, biochar can take in positively charged metals due to its electrostatic attraction. Because of this, it is anticipated that the cation exchange capacity (CEC) of soils will rise due to the negatively charged functional groups; furthermore, pH-dependent O-containing functional groups (oxonium heterocycles) of biochar will also exhibit anion exchange capacity (AEC) (Oliveira et al. 2017).

11.5.1.2 Surface Sorption

The removal of heavy metals via the diffusion of metal ions into the pores of sorbents without forming chemical interactions is called surface sorption. Surface sorption is the word used to describe the removal of heavy metals. The biochar-metal sorption process, also known as the biochar mechanism, is susceptible to the solution's pH and the point of zero charges (PZC) of the biochar (Patra et al. 2017). In addition, biochar can absorb heavy metals via various adsorption mechanisms due to its high surface area, abundance of polar functional groups, and presence of transition metals (Gholizadeh and Hu 2021).

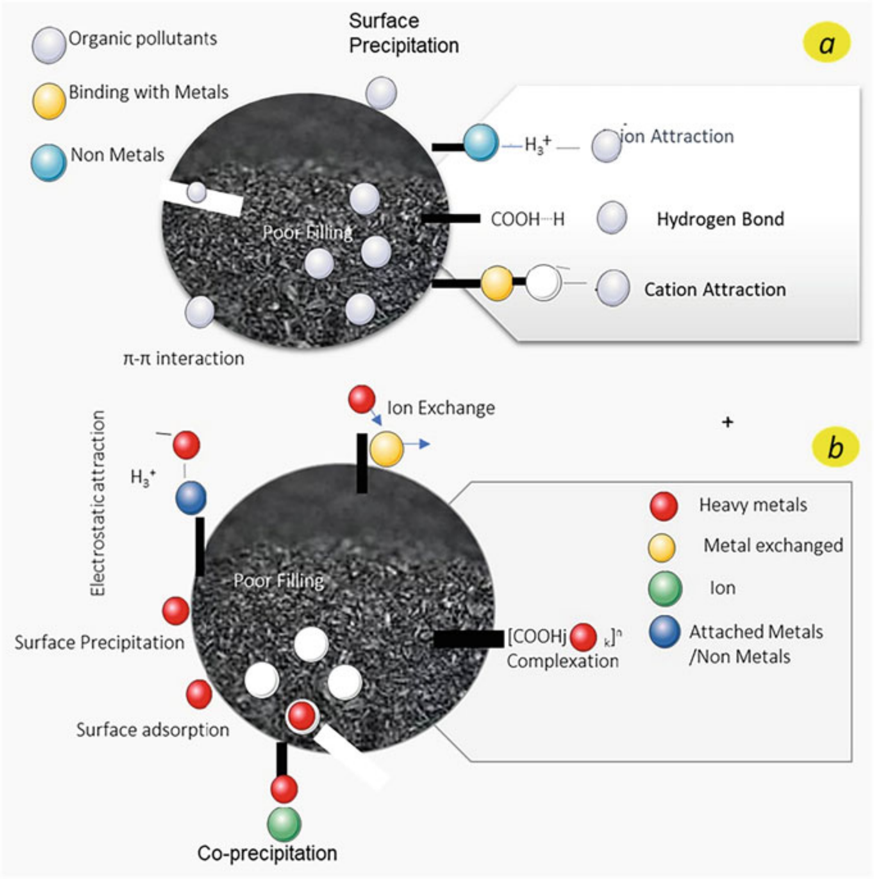

Fig. 11.1 A biochar structural diagram showing the electrostatic interaction, surface sorption, ion exchange, precipitation, functional groups, and characteristics of biochar. Reprinted from Ref (Sarma et al. 2022) with permission from Elsevier. License Number: 446421163588

11.5.1.3 Ion Exchange

Ion exchange processes are reversible ion exchanges between a solid and a liquid phase. The solid phase is known as an ion exchanger and needs to be insoluble in the medium in which the exchange occurs (Barquilha and Braga 2021). The interchange of protons and ionized cations with dissolved salts on the surface of the biochar is necessary for the mechanistic process to occur. The ability of biochar to effectively absorb heavy metals depends on both the surface functional group and the contaminated size of the biochar (Ambaye et al. 2020). In particular, metal ions are significantly adsorbed in active biochar sites with phenolic and carboxylic functional groups on the material's surface. As a result of the presence of mineral components, biochar can absorb metals by electrostatic attraction, ion exchange, surface complexation, and precipitation of metals by releasing soluble ions (Sobik-Szołtysek et al. 2021).

11.5.1.4 Complexation

By merging two or more molecules, complexation can occur, resulting in the production of a well-defined, nonbonded geometrical structure. It is predicated on the interaction of weak forces such as H-bonding and hydrophobicity. When it comes to the immobilization of heavy metals, the surface functional groups of biochar play a significant role. When these functional groups interact with HM ions, stable complexes are formed by combining the two. More oxygen functional groups are present in biochar produced at lower temperatures. Because of surface oxidation and generation of carboxyl, the amount of oxygen in this kind of biochar increases over time (Dhiman et al. 2021).

11.5.1.5 Precipitation

One of the important ways of removing the inorganic pollution caused by biochar is through precipitation. It involves the development of mineral precipitates into the solution or onto the surface of the sorbing material for biochar, which is produced from the breakdown of cellulose and hemicelluloses material by pyrolysis at temperatures higher than 300 °C and possesses alkaline characteristics (Ambaye et al. 2020). The creation of one or more solids during the sorption process is precipitation. This can take place in a solution or on a surface. There has been much discussion about precipitation being an essential part of immobilizing heavy metals by utilizing biochar sorbents (Patra et al. 2017).

11.5.2 Adsorption of Toxic Organic Metals

On the other hand, the mechanisms behind the adsorption of organic contaminants by biochar are linked to a variety of different interactions. These interactions include hydrophobic interaction, pore filling, partitioning, electron donor and acceptor (EDA) interaction, and electrostatic contact (Poissant et al. 2008). Biochar has a higher surface area, is resistant to biodegradation, and has an active adsorption affinity for various hydrophobic organic and hazardous inorganic pollutants. Because of its higher surface-to-volume ratio, biochar has a stronger and more favorable affinity for harmful and persistent pollutants such as polycyclic aromatic hydrocarbons, dioxins, furans (PCDD/Fs), polybrominated diphenyl ethers (PBDEs), and polychlorinated biphenyls. These contaminants include PCBs. According to the research from Hu et al. (2020), one of the methods that biochar employs to reduce the mobility of inorganic pollutants is a change in pH (Das et al. 2020).

As a result, biochar can disrupt source-pathway links because it can absorb contaminants on its surface, resulting in a lower concentration of contaminants in the soil solution. Biochar can remediate soil by permanently absorbing contaminants in the soil solution and preventing the pollutants from reaching receptors (Sizmur et al. 2015).

11.6 Biochar Made from Different Materials Can Be Used to Clean Up Polluted Land

Biochar is a multipurpose material that can be used in various environmental remediation procedures (Yuan et al. 2019). Because of its carbonaceous structure and high surface area, biochar, for example, can trap heavy metals and pollutants from the water and soil matrices in which they are located (Odinga et al. 2021). In general, agricultural residue and woody biomass containing lignin, cellulose, and hemicellulose are excellent sources of biochar for lowering greenhouse gas emissions and cleaning up organic pollutants. Biochars with a high ash concentration, such as those derived from manure and sludge, on the other hand, are more suited for the remediation of heavy metal and cationic organic pollutant pollution (Ji et al. 2022).

According to several research findings, soil that has been changed with biochar is more effective in absorbing a broader range of organic pollutants, reducing the quantity of those pollutants that plants take in. Herbicide bioavailability can be lowered when more charcoal is present in the soil. The accumulation of pesticides and other organic pollutants in plants can be considerably decreased by applying little biochar to the soil (Zhang et al. 2013).

11.6.1 Application of Biochar in Phytoremediation

Biochar and phytoremediation are risk-free, ecologically friendly technologies that may be at the forefront of attempts to clean up polluted soil (Paz-Ferreiro et al. 2014). The multidisciplinary discipline of phytoremediation aims to either immobilize or mobilize toxins induced by various environmental circumstances. The term “phytoremediation” refers to a wide range of remediation techniques, including rhizoremediation, phytoextraction, phytodegradation, and phytovolatilization (Narayanan and Ma 2022).

Xu et al. (2020) employed a mixture of toxicological and physiological studies to assess the effect of biochar pyrolyzed from kitchen waste (KWB), corn straw (CSB), and peanut hulls (PHB) on the immobilization of lead (Pb) and cadmium (Cd) in polluted soil by planting swamp cabbage (*Ipomoea aquatica* Forsk.). The study discovered that biochar made by pyrolyzing KWB, CSB, and PHB was better at immobilizing Pb and Cd and may raise the pH of the soil. Additionally, swamp cabbage’s levels of SOD and POD reduced, while its fresh weight and root length increased following treatment with biochar.

Bandara et al. (2016) conducted a study on heavy metal immobilization in serpentine soil by producing woody biochar from *Gliricidia sepium* (Jacq.) where tomato plants (*Lycopersicon esculentum* L.) were employed in a 6-week pot

Table 11.2 The impact of biochar feedstock application on metal bioavailability and content in soil

Biochar feedstock	Pyrolysis conditions (°C)	Effect on heavy metal	References
Sugarcane bagasse biochar	450	Concentrations of Pb, Cu, and Cd metal in cabbage plants were considerably reduced as the biochar application rate was increased in topsoil	Nie et al. (2018)
Sewage sludge biochar	500	Plant availability of the Cu, Ni, Zn, Cd, and Pb metals has been significantly reduced in Mediterranean soil	Méndez et al. (2012)
Rice husk biochar	500	Decreased levels of Cu, Zn, and Cd heavy metals in the soil from wetlands	Gholizadeh and Hu (2021)
Corn straw biochar	400	Adsorption of metals Cd and Pb from water and soil	Chi et al. (2017)
Peanut shell biochar	350–500	Biochar converted acid-soluble Pb and Zn to reducible bound speciation, which decreased the bioavailability of Pb and Zn in the soil	Chao et al. (2018)
Gliricidia sepium (Jacq.) biomass-derived biochar	300 and 500	Efficiency of immobilization for Ni, Mn, and Cr in tomato plant (*Lycopersicon esculentum* L.)	Bandara et al. (2016)
Wheat straw biochar	450	The organic functional groups in wheat straw biochar assisted in absorbing, storing, and relocating too much bioavailable Cd from solutions and soil that was polluted with the heavy metal	Cui et al. (2019)

experiment with biochar application rates of different concentrations. After germination, the plants on the control treatment were unable to survive, whereas all of the seedlings typically flourished on biochar-modified soils; the results showed that biochar emerged as the most effective method for immobilizing metals, as evidenced by immobilization efficiencies of 68%, 92%, and 42% for nickel (Ni), manganese (Mn), and chromium (Cr), respectively (Bandara et al. 2016).

Table 11.2 shows the impact of biochar feedstock application on metal bioavailability and content in soil.

11.6.2 Modification of Biochar for Assisted Remediation

Recent studies have concentrated on biochar modification using unconventional structures and surface properties to improve biochar's capacity for environmental remediation and overall positive impact (Rajapaksha et al. 2016). Efforts have been made to change biochar to have a higher porosity, surface area, or surface functional group content. Altering biochar can be done in several ways, including chemical,

Table 11.3 The impact of modified biochar feedstock application on metal bioavailability and content in soil

Modified biochar	Preparation	Effects	References
Thiol-modified rice straw biochar (RS)	Produced using mercaptoethanol in the esterification process	Remediation of Cd and Pb from polluted soils	Fan et al. (2020)
Magnetic wheat straw biochars	Wheat straw biochars magnetized with iron oxide	Removed Pb from polluted soils	Gong et al. (2020)
Oxidized and thiolated pig manure biochar	H_2O_2 and 3-mercaptopropyltrimethoxysilane were used to oxidize and thiolate pig manure	For low Cd concentrations, oxidized biochars showed the highest levels of sorption. Compared to unmodified and oxidized biochar, thiolated biochar demonstrated increased Pb sorption	Wang et al. (2021)
Bismuth-impregnated biochar	Wheat straw-derived biochar that has been treated with bismuth (BiBC)	By controlling ferrolysis, bismuth-impregnated biochar (BiBC) reduced the bioavailability of arsenic in paddy soils	Zhu et al. (2019)
Modified coconut shell biochar (MCSB)	Modified coconut shell biochar (MCSB) produced from coconut shell biochar (CSB) using a combination of ultrasonication and hydrochloric acid pickling	Immobilization of Cd, Ni, and Zn in sandy soil	Liu et al. (2018)

physical, and magnetic methods and through the impregnation of mineral oxides (Godwin et al. 2019). The effects of applying modified biochar feedstock on metal bioavailability and content in soil are shown in Table 11.3.

The effectiveness of soil heavy metal immobilization and the mechanisms of a novel phosphorus-modified biochar synthesized using K_3PO_4 were studied by Zhang et al. in 2020 (produced by pyrolyzing with biomass feedstocks of bamboo, rice husk, wood, and cornstalk pre-impregnated with potassium phosphate). According to the findings, the phosphorus (P) compounds in modified biochar played a substantial role in the immobilization of copper (II) and cadmium (II) by creating precipitates or complexes with these elements at a ratio of between two and three. The acid-soluble forms of copper (II) and cadmium (II) ions might be transformed into more stable forms with the assistance of phosphorus-modified biochars. In addition, compared to bamboo and wood P-assisted biochars, the modified cornstalk and rice husk biochars show greater immobilization efficiencies for Cd (II) and Cu (II), with percentages ranging from 14 to 24% and 19 to 33%, respectively, for each element. Phosphorus also improved the extraction and mobility of arsenic, despite the fact that the input did not change. According to this study's findings, phosphorus-modified biochar can be used as an innovative soil rehabilitation technique for heavy metal-polluted soils (Zhang et al. 2020).

Using thiol-modified rice straw biochar and mercaptoethanol in the esterification process, Fan et al. (2020) looked into the possibility of restoring contaminated soils that had been affected by cadmium and lead and lead poisoning. The thiol groups successfully placed onto the surface of the biochar served a function in the complexation of metal ions. During the 28-day incubation trials with thiol-modified rice straw biochar, surface complexation reduced the available cadmium in the soil by 34.8–39.2%. In addition, it reduced the available Pb-lead in the soil by 8.6–11.1% (Fan et al. 2020).

According to Liu et al. (2018), modified coconut shell biochar (MCSB), which was produced from coconut shell biochar (CSB) using a combination of ultrasonication and hydrochloric acid pickling, which greatly enhanced the surface functional groups and microcosmic pore structure, could be used as an ameliorant to immobilize heavy metals in contaminated soils because it outperformed CSB in immobilizing metals. Therefore, sand soil samples were subjected to an incubation period of 63 days at a temperature of 25 °C with the addition of MCSB or CSB at concentrations of 0%, 2.5%, and 5%. According to the findings, the addition of 5% MCSB resulted in a reduction in the acid-soluble concentrations of Cd (30.1%), Ni (57.2%), and Zn (12.7%), respectively (Liu et al. 2018).

Thermal pyrolysis of iron-treated cedar sawdust, as shown by Wan et al. (2020), can be used to manufacture adsorbents based on magnetic biochar that contains Fe_3O_4 particles embedded in a porous biochar matrix. These adsorbents can then be utilized to remove contaminants from aqueous solutions. According to the findings, 20–30% of the arsenic, cadmium, and lead were simultaneously removed within 24 h after the adsorbent was added to a multi-contaminated soil slurry and then separated from the soil. This method has considerable potential for treating heavy metal pollution in soil and aquatic ecosystems (Wan et al. 2020).

11.7 Conclusion

In conclusion, biochar provides a plethora of potential for boosting environmental sustainability. This could be the one option for waste treatment and lowering environmental pollution. The low feedstock cost and the simple processing procedure also make biochar useful. Furthermore, biochar's characteristics can aid in adsorption and immobilization via complexation, electrostatic interaction, and ion exchange, among other things. In addition, biochar's physicochemical features enable it to sequester carbon in the soil, improve composting, develop biochar-based organic fertilizers, clean up contaminated soils, improve soil quality, reduce groundwater and surface water contamination, and remove pollution.

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Biomass-Based Engineered Materials for Soil Remediation

12

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Contents

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Abstract

It is an undeniable fact that modern human civilization is proliferating at the cost of irrevocable damage to the primary natural resources, i.e., land, water, and air. Among these, land is one of the most crucial components as it sustains all the terrestrial life-forms. Sadly, reckless anthropogenic activities are deteriorating the soil quality at an alarming rate. Thus, soil remediation is demanding immediate attention of the scientific community. Though various conventional techniques have been developed for soil remediation, their inefficiency impels the researchers to probe for more effective and greener pathways. In that respect, biomass-based hybrid materials prove to have a huge application potential, since these engineered materials exhibit superior properties, such as high chemical resistance, large surface area, high porosity, and greater sorption capacity. Considering the significance and growing awareness of the concerned domain in the recent years, this chapter attempts to provide an overview of the synthesis and applications of various biomass-based materials for effective soil remediation. In conclusion, future prospects and the associated challenges have also been highlighted.

Keywords

Soil remediation · Biochar · Biomass · Bioengineered materials

12.1 Introduction

Soil performs crucial ecological functions that are beneficial for both natural and anthropogenic systems. The ability of the soil to conduct these functions is affected by some disturbances, which has an impact on ecosystem processes as a whole (Volchko et al. 2014). Few of the widespread disturbances are the effects of human activity, including resource exploitation, intensive farming, fast industrialization, war, and military training (Fayiga and Saha 2016; Jiang et al. 2018), that leads to the deposition of different types of contaminants. Due to the continual interactions between soil, water, and air, soil pollution is a significant environmental issue that puts ecosystems and human health at risk. According to estimates, in China, about 16.1% of soils are polluted with organic and toxic metal contaminants. Serious health issues might be caused by toxic substances in soil (Zhang et al. 2019b). Several organic and inorganic pollutants like petroleum hydrocarbons, polycyclic aromatic hydrocarbons (PAHs), polychlorinated naphthalene (PCN), perfluorochemicals (PFCs), and various radioactive pollutants and heavy metals have severely polluted the soil (Anning and Akoto 2018; Dardouri and Sghaier 2018). Exposure to such hazardous pollutants has significant negative effects on health, including cancer, neurological problems, weakened immune systems, organ dysfunction, as well as physical and mental illnesses (Fig. 12.1). The burden on society and terrestrial ecosystems has significantly increased because of the

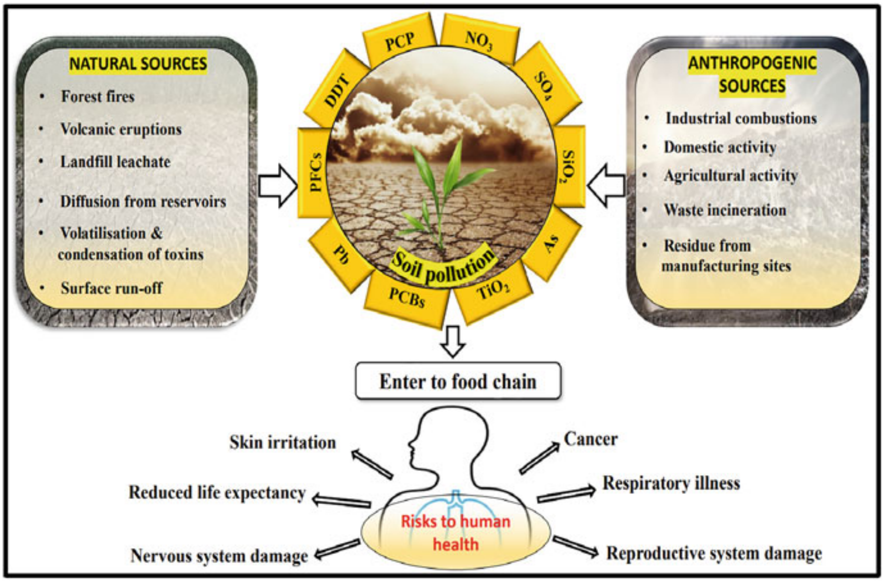

Fig. 12.1 Schematic representation of the anthropogenic and natural sources for soil pollution and their consequences (PCP pentachlorophenol, As arsenic, PCBs pentachlorobenzene, SO_4 sulfate, Pb lead, TiO_2 titanium dioxide nanoparticles, SiO_2 silicon nanoparticles, NO_3 nitrate, DDT dichlorodiphenyltrichloroethane, PFCs perfluorochemicals)

extensive and rapid spread of pollutants like heavy metals on agricultural land. Contamination in croplands can expose heavy metals such as mercury, lead, nickel, arsenic, and cadmium at almost 82.4% of the samples through soil–plant–food chain. The rest of the samples are polluted by organic contaminants like dichlorodiphenyltrichloroethane (DDT) and PAHs (Zhao et al. 2015). For instance, the World Health Organization lists mercury in top ten substances of concern (WHO 2017). As(III) has caused a number of environmental issues like human carcinogenicity due to its high toxicity (Feng et al. 2018). The use of arsenic pesticides, industrial pollutant discharge, and mining are the major anthropogenic activities attributed to continuous degradation and dispersed arsenic contamination (Ghosh et al. 2014).

The parent material of the soil (lithogenic source), as well as numerous anthropogenic sources, is the primary cause of heavy metal contamination. Most of the heavy metals are found naturally in soil-forming materials, often in the forms that are not easily accessible to plants. The minuscule levels of heavy metals (1000 mg kg^{-1}) that naturally occur in soil due to deterioration of parent materials make them scarcely poisonous. The heavy metals basically turn into contaminants in the soil environments due to the following factors: (1) their generation rate through artificial cycles is faster than that of natural processes; (2) they are switched from mining to random places with a direct exposure possibility; (3) high concentration of metals is present in waste products; and (4) based on the chemical form, metals may become more accessible in the receiving environmental system (D'Amore et al. 2005). It has been found that the organomercuric form of mercury inhibits brain function, while Hg^{2+} affects the lung and kidney (Clarkson and Magos 2006). Due to carcinogenic effects of PAHs present in the soil, exposure to such soils could be a severe threat to human health (Pei Zhang and Chen 2017). Lung cancer, stomach pains, ulcers, vomiting, diarrhea, skin issues, genetic changes, and various other human diseases are also caused by toxic metals. Itai-itai disease results in kidney failure and fragility of the bones and was first reported in Japan around the beginning of the twentieth century due to Cd poisoning through drinking water and rice contaminated by Cd (Shen et al. 2019).

12.1.1 Importance of Soil Remediation

Even though governments and academic institutions have developed several effective interventions, soil contamination persists as an important environmental issue that prevents socioeconomic progress. Soil is one of the major environmental components that contain two major contaminants like persistent organic pollutants (POPs) and heavy metals, which needs to be remediated. Contamination of soil interferes or prevents various soil functions that harms human health. As a result, removal of contaminants is necessary to reduce the exposure risk and improve soil quality to maintain ecosystem. To ensure sustainability of the remediation process, "greener" remediation technologies are encouraged by introducing the "green and sustainable remediation" (GSR) movement (Hou and Al-Tabbaa 2014; Zhang et al. 2020b). Therefore, it is essential to investigate remediation techniques with a reduced carbon footprint that provides greater environmental sustainability.

12.2 Techniques for Soil Remediation

Excavating the contaminated soil, putting it in a landfill, and then backfilling the area with new material are a widely used technique for handling soil contamination. High energy costs and scarcity of resources available naturally for backfilling make this technique complicated. Controlling the sources and improving the effectiveness of the remediation technology are both essential for complete removal of contaminants from polluted soil. For soil cleanup, a variety of remediation technologies have been developed globally, including thermal remediation for Hg (Hseu et al. 2014), soil washing for As (Ko et al. 2006), chemical leaching for Cd (Makino et al. 2007), solidification/stabilization for Zn (Al-Wabel et al. 2015), and phytoremediation for Pb (Babu et al. 2013). Cost, long-term effectiveness/persistency, commercial viability, public acceptability, and physicochemical qualities such as mobility, toxicity, and volume are the important variables impacting the applicability and choice of such technologies.

Two major categories of remediation technologies are in situ and ex situ remediation methods. Flowchart of different types of soil remediation techniques is

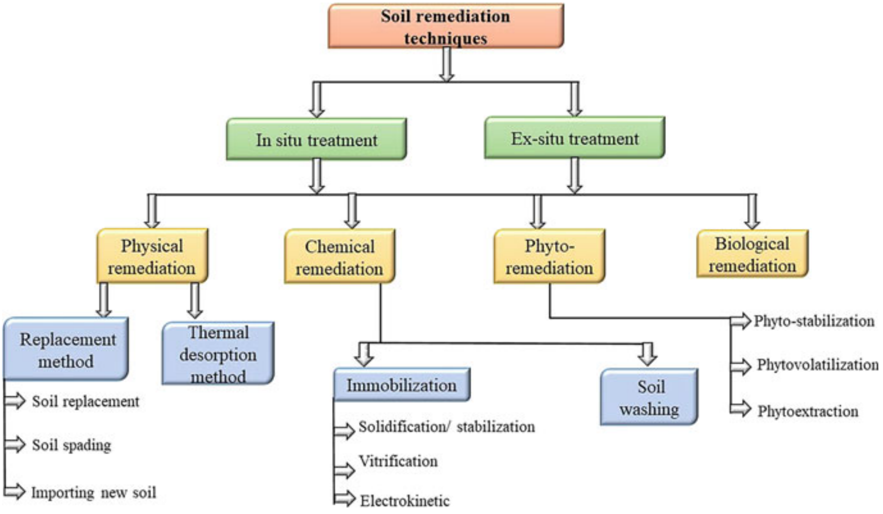

Fig. 12.2 Flowchart of various soil treatment techniques

depicted in Fig. 12.2. Both the techniques have benefits and drawbacks depending on the soil characteristics, soil condition, and pollutant content.

12.2.1 In Situ Remediation Technologies

It is an effective and affordable ecological remediation method for the treatment of polluted soils. The main advantage of "in situ treatments" is that soil that is contaminated does not need to be evacuated. It includes a range of techniques for the remediation of polluted soils without eradicating them from the site. Two categories of in situ treatment are solidification/stabilization treatment methods and biological/chemical treatment methods (Hussain et al. 2022). To decrease the pollution below standard levels, these remediation approaches may be employed independently or in combination. By using in situ treatment, soils remain in place, which lowers the possibility of increased contamination due to resuspension of pollutants. Because handling soils is relatively easy, in situ remediation technologies lower the exposure risk and subsequent soil spills. Additionally, these treatments help to decrease mobility and volume of toxic materials, as well as their subsequent emission and loss to the atmosphere. The significant disadvantage of this method for removal of contaminant is its less proficiency than "ex situ remediation" technique.

12.2.2 Ex Situ Remediation Technologies

Ex situ remediation, which treats polluted soils elsewhere by excavation, is not cost effective (Kuppusamy et al. 2016). Because excavation is expensive and exposes workers to health risks from contaminants, the preferred method is in situ remediation. However ex situ treatment often provides more consistent results, is easier to monitor, and requires less time to complete than other methods to effectively remove contaminants despite the high expense. Ex situ treatments mainly comprise electrical, chemical, physical, biological, and thermal treatment. Generally, digestible physical, electrical, and chemical methods have been condensed in a single category known as physicochemical treatment. The purpose of this treatment is to destroy and segregate the contaminants depending on the physiological properties of the pollutants and medium (Zhang et al. 2021). Using decontaminated soils for landscaping is possible after ex situ treatment. Equipment for these treatments is easily accessible and typically neither engineering nor energy intensive.

12.2.3 Physical Method of Soil Remediation

This technique involves soil replacement procedure (Derakhshan Nejad et al. 2018, b) and thermal desorption methods (Samaksaman et al. 2016). Land excavating method uses non-contaminated land to replace the polluted land completely or partially in order to reduce the contamination and to improve soil quality. This technique can reduce the environmental impact of contaminants by adequately separating the soil and ecosystem. This method is expensive and fitting only for land in small regions. The three types of soil replacement techniques are as follows: (1) soil spading, (2) soil replacement, and (3) importing non-contaminated soil. In land replacement technique, fresh/new soil is used to replace contaminated soil. This technique can be used to treat small-scale contamination. However, to accomplish dilution and natural deterioration, soil spading technique is used, i.e., digging the contaminated soil out and causing the contaminant to disperse. Importing new soil involves covering the surface of the polluted land with a significant amount of non-polluted soil to lower pollutant levels. In thermal desorption technique, infrared radiation is used to volatilize the contaminants (e.g., Hg, As) and steam, and microwaves are used to heat the contaminated soil (Derakhshan Nejad et al. 2018b).

12.2.4 Chemical Method of Soil Remediation

Chemical remediation process involves addition of chemicals in the polluted soils to remove or stabilize contaminants from contaminated surfaces. This process converts the polluted soils into less harmful forms that become useful for plants, waterbodies, and human beings. Metallic oxides, clays, or biomaterials are generally used for chemical treatments. Two different types of chemical remediation techniques are immobilization method and soil washing (chemical leaching) Tampouris et al. 2001.

12.2.5 Phytoremediation

In this technique, green plants are utilized in fixing contaminants that lowers the risk of environmental damage. The three major types of phytoremediation techniques are phyto-stabilization, phytovolatilization, and phytoextraction. The main feature of this technique is that it relies on the solar energy-driven technology. It is an economic technique that can be implied to treat soil having a mixture of contaminants without producing secondary waste. The major disadvantage of this method is that it requires a large span of time (Sarwar et al. 2017).

12.2.6 Biological Remediation

Biological remediation/bioremediation is an eco-friendly technique where microorganisms are used for treating pollutants through intrinsic bioremediation techniques (Aparicio et al. 2022). Addition of several enhancing agents (electron donors, electron acceptors, microbes, and nutrients) will enhance the capacity of such technique that results in enhanced bioremediation. Different types of mechanisms like precipitation, intracellular accumulation, extracellular complexation, and oxidation–reduction reaction are involved in this remediation method. This technique is useful for the treatment of industrial wastes, treatment of mining sites, and cleansing sewage sludge (Ye et al. 2017).

12.3 Bioengineered Strategy for Soil Remediation

Soil contamination causes several environmental problems, lowers the quality of agriculture, and has negative impact in all forms of life. The existing conventional physicochemical technologies (soil washing, vitrification, soil replacement, and electrokinetics) have shown to be efficient for treating polluted soils. Nevertheless, certain minor and major defects in these technologies continue to put them in trouble. High cost, poor feasibility, unsustainability, and inefficiency are some examples of this. Additional methods have the potential to deteriorate soil quality and remove other precious metals or only work in specific circumstances as low carbonate levels and insufficient soil permeability (Hou and Gao 2003; Khalid et al. 2017). Other techniques such as stabilization and solidification have the potential to trap pollutants but are unable to remove, alter, or destroy the pollutants. On the other hand, bioremediation process is more economic and environmentally beneficial and consequently garnered more attraction in recent times. However, there are certain drawbacks of using bioremediation techniques. For instance, phytoremediation technique shows slower rate of accumulation of pollutants as a result of using of hyperaccumulators, which are often extremely slow growing.

In laboratory-scale experiments, it has been shown that other biological techniques (bioaugmentation, digestate, etc.) provide significant possibilities for bioremediation of organic-inorganic pollutants and heavy metals. However, only a small number of industrial and field applications have been made to ascertain the feasibility and viability of these technologies in the environment. Particularly, application of biochar in environmental engineering is one such technology that has attracted more attention. Recently, researchers have found that using biochar generated from biomass is a viable way to reduce contamination of polluted soil. Such materials played an important role for enhanced bioremediation by serving as a strong, sustainable adsorbent. Pyrolysis conditions, type of biomass material, and carbonization method largely affect the efficiency of biochar for adsorption of pollutants. During the last decade, implementation of biologically and chemically modified biochar materials to enhance the effectiveness of pollutant removal capacity has gained large interest. Hence, the development and application of bioengineered biomass-based materials and their composites in contaminant and risk management, linked with the remediation of contaminated soil, have become one of the emerging areas of research.

12.4 Biomass

Shortage of nonrenewable resources and environmental issues have pressurized the researchers to think of sustainable and cost-effective resources that can be obtained via green routes to develop advanced functional materials. Researchers have identified biomass as one of the resources that can meet the demands of nonrenewable resources and have various potential applications. Biomass can be described as plant-based organic matters, which are synthesized via photosynthesis to produce carbohydrates. Apart from plants, biomass can also refer to animal wastes, industrial wastes, agricultural wastes, and industrial and urban wastes.

12.4.1 Biomass Feedstocks

Plant and animal resources as well as any other materials derived from their wastes can be included in the biomass feedstocks. Biomass feedstocks mainly cover lignocellulosic materials, including wood and agriculture wastes and non-lignocellulosic materials such as food wastes and industrial and urban wastes (Janu et al. 2021). These biomass resources can be converted to different advanced engineered materials directly or after a chemical/physical treatment. Biomass feedstocks can be classified into five main sources, livestock wastes, woody biomass, agricultural biomass, aquatic biomass, and industrial and urban waste (Fig. 12.3) (Jeguirim and Limousy 2019).

These feedstocks can be used to produce materials like biochars, which have various applications in land and water remediation. In Table 12.1, we have compiled various biomass sources for char production and its applications.

Plant resources are the oldest biomass derived from forests, woodlands, and different plantations. Woody biomass residues in forms of sawdust, chips, barks, shavings, etc. generated in large amount from all over the world can be converted to

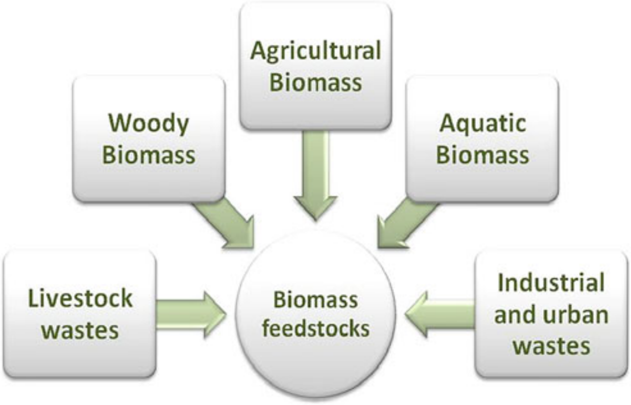

Fig. 12.3 Schematic outline of different biomass feedstocks

various potential resources. Moreover, wood is a natural composite material comprising natural fibers, cellulose, hemicellulose, and lignin and other biomaterials, which have major emerging applications in various fields (Papageorgiou et al. 2021). Nowadays, the materials derived from wood have been explored in areas such as electronics, optics, catalysis, biomedical devices, and energy.

Agriculture biomass includes the residues from agriculture crops such as husks, straws, stover, pulps, and other by-products. Some of the major agriculture residues for biochar production are paddy straws, sugarcane bagasse, palm kernel shells, empty fruit branches, wheat, and corn straws. A number of biomasses produced from agriculture have been used for soil enhancement and its remediation. Biochar production from agriculture wastes is recognized as an interesting route for development for advanced engineering products for pollution control.

Aquatic biomass is another important category of biomass feedstock that has been immensely used in water and soil remediation. Chars derived from these biomasses have a high content of carbon and can enrich the soil by adding up nutrients. Microalgae, macroalgae, and marine and freshwater plants are the main sources of aquatic biomass.

A large number of livestock feces is being generated every year around the globe, which puts the ecosystem at great risk. Therefore, converting these animal manure to char is an interesting technology for reducing and endorsing these wastes. Bio-oil and gas obtained from animal wastes can be used directly as fuel, and biochar has a wide range of applications such as fertilizer, adsorbent, catalysis support, and energy storage. Numerous studies were done on soil remediation and its enhancement from biomass derived from livestock wastes.

Waste from cities and industries that is accumulating in landfills has become a serious ecological and public issue across the world. Therefore, new strategies have been made for minimizing these wastes by converting them into useful materials for energy production and other advanced materials. Urban wastes mainly include household and commercial wastes such as metal, glass, paper, plastic, and food.

Table 12.1 Biomass sources for char production and its applications

Biomass sources	Form/part	Methods of char preparation	Operating conditions	Applications	References
Rubber wood	Sawdust	Slow pyrolysis	10 g, 5 °C/min, 300–700 °C, 1–3 h	Property characterization	Shaaban et al. (2014)
Cypress	Sawdust	Slow pyrolysis	5 °C/min, 500 °C, 1 h	Biofertilizer	Haddad et al. (2018)
Rape sunflower	Petals and seeds	Slow pyrolysis	30 g, 30 °C/min, 550 °C, 1 min	Biochar for soil management	Sánchez et al. (2009)
Danshen	Herb residues	Slow pyrolysis	10 °C/min, 250–800 °C, 3 h	Adsorption of sulfamethoxazole	Lian et al. (2014)
Scenedesmus dimorphus	Algae residues	Slow pyrolysis	40 °C/min, 500 °C, 100 mL/min	Adsorption of cobalt	Bordoloi et al. (2017)
Spirulina platensis	Microalgae residues	Pyrolysis	450 °C, 2 h	Methylene blue adsorption	Nautiyal et al. (2017)
Water hyacinth	Leaves and stem	Slow pyrolysis	15 g, 30 °C/min, 300–600 °C, 10 min	Chromium adsorption and reactivity	Lin et al. (2018)
Municipal solid waste	Paper, textiles, plastics, organic wastes, etc.	Slow pyrolysis	400–600 °C, 30 min	Removal of aqueous As(V)	Jin et al. (2014)
Rice-straw biochar and calcite	Straw residues	Pyrolysis	500 °C, 2 h	Ni removal from soil	Ali et al. (2020)
Orange peel		Oven dried and finely grounded	80 °C, 12 h	Cadmium removal	Akinhanmi et al. (2020)

On the other hand, industrial wastes include medicinal wastes, textile wastes, waste lignin, paper sludge, sewage sludge, metallic wastes, and petrochemical residues. Char production from urban and industrial wastes is becoming a hot research topic for degradation of environmental pollution.

12.5 Biochar (BC)

The complexity that soil bears creates immense challenges for soil remediation as they are expensive, time consuming, and hard to handle. Various methods for soil remediation have been discussed where sustainable materials were particularly emphasized due to their green aspects. Out of all the aforesaid materials, biochar, a carbonaceous substance, produced when biomass is gasified and subjected to pyrolysis, is a very useful and abundant material that can be easily derived from various biomass found in nature. BC's unique properties, such as its resistance to degradation, negative charge, and large internal surface area, make it ideal for the rehabilitation of contaminated soils (Lua and Guo 1998). BC's surface has a significant negative charge, which draws positively charged metals and organic molecules from the soil solution to its interior surface. By doing this, it will be possible to decrease the number of hazards in the soil solution along with their current and potential availability for microorganism's uptake (Beesley et al. 2010; Mukherjee et al. 2011).

12.5.1 Methods of Preparation of Biochar

Carbonaceous material made from biomass by applying temperature above 300 °C is called biochar.

Different methods have been adopted to prepare biochar, which are mainly divided into microwave carbonization, hydrothermal carbonization (HTC), and pyrolysis. Biochar has various physicochemical characteristics, such as number of functional groups, ash content, specific surface area, pore size, and yield, that mostly depend on BC's preparation methods and raw materials. Among the other preparation methods, BC's production from HTC is the highest (Sabio et al. 2016). However, microwave carbonization process is a controllable process with no hysteresis, energy efficiency, and fast heating (Afolabi et al. 2017; Liu et al. 2019). But BCs synthesized from microwave and HTC-controlled process are rarely considered as soil remediation material due to high content of organic materials.

Pyrolysis is an efficient method for the preparation of biochar by thermal degradation of biomass at elevated temperature. Electric heating or high-temperature medium is typically used in this procedure to achieve temperatures more than 400 °C in inert atmospheres.

The cellulose, hemicelluloses, and lignin content of the materials used in the production of biochar differs. Since different materials produce different amounts of cellulose, hemicellulose, and lignin in the biochar, its various physical and chemical compositions are different (Crombie et al. 2013; Williams and Besler 1993). Thermal degradation of hemicelluloses requires the lowest temperature in the range of 220–350 °C, while cellulose requires temperature between 315 °C and 400 °C. On the other hand, lignin covers a range from 150 °C to 550 °C or even 900 °C (Enders et al. 2012; Yuan et al. 2011). At a temperature below 500 °C, pyrolysis of hemicelluloses and cellulose is an exothermic reaction while at a temperature above 500 °C, the reaction is exothermic in nature (Park et al. 2015). It has been observed that biochar from straw contains more ash than that of other biochar, which is due to the higher Si content in straw (Enders et al. 2012; Yuan et al. 2011). It has also been investigated that the BC yield and the quantity of acidic functional groups (–COOH, –OH) decrease as the pyrolysis temperature rises, while the pH, content of ash, and basic functionalities increase. According to different heating rates, there are two types of pyrolysis method, fast pyrolysis (FP) and slow pyrolysis (SP) (Meyer et al. 2011). Thermal process in which biochar is degraded at a slow heating rate with limited supply of oxygen and long gas residence time is the slow pyrolysis process (Bruun et al. 2012; Mohan et al. 2006). The heating rate in FP process is a few hundred seconds and gives different products than SP (Laird et al. 2009). Biochars produced from FP and SP have different impact on the soil environment due to its different physical and chemical properties. Moreover, biochar obtained from slow pyrolysis contains complete pyrolyzed biomass fraction, while FP-BC consists of un-pyrolyzed labile fractions (Bruun et al. 2012).

Biomass feedstock can be effectively converted into biochar using hydrothermal carbonization. This process involves introducing the feedstock into water at relatively low temperatures, typically between 180 and 220 °C. When compared to SP, HTC produces biochar with higher carbon content, but when it is compared to biochar made through SP, which is less acidic and richer in oxygen-containing functional groups and surface charge, HTC produces biochar with higher acidity (Román et al. 2018).

Other techniques for transforming biomass include flash carbonization and torrefaction (Chen et al. 2015a), in addition to the microwave carbonization, hydrothermal carbonization, and pyrolysis. Thermochemical process such as torrefaction needs operating temperatures lower than 300 °C at a lower heating rate of 50 °C per minute, atmospheric pressure, a lengthy residence period of 1 h, and little or no oxygen supply (Van Poucke et al. 2019). In flash carbonization method, the flash fire is inflamed on the biomass-packed bed at a pressure of about 1–2 Mpa to convert the biomass into gas- and solid-phase products (Cha et al. 2016). At 1 Mpa, about 40% conversion of biomass to solid-phase BC takes place (Mochidzuki et al. 2003).

In addition to microwave pyrolysis, new pyrolysis techniques such as plasma cracking and laser technologies have also been created. Laser pyrolysis method uses small samples and allows for rapid cooling and heating, which successfully inhabits the development of secondary reactions (Metz et al. 2004). The synthesis of coke and syngas is the primary application of plasma pyrolysis technology. It can significantly enhance syngas production while lowering bio-oil yield as compared to conventional cracking technologies (Tang and Huang 2005; Yaman 2004). Since this technology is expensive and consumes a lot of energy, these new pyrolysis techniques are, nevertheless, hard to spread.

12.5.2 Biochar for Soil Remediation

Soil pollution is getting worse with time as a result of increased industrialization and anthropogenic activities. This is primarily because of the receding of soil area and increasing chemical pollution from substances like heavy metals, pesticides, acidic substances, petroleum wastes, and persistent organic pollutants. Along with heavy metals, organic pollutants such as medicinal residues, fertilizers, polycyclic aromatic hydrocarbons (PAHs), pesticides, polychlorinated biphenyls (PCBs), and antibiotics make up the majority of pollutants in soil (Renella et al. 2004; Yang et al. 2014). These pollutants have carcinogenic, teratogenic, mutagenic, and genotoxic effects that put human health at risk through the food chain. In addition to affecting crop yield and quality decline, it further degrades the quality of the air and water ecosystems (Tang et al. 2010).

Biochar was generally derived from waste solids and biomass, like animal, plant, and sludge waste. The ability of BC to eliminate contaminants, clean up polluted soil, and lower emission of greenhouse gases is the reason for its widespread use. Biochar provides benefits in immobilization of heavy metals and degradation of organic contaminants from soil due to its outstanding impact, economic advantage, and ease of use. BC is a promising amendment with great qualities that can be utilized to treat various types of soil contamination. However, not every biochar performs equally well in terms of enhancing soil quality. Biochar generated from plant biomass, agricultural residues, aquatic biomass, and urban wastes does not show equal performance in the enhancement of soil quality.

12.5.2.1 Biochar from Industrial and Urban Waste for Soil Remediation

Globally, the increasing levels of municipal and industrial trash in landfills are becoming a severe environmental and social problem. Therefore, new strategies for reducing these wastes have been developed by transforming them into beneficial materials for energy generation and other sophisticated technologies. Pathogens, contaminants, and toxic substances that are found in industrial and urban wastes can be eliminated by converting wastes to BCs, which is a potent method of waste eradication.

Karimi et al. have showed that BC made up of industrial sludge from sewages alters soil pH and electrical conductivity values. Additionally, BCs might change readily found cadmium and lead in soil into their more stable form, decreasing their bioavailability and mobility. This study also noted the effect of changing pyrolysis temperature that alters the volume and micropore size. With increase in temperature, volume and microporous area of BC decrease (Karimi et al. 2020).

One important factor affecting the porous characteristics of the biochar is the temperature used to create it. BC was produced in a study by Xing et al. by pyrolyzing sludge at temperatures of 900, 700, 500, and 300 °C. Outcomes showed a drastic decrease in the amount of Cu, Zn, As, and Pb (Xing et al. 2019).

Municipal solid waste has recently attracted interest as a means of waste management among the many feedstock (Ateş et al. 2013). Few studies have highlighted the use of BC made by solid waste from municipality, which decreases the amount of waste in landfills, as well as a material to clean up environmental contamination and add value to compost (Jayawardhana et al. 2016).

Cd adsorption mechanism on biochar, which is produced by pyrolyzing biophysically dried sludge from sewage at 900 °C, has been studied using static equilibrium experiments under various conditions. It was observed that with increasing pH, the removal ability increased, thus making pH the most significant element controlling the adsorption process. In contrast, temperature (between 15 °C and 35 °C) has a minor and insignificant impact on the adsorptive function (Chen et al. 2015b).

A composite of chitosan and textile waste BC (TWB) was used to remedy Cd-polluted soil. When chitosan was coated with TWB, the mobility of Cd was lessened and its availability to moringa decreased. The strategy for cleaning land contaminated with Cd by this method showed excellent result. The toxicity of Cd was also reduced, and availability of vital nutrients increased in the plants (Zubair et al. 2021).

The usage of recycled fibers in the paper industry is rising. De-inking paper wastes are produced in enormous quantities when pollutants, ink, coatings, and clay are removed to make recycled fibers. An intriguing alternative to waste valorization could be the production of BC by pyrolyzing the waste to apply it in repairing heavy metal-contaminated soil. In Zn-polluted soils, de-inked paper sludge-based BCs have been used under laboratory condition, soils was incubated, and soluble Zn was measured. It was found that the amount of mobile Zn decreased and Zn solubility dropped noticeably by BCs produced at higher temperature (Méndez et al. 2014).

12.5.2.2 Biochar from Livestock Wastes for Soil Remediation

Char production from livestock wastes is an interesting technology for the management of animal manure by reducing and valorizing these wastes. As farming of cattle increased rapidly for human needs, the waste generated from them has also heightened which poses threat to human health (Chen et al. 2018). Due to the increased potential of microbial transmission, cow manure has caused serious ecological and health issues (Chen et al. 2020b). Therefore, one of the major difficulties facing the livestock industry is the proper disposal of contaminants from cow manure. It is generally recognized that turning cow manure into biochar is an efficient way to reuse animal pollutants (Van Poucke et al. 2019). Numerous studies have shown that biochars made from cow dung can be used as wastewater adsorbents and land remedial materials, and both the methods were widely used in environmental cleanup (Clancy et al. 2013; Khan et al. 2020; Qin et al. 2016; Yue et al. 2019).

Though lodgepole pine BC had varying degrees of success for soil treatment, the removal of Zn and Cd using BCs obtained from cow dung and poultry litter showed satisfactory result. Moreover, when compost was added to either of the BCs, the soil demonstrated large production of switchgrass sprout and roots. Among them, when a mixture of 5% cow dung and 5% compost was used, a considerable decrease in Zn and Cd in the roots and switchgrass shoots was observed. There were significant performance differences among the BCs and compost combinations, when applied to mine-impacted soil and heavy metal to increase switchgrass productivity. The application of compost along with BCs considerably enhanced the growth of switchgrass. This may be explained by the elevated pH in soil, which encourages the immobilization of Zn and Cd, reducing the amounts of heavy metals found in soil. Therefore, generating designer biochars is a crucial managerial element for building effective mine-site phyto-stabilization programs (Meier et al. 2017).

Meier et al. used BC derived from chicken manure (CBC) to immobilize Cu for growing metallophyte *Oenothera picensis*. The CBC showed decrease in Cu uptake by plants by changing its spatial distribution, bioavailability, and mobility. Plant development was aided by the rise in nutrients that were available and the reduction in Cu toxicity. The enhanced microbial activity most likely also aided in the promotion of plant development and decreased the bioavailability of copper. Therefore, it was concluded that Cu-contaminated soils can be cleaned up with CMB (Novak et al. 2019).

12.5.2.3 Biochar from Agricultural and Plant Residues for Soil Remediation

Accumulation of hazardous compounds within the soil mainly causes soil contamination, which is difficult to manage with conventional treatments. Among the various technologies, remediation techniques using plant-based materials have gained attention for soil remediation and rehabilitation from several years due to their ability to improve soil conditions, potential benefits in terms of cost, and public acceptance. Biochar derived from various plant-based feedstocks has been employed for the remediation of contaminated soil (Table 12.2) due to their ease of preparation and versatile application.

Papageorgiou et al. have used wood waste as biomass source and converted it into biochar by pyrolysis, which was further implied for treating heavy metal and PAH-contaminated soil (Papageorgiou et al. 2021). The purpose of this study is to utilize wood waste-based biochar and evaluate its effect on the environment, considering the life cycle. The specific objectives are to (1) quantify and show the supplies and flows of metals and PAH present in contaminated soil, (2) assess the impact of these systems to the environment, and (3) manage contaminated soil by recovering energy from wood waste.

Soil contamination by cadmium has proven to be a severe environmental issue. For reducing its mobility through biochar, Bashir et al. have evaluated the study of effectiveness of biochar (from maize stover (MSB), rice hull (RHB), and rice straw (RSB)) on the mobility of Cd and its augmentation in Chinese cabbage (Bashir et al. 2018). The study demonstrated that raising the rate of biochar from 1.5% to 3% considerably enhances soil chemical properties (nutrients, organic carbon, and pH). Cd concentration reduced in $CaCl_2$ extract at 3% utilization rate, by 46.49%, 39.7%, and 58.6% of MSB, RHB, and RSB, respectively, which was proven by toxicity characteristic leaching procedure (TCLP) and simple bio-accessibility extraction test (SBET). RSB validated positive outcomes for immobilization of Cd and lowering of its bioavailability to reduce risks to food security.

Table 12.2 Use of biochar derived from various plant-based feedstocks for remediation of contaminated soil

S/N	Plant-based feedstocks	Pollutants	Remediation effect	References
1	Cotton straw chips	Chlorpyrifos and fipronil	Reducing bioavailability of both pesticides from the soil	Yang et al. (2010)
2	Red gum wood	Acetamiprid	Increase the sorption of acetamiprid by 52.3% for red soil	Yu et al. (2011)
3	Wheat straw	Atrazine and trifluralin	Lowering herbicide in soil using biochar amendments	Nag et al. (2011)
4	Rice straw	*Cu (II), Pb (II)*	Decreased acid-soluble lead and copper by 18.8–77.0% and 19.7–100.0%, respectively	Jiang et al. (2012)
5	Miscanthus straw	Cd, Zn, and Pb	Using 10% BC, lead, zinc, and cadmium were lowered to almost 92%, 87%, and 71%, respectively	Houben et al. (2013)
6	Soybean stover	Pb	Soybean stover-based BC was used in 20 wt.% to reduce lead leachability in military firing range up to 90%	Moon et al. (2013)
7	Rice, canola, soybean, and straws of peanut	Pb (II)	Treating soil with different BCs increased the adsorption of lead by 42.5%, 50.5%, 56.9%, and 66.8%, respectively	Jiang et al. (2014)
8	Unfertilized dates	Ni	Reduction of 53% of Ni by using BCs	Ehsan et al. (2014)
9	Peanut shell	PAH	PAH bioaccumulation reduces by 71–84%	Khan et al. (2015)
10	Rice straw	Cd, Pb, Zn	An increase of vegetable yield was observed by reducing metal bio-accessibility by 34–67%	Niu et al. (2015)
11	Rice straw, wheat straw	Imidacloprid, isoproturon, and atrazine	Stabilize the soil contaminated with organic pollutants	Jin et al. (2016)
12	Soybean stover	Pb and Cu	Immobilizing Pb up to 88% and Cu up to 87%	Ahmad et al. (2016)
13	Rice hull	Fomesafen	Increases the adsorption of fomesafen 4–26 times compared to unamended soil	Khorram et al. (2017)
14	Tomato green waste	Cd	Effectively reduces mobilization of Cd in soil by 35–54% and 34–76% reduction in the accumulation of Cd in the shoots of pak choi cultivars	Yasmin Khan et al. (2017)
15	Corncob	Bisphenol A (BPA)	Immobilization of BPA was observed due to mineral dissolution by BC	Li et al. (2017b)
16	Walnut shell, corn straw, and rice straw	Chrysene	Biodegradation rate of chrysene increases by 3–45%	Zhang et al. (2018a)

(continued)

Table 12.2 (continued)

S/N	Plant-based feedstocks	Pollutants	Remediation effect	References
16	Corn straw	PAH	Using rice root BC, a reduction of 2(+3)-, 4-, and 5(+6)-ring PAH uptake was observed up to 10%, 40%, and 40%, respectively, and PAH bioaccumulation reduced by 14%, 37%, and 46%, respectively	Ni et al. (2018)
17	Grape prune residue	Cd, Pb, Cu, and Zn	Decreased the mobility of Cu, Pb, Zn, and Cd by 70%, 62%, 49%, and 47%, respectively	Hamzenejad Taghlidabad and Sepehr, (2018)
18	Maize straw	PAH	Decreased 30% PAH from contaminated soil	Li et al. (2019)
19	Vegetable wastes	Pb	Achieved immobilization of Pb 87%	Igalavithana et al. (2019)
20	Peanut vine and rice straw	Cd	Cd exchange rate was lowered in biochar-amended soil by 35.80% and 28.48%, respectively, by two biochars	Chen et al. (2020c)
21	Rice straw	Cd	Reduction of Cd accumulation and enhancement in Cd immobilization in rice were observed using Si-modified BC	Sui et al. (2020)

Another field study revealed the use of *Brassica chinensis* L. (pak choi) as test plant in a field experiment to examine the impact of biochar (sugarcane bagasse) on the health of soil microbiota as well as the availability of lead (Pb), copper (Cu), and cadmium (Cd) in polluted land. This study reveals that, with increase in biochar application, concentration of Cd reduced by 8.5% and availability of heavy metals to plant roots and shoots considerably decreased (Nie et al. 2018).

Zhang et al. have conducted an incubation experiment using biochar from corncob, rice straw, walnut shell, and corn straw in order to determine how biochar properties, feedstocks, and heat treatment temperatures (HTTs) affect the biodegradation of PAHs, microorganisms' quantity, activity of enzyme, and microbial community shift in polluted land. Rather than the feedstocks, the HTTs had a stronger influence on microbial quantities and enzyme activity (Zhang et al. 2018).

Agricultural residue-based biochar shows superior property to reduced high surface area and ash content over biochar from feedstocks due to the presence of higher proportions of lignocellulose components (Cao et al. 2019; Shi et al. 2019). So, it has been considered that biochar made from crop leftovers is a potential substance for the restoration of soils that are polluted with trace elements (Bian et al. 2016).

Production of oil mallet and wheat chaff-based biochar at 550 °C on nascent plants in wetland such as *Juncus subsecundus* with various dosages and its effect in

Cd concentration under waterlogged soil conditions were examined by Zhang et al. in a glasshouse study.

By using wheat chaff biochar at lower concentration rates (0.5%), greater Cd removal results were observed. By using oil mallet biochar treatment, no significant difference was observed. Both biochars lowered Cd accumulation; however, because of the interaction between the biochar and the wet environment, *Juncus subsecundus* growth was not improved (Zhang et al. 2013).

Liang et al. employed rice husk-derived biochar to remedy contaminated land near Dongting Lake. 40 g Biochar, prepared using pyrolysis at 500 °C, was added to 400 g of soil, and the mixture was incubated for no more than 2 months. The findings showed that Zn, Cu, and Cd levels dropped in concentration (Liang et al. 2017).

Undoubtedly, the effectiveness with which heavy metals are removed from soil by biochar depends on various biomasses they are derived from. This might be caused by the varied structures of the biochar made from various types of biomasses. In an investigation, two samples of biochar were created by pyrolyzing pig manure and corn straw. The outcomes displayed significant reduction of Hg, Cd, Pb, and Cr. For instance, the usage of biochar samples using pig manure and corn straw resulted in reduction in the concentration of Hg from 0.79 to 0.34 and 0.59 mg/kg, respectively (Zhang et al. 2018c).

12.6 Engineered Biochar and Composites for Soil Remediation

Various modifications to activate biochar for improving its physical and chemical properties are becoming an emerging trend (Wang et al. 2020). “Engineered biochar” refers to the modification made to improve its properties using physical, biological, and chemical means to achieve specific objectives (Panahi et al. 2020). Innumerable attempts to activate biochar without external doping agents have been performed including steam, gas, alkalis, acids, microwave, and oxidants (Panwar and Pawar 2020; Sajjadi et al. 2019b). A different strategy is to make composites of materials aside from biochar itself that have distinct and desirable properties. The range of applications for biochar for immobilization (Bandara et al. 2020), soil redox management (Yuan et al. 2017), carbon sequestration (Ennis et al. 2012), and greenhouse gas reduction (Kammann et al. 2017) accelerated the interest in its study. But compared to pristine biochar, biochar nanocomposites have shown promise for improving soil qualities through carbon mitigation (Bolan et al. 2022), nitrogen enrichment (Khajavi-Shojaei et al. 2020), microbial activity (Zhang et al. 2020a), and elimination of toxic heavy metals (Gholizadeh and Hu 2021). Therefore, biochar and their composites impart great interest as a greener and more economic material. Here, in this section, we will discuss how we can tailor properties of biochar by modifying it and with addition of different agents such as metal oxides, surface agents, and nanomaterials. Also, we will address the advantage of biochar composites over their relatively pure form.

12.6.1 Modification of Biochar

Researchers investigated the effects of several modification techniques to produce biochar with better properties. In order to obtain the desired outcome, modification of the pure biochar using chemical or physical techniques is carried out (Fig. 12.4). Various parameters like the type of activator, activation period, temperature, and soaking period have significant influence on the properties of biochar.

12.6.1.1 Chemical Oxidation and Reduction

Surface oxidation of biochar to increase oxygen functionalities such as -COOH and -OH increases its hydrophilicity. The biochar's pore structure and size would alter concurrently, and this would ultimately result in an improvement in the biochar's ability to adsorb polar adsorbates. HCl, HNO_3, H_2O_2, H_3PO_4, and other common oxidants are utilized (Sajjadi et al. 2019a). The biochar modified by HNO_3 has a higher concentration of acidic oxygen functionalities (Ho et al. 2014) and a higher NH_3-N adsorption, despite the fact that the surface area of biochar altered by HNO_3, H_2O_2, and HCl is similar to that of biochar treated by HCl. In terms of eliminating Pb pollution, biochar that has been treated by H_3PO_4 is superior to other acids. The extent of adsorption of Pb in biochar is enhanced by increasing porousness, surface area, and phosphate precipitation (Zhao et al. 2017).

Modification using alkalis is referred to as chemical reduction. Here, various reducing agents are introduced in order to increase the biochar's non-polarity. The porousness and surface area (SA) of biochar can also be increased by reducing the surface-located functional groups of biochar that results in improved adsorption

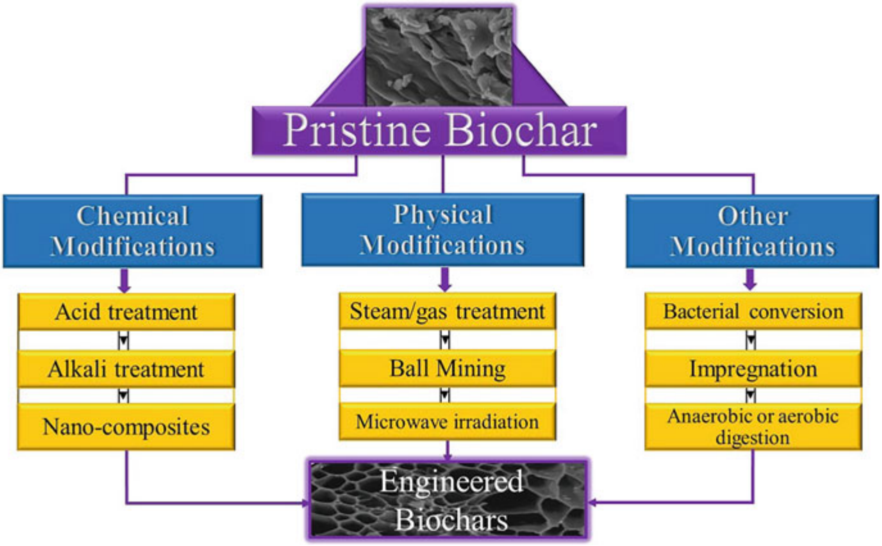

Fig. 12.4 An outline for modification of biochars

capacity for contaminants, particularly nonpolar adsorbates. Reducing agents such as NaOH (Li et al. 2017a), KOH (Wang et al. 2018), NH_4OH, and others are frequently utilized. Modification effects vary depending on the reducing agent. Li et al. (2011) used chemically reduced carbon produced from coconut shell using NH_4OH, NaOH, HNO_3, H_2SO_4, and H_3PO_4 to determine which altered biochar will best increase the ability to absorb volatile organic compounds (VOCs). The results demonstrate higher adsorption of o-xylene in alkali-treated carbon than acid-treated carbon due to increased surface area, porosity, and decreased oxygen functionalities, although acid treatment had the opposite effect.

12.6.1.2 Physical Modification

Physical methods for biochar modification are more affordable and environmentally beneficial compared to chemical approaches. With simple and moderate treatments, it enhances the chemical and physical characteristics of BCs, its permeability, and porousness. The most often employed methods for physically altering biochars include microwave irradiation, steam/gas activation, magnetization, and ball milling.

The mechanism of inducing porosity by steam/gas is due to elimination of the residues that are trapped inside the porous biochar (BC) structures as a result of incomplete combustion. Activation of BCs by carbon dioxide and hydrogen can be achieved through surface oxidation processes (Wang et al. 2019). As a result, compared to the pristine BCs, the steam-activated engineered BCs (E-BCs) exhibit increased adsorption capacity for methane and nitrogen dioxide.

Another developing method for altering BCs is microwave irradiation, which raises their temperature by 200–300 °C using microwave heating in a brief period of time. In comparison to E-BCs made by conventional pyrolysis, those made through microwave irradiation have larger surface areas and exhibit greater absorption for numerous contaminants (Li et al. 2016). The physicochemical characteristics of BCs, such as water-holding ability and cation exchange capacity (CEC), are greatly enhanced when microwave irradiation is combined with steam activation or impregnation (Lee et al. 2020).

Another typical physical modification technique is ball milling, which reduces raw BCs to powder or nanoparticles. The adsorption capabilities of BCs significantly increase because of the simultaneous increase in particle size and surface area (Lyu et al. 2018). Introducing chemicals while ball milling can change the chemical characteristics of the BCs like micropore structure and surface functionalities. A major drawback in using ball-milled BCs is that they can easily transmit via soil pores and may pose risk to groundwater. In addition, biochar stability after pollutant adsorption is a complication. Using an external magnetic field, magnetic BCs produced by chemical ball milling are easily recoverable. Reusable magnetic BCs have been noted to demonstrate effective adsorption for inorganic and organic contaminants from wastewater (Yi et al. 2020). Additionally, the magnetization procedure increases BCs' catalytic activity and surface charge, improving their suitability for environmental remediation.

12.6.1.3 Other Modifications

Feedstock when introduced to anaerobic digestions or bacterial conversion produces biofilms on the surfaces of BCs; this process is the biological modification of BCs. The generation of biofuel and biofertilizers, by aerobic or anaerobic digestion of waste biomass, creates economic value. BCs altered by pyrolyzed digestion of waste are reported to have strong anion exchange capacities, large surface areas, and hydrophobicity, which is extremely effective at removing cationic dyes and heavy metals (Wang et al. 2017). By creating biofilms, microorganisms improve BCs' efficiency in the removal of soil pollutants. Elimination of pharmaceuticals and other contaminants by immobilization and biotransformation processes using biologically modified BCs through biofilm has proven to be extremely promising (Li et al. 2020a).

Minerals impregnated in biochar have shown higher CEC, mineralogical structure of clay minerals, and surface charge that can be employed for soil pollutant removal (Yao et al. 2014).

The most popular clay minerals employed as inexpensive sorbents include montmorillonite, gibbsite, and kaolinite as well as iron oxides (Rajapaksha et al. 2012). Introducing functionality in biochar matrix was achieved by combining bagasse, bamboo, and hickory chips with the clay (montmorillonite and/or kaolin) by pyrolyzing for 1 h at 600 °C in N_2 atmosphere. Biochar serves as a good porous structure in biochar-clay composites to host and supports the distribution of the small particles of clay inside the matrix.

12.6.2 Biochar Composites

Due to all the constraints limiting the use of pristine BCs in environmental remediation, the concept of engineered biochars came into existence. Among them, chemically modified composites of biochar emerged as one of the most useful and popular, due to their high stability and various uses in multiple environmental remediation unlike their raw form. In addition to enhancing the physicochemical characteristics of BCs, composites of it combine the benefits of BCs with the additional materials. In many literature, biochar composites are divided into many categories. Here, we will classify biochar composite into major five categories, mineral-BC composites, metal-BC composites, carbonaceous engineering nanocomposites, microorganism BC composites, and layered double hydroxide (LDH)-BC composites (Wang et al. 2022).

There are essentially two methods for making biochar composites (Fig. 12.5):

- *Pre-treatment of biochar with different nanomaterials:* In this synthesis technique, biochar is doped with nanomaterials before pyrolysis to produce biochar composite. For example, Lawrinenko et al. (2017) used corn stover, alfalfa meal, and cellulose to synthesize biochars. These BCs were pre-wetted, either with $AlCl_3$ or $FeCl_3$, and thereby using programmable muffle furnace were slow pyrolyzed to 500 °C and 700 °C (i.e., highest treatment temperature) in N_2

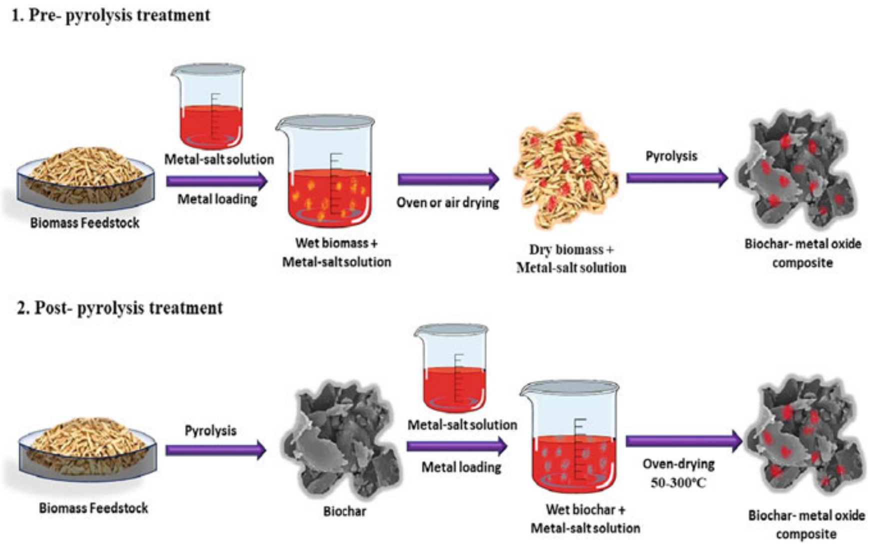

Fig. 12.5 Schematic representation of pre- and post-pyrolysis treatment used for modification of BCs

atmosphere. The biochar composite produced became surface functionalized by Al-O-C moieties resulting in higher (AEC) than pristine biochar at acidic pH.

- *Posttreatment of biochar with nanomaterials*: After pyrolysis, pristine BC may have enhanced qualities if impregnated with nanoparticles. Biochar is frequently treated via wet impregnation, heat treatment, and direct hydrolysis post-pyrolysis to produce biochar composites. Lin et al. (2019) employed Fe-Mn-modified BC to lower the amount of arsenic (III, V) present in soil by raising soil redox potential. Corn straw was used as a precursor to prepare BC by pyrolysis. Fe $(NO_3)_3$ and $KMnO_4$ were precoated on BC before pyrolysis for 30 min at 600 °C. The resultant composite, when compared to the original BC, had substantial arsenic removal efficiencies. This was brought on by the soil's elevated redox potential in the presence of the BC composite. The growth of crystalline and amorphous hydrous oxide bound of As was used to explain the process of arsenic reduction in soil due to the presence of Mn and Fe in BC composite.

12.6.2.1 Classification of Biochar Composites

Mineral-BC Composites

Minerals found in nature can effectively enhance soil remediation when used with biochar, which also results in increased soil fertility and helps with soil remediation.

Herath et al. (2020) conceived of montmorillonite as a silicon source as opposed to using it as a cation exchange material. The development of Si-ferrihydrite-mediated montmorillonite rich in Si-BC composite was effective in microbe-mediated immobilization of As in soil.

A nutrient-rich mineral known as struvite (NH_4MgPO_4) has long been used as a fertilizer. Struvite coprecipitated onto biochar may improve gradual liberation of PO_3^{4-} and favor metal immobilization (Li et al. 2020b) as well as improved fertility (Hu et al. 2019). Mineral additions can help lessen the potential toxicity of biochar made from waste materials, allowing for the productive use of a resource that might otherwise go to waste (Mumme et al. 2018).

For adsorptive immobilization of Pb (II) and Cd (II) in soil, a hierarchical porous biochar (HA-HPB) tailored with $Ca_{10}(PO_4)_6(OH)_2$ (hydroxyapatite) was created. Through the use of molten salt to assist the pyrolysis process, rice husk was converted into hierarchical porous biochar (HPB). HA-HPBs lowered the bioavailability of Pb and Cd up to 93% and 88%, respectively. Precipitation, complexation, ion exchange, and cation-cation interaction lead to the elimination of metals Pb (II) and Cd (II). Langmuir adsorption capacities for Pb (II) and Cd (II) were found to be 110.2 and 88.1 mg/g, respectively (Wu et al. 2022).

To reduce soil Pb mobility and bio-accessibility, a study investigated on Pb-polluted soils using Bauxsol™, a modified bauxite refinery residue (MBRR) (Burton et al. 2022). Four soils that had been polluted with lead from paint waste, shooting range activity, and smelting were used in this study. At low Pb loadings, Pb was retained by MBRR by surface-assimilated Al and Fe (hydr)oxides, while high Pb loadings result in the formation of $Pb_3(CO_3)_2(OH)_2$ (hydrocerussite). Bio-accessibility of lead during the intestinal phase was decreased as a result of Bauxsol™.

Elimination of pesticides in polluted land has become very crucial. Liu et al. (2022) used original BC (OBC), walnut shell BC, illite BC (IBC), montmorillonite-tailored BC (MBC), and kaolinite (KBC) to investigate metolachlor (MET). According to the findings, MBC was most stable, with IBC, KBC, and IBC all having higher thermal and chemical stability than OBC. Adsorption mechanisms and outcome of the kinetic fitting demonstrated that adding minerals to BC improved MET's physical adsorption. The main sorption processes were hydrophobic interactions, hydrogen bonds, and coordination bonds.

Metal-Biochar Composites

Iron species shows excellent improvement in the performance of biochar. The three main composite types are nZVI (nano-zerovalent iron)-biochar, FeO-biochar, and FeS-biochar. The mechanistic improvement, fabrication processes, and their applications have all been thoroughly explored in several literature (Lyu et al. 2020). Improved electrostatic interactions, precipitation, and surface complexation of iron-biochar composites favor the adsorption and immobilization of heavy metals and organic pollutants (Alam et al. 2020; Vickers 2017). Out of all the iron species, nZVI-biochar and FeS-biochar are two forms of iron-biochar composites that have a strong reduction capacity for organic pollutants and Cr (VI) (Chen et al. 2021). Additionally, reactive oxygen species (ROS) can be produced by oxidants when iron-biochar composites are used to oxidize organic pollutants (Diao et al. 2021).

The impact of FeS-based sludge BC on vanadium fractionation, mobility, bioaccumulation, and speciation in polluted land from mining place was investigated by Aihemaiti et al. (2022); after ferrous sulfate modification, amorphous FeOOH gets functionalized on BC surface. Vanadium mobility in soil was significantly inhibited by ferrous sulfate-treated biochar. Proteobacteria leads to biotic conversion of V(V) to V(IV) in soil.

A new biochar nanocomposite with g-MoS_2 coating was created by Yang et al. (2020) to treat ciprofloxacin. More π-electrons were provided by the composite than by the pristine biochar, improving the "π-π EDA interactions."

Yuan et al. (2022) created magnetic silicate composite biochar (MSCB) and silicate composite biochar (SCB) as a recoverable BC with the intent of reusing. The result showed that the prepared MSCB has strong magnetism and good hydraulic properties; after three cycles of "application-separation-desorption-reuse," the MSCB was used to remove Cd by either precipitation or pore interception up to 30.32–38.80% in the soil, while the SCB can remove 28.30–35.78%.

It is interesting that innovative trend to metal-co-doped biochar which inculcates phenomena like chemical-precipitation resulted in Mg-Al-biochar composites having excellent phosphate adsorption capability (Zheng et al. 2020).

Therefore, one of the simplest techniques for improving the characteristics of biochar is metal co-doping. The remediation of the environment with this technique has proven to be efficacious. To determine whether further applications are feasible, more research should be done. In many literatures, it has been proposed that nutrient (like Mg, Ca, and K) co-doped BC may directly boost fertility of soil and subsequently improve BC's capacity to sequester carbon. Also, co-doped biochars, if created appropriately, could release nutrients while immobilizing metals in soil (Mašek et al. 2019).

Carbonaceous Engineering Nano-Biochar Composites

Composites made of graphene and carbon nanotubes (CNT) with biochar improve the adsorption of organic pollutants. These carbonaceous tailored nanocomposites' exceptional adsorption performance is a result of the amount of π-electrons present in them. There are numerous organic dyes that contaminate groundwater and impair soil fertility. Carbonaceous designed nanocomposites may be utilized to adsorb and break down these organic dyes from the soil's groundwater.

Due to electrostatic interactions, composites of multiwalled carbon nanotube (MWCNT) and BC demonstrated high methylene blue adsorption capability (Inyang et al. 2014). It is interesting to note that a designed MWCNT-BC composite has a remarkable ability to encapsulate a phase transition material n-dodecane, for energy storage. BC composites had steady networks that encouraged surface tension and capillary forces to hold organic molecules in place (Atinafu et al. 2021).

A study demonstrated the performance of a new adsorbent for zinc (Zn) and copper (Cu) using poultry litter BC and graphene oxide composite (PLB-GO). In addition, its fertilizing benefits on plant growth, nutrient utilization effectiveness, and effect on soil fertility were investigated. PLB-GO demonstrated Zn and Cu adsorption efficiency that was 17.7% and 16.2% higher than that of pure PLB, respectively (da Silva Carneiro et al. 2022). It is also worth mentioning that according to Liu et al. (2016), cation interactions may also play a role in promoting CNT-BC and GO-BC composite for adsorption of pollutants.

Layered Double Hydroxide (LDH)-Biochar Composites

"LDHs are anionic clay minerals made up of layers of positively charged metal hydroxide and anions for charge neutralization in the interlayer region." Numerous LDH-BC composites with various M^{2+} and M^{3+} metal cations, such as Ni-Fe, Ca-Al, and Zn-Al, are employed extensively in pollutant adsorption (Wang and O'Hare 2012).

LDH composites are suitable materials that are frequently employed for the adsorption of pollutants because to their diverse features, which include high anion exchange capacity, improved coprecipitation, presence of hydroxyl groups for surface complexation, and hydrogen bonding.

A porous Mg/Fe-LDH@biochar composite synthesized by Zhang et al. has signified an excellent reduction property of agricultural pollutants (Zhang et al. 2018b). Following the inclusion of the composite, leaching of metals, NO_3, and NH_4^+ fell by 90%, 40%, and 60%, respectively.

It is essential to use highly effective amendments to reduce soil arsenic (III, V) in order to boost land quality and increase agricultural output. Using a straightforward coprecipitation technique, LDHs with three different M^{3+} like Cu, Zn, and Mg with M^{2+} as Al were functionalized using cornstalk BC. As a result, improved hydroxyl surface functionalities and thereby higher "anion exchange capacity" (AEC) by LDH@BCs were displayed for As (Gao et al. 2020).

To decrease the uptake of lead and uranium(U) by Indian mustard in U-polluted land, a novel "phosphorus-modified bamboo BC" (PBC) composite with Mg-Al LDH, i.e., PBC@LDH, was developed by Yin et al. (2022). U contamination of soil poses a major threat to both human health and ecological stability that results from uranium mill tailing (UTM). Lead and uranium absorption and translocation by Indian mustard might be inhibited by stabilizers. Immobilization is a result of several reactions, including complexation, reduction, and others; therefore, the presence of stabilizer could hinder the development of complex containing U.

Research has long been focused on developing materials, which could remove anionic and cationic heavy metal pollution. A simple coprecipitation method was employed to create a biochar-supported Fe-Mn-Mg@LDH composite that can concurrently treat As and Cu in land and water. It was shown that 1% of this composite dosage increases microbial activities, which helps for heavy metal passivation. These findings demonstrated that Fe-Mn-Mg@LDH considerably enhanced the soil quality (Shao et al. 2023).

Microorganism-Biochar Composites

In the light of soil treatment, microorganism-based biochar composite can be used in three different strategies to enhance biochar's ability to remove pollutants.

First off, inoculating a biochar with microorganisms that have a high capacity for degrading organic pollutants immediately improves the biodegradation process as a whole. Rice husk BC is infused with "bacterium *Bacillus siamensis*" for degrading "dibutyl phthalate" (DBP) (Feng et al. 2020). A different work by Xiong et al. (2017) discovered that modified BC worked better than unmodified BC at degrading soil polycyclic aromatic hydrocarbons (PAHs).

Second, microbial cells contain amine, hydroxyl, and carbonyl groups, which makes them suitable to enhance BCs' property for metal immobilization. Surface complexation can be used to immobilize Cu, Cd, and As (Ma et al. 2020; Lu Wang et al. 2021).

Microbial agent (including *Citrobacter* sp., *Bacillus cereus*, *Bacillus subtilis*) incorporated BCs have shown superior performance in Cd and U removal. "Biochar-based microbial agent" BMA boosted CEC, soil organic matter, fluorescein diacetate dehydrogenase activity, and fluorescein diacetate hydrolysis activity. In BMA-treated soil, the availability of Cd and U was dramatically fell by 54.2% and 67.4%, respectively, limiting their accretion in crops. Vegetable growth was considerably aided by BMA, which also drastically changed the composition and efficiency of rhizosphere soil microbial populations (Qi et al. 2022).

Third, precipitation can also immobilize soil metals via the phosphate produced by the microbes (Tu et al. 2020). The capacity of microbial agents to liberate and fix N_2 and PO_4^{3-} makes microorganism-biochar composites useful for enhancing soil fertility.

12.7 Sorption Mechanism for Removal of Contaminants

Despite having significant difference in the physicochemical properties in organic and inorganic pollutants, surface-modified BCs can mitigate both the pollutants. The mechanism followed for pollutant remediation by BCs is quite different. We can generally classify the remedial mechanism for organic and inorganic pollutants (Fig. 12.6).

12.7.1 Adsorption Mechanism of Organic Pollutants

Adsorption mechanism for organic pollutants includes various interactions like hydrogen bonding, hydrophobic interactions, pore filling, and electrostatic adsorption/chemisorption.

Pollutant mitigation using hydrogen bonding mainly comprises the modification of surface functionalities of BCs by heteroatoms such as O, N, and F. These atoms are well known to form hydrogen bonding due to their electronegative characteristics, which can share a pair of electrons as hydrogen bond acceptor to form a bond stronger than van der Waals forces but weaker as compared to covalent bonds. As a result, BC's O-containing functional groups may attract organic contaminants with electronegative elements via H bonding (Namgay et al. 2010). BCs produced by different starting feedstocks contain a number of O functional groups, which leads to the formation of H bonding (Dai et al. 2019).

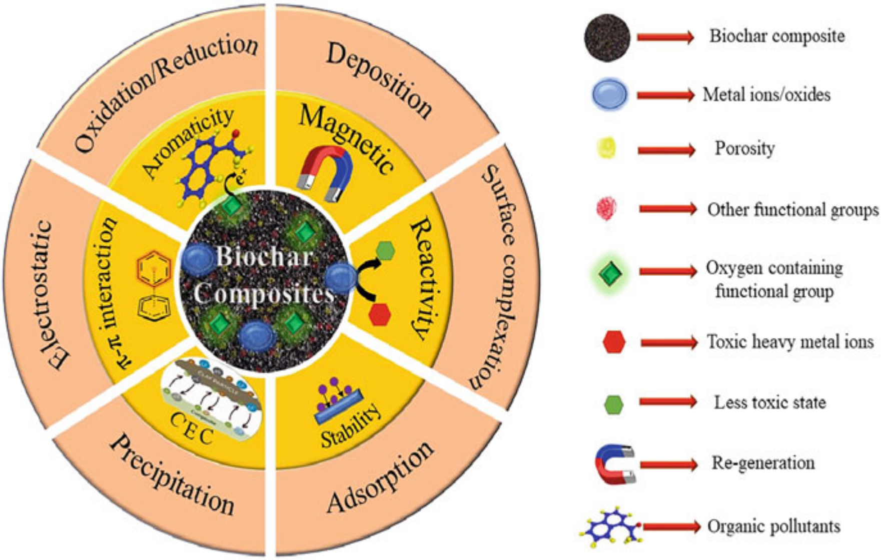

Fig. 12.6 Methods used and characteristics of BC-based composites used in soil remediation

Hydrophobic interaction results in the formation of anhydrous domain that arises from entropic impact caused by the division of H bonding, which holds H_2O molecules to the nonpolar solute in aqueous medium. Less energy is needed for hydrophobic interaction compared to partitioning mechanism (Ambaye et al. 2021). The adsorption of “perfluoro-octane sulfonate” (PFOS) on BC obtained from corn straw occurs through hydrophobic contact. The degradation of surface functionalities which are polar can increase the adsorption capacity of BCs towards organic pollutants (Chen et al. 2011).

The presence of tiny mesopores (2–50 nm) and micropores in BCs can adsorb organic hazards by pore filling. This mechanism is heavily dependent on pore volume and size distribution present on the surface of biochar. According to the reports, pore filling process was mostly responsible for the carbaryl and dye adsorption on BCs made up of pig manure and rice husk (Yuan et al. 2017).

The charge surface of BCs attracts ionizable organic contaminants through electrostatic interaction. The two crucial parameters that influence the interaction between adsorbent and adsorbate are ionic strength and pH of solution (Guo et al. 2020). A study on methylene blue (MB) dye was carried out by Inyang and colleagues, which showed that an increase in ionic strength of the solution by NaCl decreased the total adsorption of MB on BC (Inyang et al. 2014). As opposite charge attracts, altering the charge on BCs by changing the pH can enhance adsorption.

12.7.2 Immobilization Mechanism for Inorganic Pollutants

The immobilization of inorganic pollutants, mainly heavy metals, can be removed by precipitation/reduction, complexation, and ion exchange processes.

An important process to immobilize heavy metals on BCs is precipitation/reduction. According to reports, after applying BCs with alkaline substances, pH of land may rise which causes heavy metals to precipitate as hydroxide, phosphate, and carbonate salt (Fidel et al. 2018). It is the primary route for removing heavy metals in the form of solid precipitation. The biochar's high pH and the presence of metals can help heavy metals precipitate out of solution and become trapped as solids inside the biochar matrix (Cao and Harris 2010; Koutcheiko et al. 2007).

In complexation, the removal of inorganic contaminants is carried out by the formation of metal ligand bonds, which arises due to specific interactions created while complexation takes place (Mandal et al. 2021; Xu et al. 2013). Outer d-orbitals of heavy metals can interact with oxygen-containing functional groups during this process (Leng et al. 2015). Effectiveness of adsorption through complexation can be improved by increasing the O-functionalities on BC surface (Mandal et al. 2021). Heavy metals that had interacted with -OH, -COOH, etc. during complexation process get immobilized on BC composite surface, thereby getting eliminated from contaminated land.

In ion exchange process, the heavy metals may get exchanged with ionic elements such as metals, which are found on BC composite's surface that may have been present in biochar itself (Hamid et al. 2020; Liu et al. 2018; Zhang et al. 2019a). Depending on various parameters like charge differences, ionic radii, and bond properties, certain transition metals may get exchanged with alkali and alkaline earth metal such as Ca^{2+} and Na^{+} and also some nontoxic transition elements such as Fe^{2+}. In a study using hydroxyapatite/calcium silicate hydride with wood BC, a composite was created which was used to trap Pb^{2+} in hydroxyapatite matrix. The Ca^{2+} present on the BC composite got replaced by Pb^{2+} due to similar ionic radii (Chen et al. 2020a).

12.8 Conclusion and Future Prospects

Soil is considered to be one of the most crucial natural resources as the health of all the plants and animals is connected to the health of soil. Its degradation adversely affects all the life-forms on earth. The quality of soil controls the quality of the food we consume and the water we drink. However, various human activities, such as severe deforestation, excessive use of pesticides, fertilizers, reckless waste disposal, rapid industrialization, and mining, have radically altered the natural composition and properties of soil, thereby brutally deteriorating its inherent fertility. Therefore, the remediation and management of contaminated land have become a matter of major concern in recent years.

In order to address this issue, a number of in situ as well as ex situ soil treatment techniques were developed. However, all these techniques have their own advantages as well as drawbacks based on the geographical structures of land, soil conditions, and nature of contaminants. Thus, the applicability and choice of a suitable technology are governed by factors such as the cost of remediation, long-term effectiveness, commercial viability, public acceptability, and physicochemical qualities such as toxicity, mobility, and volume of soil. The most frequently used physical remediation techniques include off-site landfilling, thermal desorption, steam extraction, and soil leaching. Chemical remediation techniques, like chemical leaching and immobilization, are being widely used to convert the pollutants in their less toxic forms that are safe to waterbodies, human beings, and plants. Phytoremediation technique utilizes green plants to remove pollutants from soil. Bioremediation method includes biodegradation of the hazardous materials by benign microorganisms present in soil.

Engineered biomass-based materials and their composites have been extensively studied for soil management and decontamination as the biomass-based hybrid materials exhibit huge application potential owing to their superior properties, like high chemical resistance, large surface area, high porosity, and greater sorption capacity. Biomasses are the plant-based organic matters synthesized via photosynthesis to produce carbohydrates. They can meet the demands of nonrenewable resources and have diverse applications. A carbonaceous substance, biochar, is produced when biomass is gasified and subjected to pyrolysis. This abundant material possesses several unique properties, like resistance to degradation, negative surface charge, and large internal surface area, which makes it highly useful in soil remediation. It has been particularly effective in land remediation due to its property to adsorb heavy metals, like lead, zinc, and cadmium, and organic contaminants such as herbicides and pesticides from soil.

Chemical and physical alteration of BC further enhances its physicochemical properties. Engineered biochar composites, such as mineral-BC composites, metal-BC composites, carbonaceous BC nanocomposites, LDH-BC composites, and microorganism-BC composites, have shown improvement in soil qualities through carbon mitigation, nitrogen enrichment, increased microbial activities, and better sorption of toxic heavy metals. Here, we have discussed all these engineered biochar nanocomposites in detail. Moreover, the mechanism of their interaction with soil pollutants as well as the chemistry involved in those processes have also been elaborated.

Biomass-based engineered nanomaterials undoubtedly hold enormous potential in improving the soil quality. However, the current scientific advancements in this domain of research are still not adequate to mitigate the burning issue of soil pollution fueled by widespread industrialization and chemical-assisted agricultural boom in the past few decades. This unprecedented rise in pollution is seemingly an inevitable side effect of our fast-growing modern civilization. The task at hand is further complicated by the diversity and novelty of the emerging soil contaminants. Thus, in the coming years, it is quite evident that issues like diminishing soil fertility, destruction of natural structure and composition of the soil, and pollution caused by heavy metals, pesticides, herbicides, and other toxic chemicals are bound to escalate, generating formidable challenges as well as scopes for the people working in the area of soil remediation to design and develop novel materials capable of alleviating these issues in a greener way.

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Bioremediation of Asa River Sediment Using Agricultural By-Products

13

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Abstract

The bioremediation of Asa River sediment using agricultural wastes such as rice husk and abattoir effluent was investigated through characterization of the river sediment and agricultural wastes with the aim of finding a solution to Ilorin's low soil fertility. The physicochemical characteristics of the sediment were evaluated. Using a serial dilution method, various fungi were isolated from the river sediment as well as the organic amendments. The isolated fungi were utilized for the bioremediation of the river sediment, and the biological activities (basal respiration, dehydrogenase activity, phytotoxicity, and microbial biomass) during the remediation process were studied. The ANOVA method was used to analyse the data obtained from the bioremediation experiments. The results showed that the sediment sample contains high concentrations of organic carbon, organic matter, and heavy metals, which were attributed to industrial wastes and agricultural run-off. Results also showed that higher amounts of the metals present in the river sediment were very phytotoxic ($p < 0.05$) and prevented crop germination. A total of 21 fungi were isolated from the sediment and agricultural wastes, and they significantly degraded the heavy metals in the sediment. Among the fungi, *Aspergillus niger* was the most effective in degrading most of the heavy metals, except for nickel, where *Fusarium solani* had the highest degradation. This study presents bioremediation as a low-cost and environmentally benign technique for remediating Asa River sediment.

Keywords

Abattoir effluent · Adsorption · Bioremediation · Heavy metal · Rice husk · River sediment

13.1 Introduction

For its considerable contribution to economic growth and human well-being, industrialization is considered the cornerstone of development initiatives (Iloamaeke and Iwuozor 2018; **Iwuozor et al.** 2021b; Kartam et al. 2004). Industrialization frequently results in pollution and degradation of the environment, just like many other anthropogenic activities that have an impact on the environment (Iwuozor 2019; Ogunfowora et al. 2021; Zhul-quarnain et al. 2018). Depending on the type of industry and the population that utilizes the product, industries produce waste that is unique in terms of composition and quantity. The continuous increase of industries has resulted in a significant increase in the discharge of industrial waste into the environment, mostly soil and water, resulting in the deposition of various pollutants, particularly in metropolitan areas (Colombo et al. 2003; Iwuozor and Gold 2018).

Sediments, sometimes referred to as silt or alluvium, are made up of solid mineral and organic particles that are moved by water (Bruins et al. 2020; Yanin 2019). The sediment of a river serves as a sink for pollutants that enter the stream (Emenike et al. 2022; Pak et al. 2021). Both the transport capacity of the flow and the supply of sediment determine the quantity of sediment transported in river systems. The suspended sediment load refers to fine sediment transported in suspension, which might include material collected from the river bed (suspended bed material) as well as material washed into the river from the surrounding land (wash load). The suspended bed material is frequently finer than the wash load. The “bed load”, on the other hand, consists of larger sediment particles carried along the river bed by rolling, sliding, or saltation. Depending on the flow conditions, most rivers will deliver silt in each of these load types (McKenzie et al. 2021; Sulaiman et al. 2021; Sumaiya et al. 2021).

Industrial pollution, overuse of water, ecosystem loss, and deterioration of aquatic habitats are all affecting river systems across the world (Haryani 2021; **Iwuozor et al**. 2021a; Marimuthu et al. 2020). As a result of pollution from atmospheric deposition, petrochemical spillage, coal combustion residues, wastewater irrigation, pesticides, sewage sludge, animal manures, land application of fertilizers, leaded gasoline and paints, disposal of high metal wastes, and rapidly expanding industrial areas, heavy metals and metalloids accumulate in dredged sediment (**Iwuozor** et al. 2021c; Ogemdi 2019a; Ogemdi 2019b; Ogunlalu et al. 2021). Sediment can also be useful or harmful to the society or the environment, depending on local variables. From an economic, social, and environmental standpoint, effective sediment management in rivers is becoming increasingly vital. The global geochemical cycle relies heavily on sediment delivered by rivers (Al Masud et al. 2018; Lin et al. 2020; Zhang et al. 2021). A large quantity of soil nutrients (nitrogen, phosphorus, and potassium) and cations are also present in river sediments, making the sediment beneficial for agronomy operations (Offiong et al. 2021; Yu et al. 2020). Bioremediation is commonly preferred for the remediation of soil or river sediments due to its low cost in comparison to other conventional techniques, its use as a permanent solution, its non-invasive nature, and its ability to clean up contaminants even at low concentrations, which chemical and physical techniques may not be able to do (Fragkou et al. 2021; Fu et al. 2020; Perelo 2010).

The Asa River runs south-north through Ilorin, splitting the plain into two parts: western and eastern. It is an important river in Ilorin, the capital city of Kwara State, with economic, environmental, and agricultural significance. The river covers around 303 hectares of land (Ighalo et al. 2021; Oladipo et al. 2020; Opasola et al. 2019). This river is very susceptible to pollution due to its proximity to industrial congestion, which exposes it to misuse such as effluent receptacles, which can lead to contamination. It collects waste from industries placed along its path on a regular basis, in addition to domestic waste and other activities that contribute to pollution. When portable water is not easily accessible, residents living along the river’s channel utilize the water for various domestic activities such as drinking, nursing wet vegetables, washing automobiles, and other household necessities (Ajala et al. 2018; Akinboro et al. 2021; Jimoh and Kolawole 2021). Local farmers use the sediment from the Asa River for agricultural cultivation in its existing form, without taking into account the level of contaminants present in the sediment. The bioremediation of the sediments could be implemented as a simple treatment to solve the problem of low soil fertility status in some areas of Ilorin. This presents an interesting novelty for the current investigation.

Some researchers have studied the characteristics and remediation of the sediment of the Asa River. Fawole et al. (2017) determined the physicochemical characteristics of the river sediment and also isolated six different fungal species from the river sediment. In different studies, the physicochemical properties of river sediment were also explored, and the heavy metals in the sediment were remediated with the use of abattoir effluent and poultry droppings (Adegbite et al. 2018; Augie et al. 2018). However, these studies were limited as they did not monitor the biological activities of the microbial isolates obtained from the wastes and utilized for the bioremediation process. The aim of this study was to bio-remediate Asa River sediment with the use of two agricultural by-products: rice husk and abattoir effluent. It involved the characterization of the river sediment together with the agricultural by-products, observation of biological activities (basal respiration, dehydrogenase activity, phytotoxicity, and microbial biomass) during the remediation process, and evaluation of the effects of individual fungal isolates on the detoxification of the river sediment. Given the need for eco-friendly and cost-effective strategies for sediment treatment, the relevance of this study is justified.

13.2 Methodology

13.2.1 Sample Collection

The collection of sediment samples was obtained at the Asa River, located in Ilorin, North Central Nigeria (8° 28’N, 4° 38′E to 8° 31’N, 4° 40′E), which receives effluent from major industries in the city of Ilorin. The sediment samples were collected from four different points on the river, Coca-Cola (an area that was not dredged), Unity (dredged), Post Office (dredged), and Amilegbe (dredged), and were properly labelled as C, U, P, and A, respectively. Samples were collected into clean polythene bags using a hand trowel and mixed to ensure uniformity, which was then dried in the air for 48 h and sieved through a 2 mm mesh. The organic amendments (rice husk and abattoir effluent) were collected from the National Cereals Research Institute Badeggi, Bida, and Ilorin Abattoir Centre, Ipata Market, Ilorin, respectively, and were properly kept in clean containers to avoid contaminants.

13.2.2 Physicochemical Properties of Sediment

The sediment was analysed for particle size, pH, nitrogen, organic carbon, organic matter, acidity, available phosphorus, and cation exchangeable capacity, as described by Adegbite et al. (2018). Metals such as calcium, magnesium, sodium, potassium, lead, nickel, cadmium, chromium, cobalt, copper, zinc, manganese, and iron were analysed with the aid of an atomic absorption spectrophotometer (AAS) (Perkin Elmer 200 AAS).

13.2.3 Microbial Analysis

13.2.3.1 Fungi Isolation

Fungi were isolated from the Asa River sediment and the two organic amendments (abattoir effluent and rice husk) using a serial dilution method. The sediment sample (10 g) was introduced into 90 mm of sterile water in a conical flask and shaken vigorously. Tenfold serial dilutions were thereafter carried out in sterile water. The 10^{-3} dilution (1 mL) was plated out on sterilized potato dextrose agar (PDA) using the pour plate method. After 5 days, the fungal colonies growing on the plate were counted. Pure cultures of isolates were made on freshly prepared PDA and incubated at 28 ± 2 °C for another 5 days. Stock cultures were made on PDA slants in McCartney bottles and stored in the refrigerators for further microbial analysis. The same process was repeated for each of the organic wastes (abattoir effluent and rice husk).

13.2.3.2 Identification of the Isolates

Microscopic identification was confirmed at the Department of Crop Protection, International Institute of Tropical Agriculture (IITA).

13.2.3.3 Morphology Characterization

Colony and microscopic morphologies were employed for fungal isolates based on the colony appearance on the PDA. The cultural characteristics of fungal isolates, such as mycelia growth form, spore presence or absence, pigmentation, and back colour of colonies on PDA, were also recorded.

13.2.3.4 Microscopic Features

Each fungal isolate was mounted on a slide with a cotton blue lactophenol stain. Microscopic features were observed at × 40.

13.2.4 Experimental Bioremediation

As a method to collect sediment samples, the top 0.25 m of the river bed was dredged from the bottom of the Asa River. Laboratory-scale bioremediation tests were performed in a microcosm.

13.2.4.1 Bioremediation Consortium for Microbes

Soil samples were taken from a number of possible contamination sites along the Asa River's industrial zone. The soil samples were mixed and cultured in a culture medium containing 2 g of NH_4Cl, 0.25 g of NaCl, 0.2 g of sulphur, 0.2 g of $MgSO_4.7H_2O$, and 0.5 g of KH_2PO_4 in 1 L of H_2O. Every 5–7 days, 250 mL of fresh medium was added to 2 mL of a fully established culture in an Erlenmeyer flask. The pollutants added during the acclimatization stage provided the carbon source. A rotary shaker with a temperature setting of 350 °C and 250 rpm was used to provide the microorganisms with the mineral nutrients they require to survive and grow.

13.2.4.2 Procedure for Acclimation

Roughly one millilitre of the culture was moved to a new solution after a 7-day interval. After that, 0.01 g of the sediment sample was placed in a 24-h culture at 350 °C and 250 rotations per minute. A total of 0.5 g of sediment was added to the tank after 0.1 g of sediment was added at the expiration of the first day, which permitted the cell population to develop adequately. This process was repeated incrementally until 0.5 g of sediment had been added in total. The consortium was used in bioremediation studies after several enrichment steps (109 CFU/mL). It was also put to the test to see if it could use organic molecules in sediments under aerobic conditions.

13.2.4.3 Developing an Experimental Design

In six pans, each with a surface area of 498.1 cm^2 and a capacity of 1785 cm^3, the sediment was agitated weekly with a sterile spatula to supply it with appropriate oxygen and air. To achieve a sediment moisture level of roughly 60% of the microcosms' water retention, aluminium foil was placed over the pans and maintained at room temperature (28 ± 2 °C). Deionized water was then added every week until the sediment moisture content was achieved.

All treatments were subject to these conditions. They were as follows:

- Treatment 1: A three-time autoclave at 121 °C for 30 min was used to sterilize the sediment in Pan 1 (control).
- Treatment 2: In Pan 2, no nutrients or culture supplements were applied. Biostimulation was performed with simple aeration.
- Treatment 3: It was determined if biostimulation could be achieved by aeration and addition of nutrients to Pan 3, which contains urea, $(NH_4)_2SO_4$, and K_2HPO_4 at a ratio of 100:10:1.
- Treatment 4: An experiment was conducted with bioaugmentation using aeration and nutrients for Pan 4, which was treated with nutrients and a 50 mL inoculum of 3.2×10^9 CFU/mL of a previously enriched microbial consortium from toxic soil.
- Treatment 5: Pan 5 received 50 mL of abattoir effluent for bioaugmentation with aeration and abattoir effluent.
- Treatment 6: Pan 6 was evaluated with bioaugmentation using aeration and rice husk, which received 50 g of rice husk.

13.2.5 Biological Activity in Different Treatments Was Measured Using Basal Respiration, Dehydrogenase Activity, Microbial Biomass, and Phytotoxicity

Biological activity was assessed by measuring variables such as microbial biomass carbon, basal respiration, dehydrogenase activity, and dissolved oxygen content in the sediments of the treatment units at 0, 2, 4, 6, 8, and 12 weeks. To monitor the above-mentioned parameters, sample composites were collected from various parts of the microcosm, and the analytical procedures are listed below.

13.2.5.1 Basal Respiration

In order to measure the CO_2 concentration in sediments, 2 g of sediment samples were collected from different treatment units and placed in sealed plastic vials inside 1 L glass jars. The NaOH trap used in each jar contained 10 mL of 0.2 N NaOH to trap CO_2 released as a result of substrate mineralization. The NaOH trap was periodically replaced. A titration with 0.1 N HCl was used to determine the amount of CO_2 generated by each microcosm after adding 10 mL of $BaCl_2$ to the NaOH trap.

13.2.5.2 Dehydrogenase Activity

The frequency of decrement of 2,3,5-triphenyltetrazolium chloride into triphenylformazan, as described by Alef (1995), was used to measure the dehydrogenase activity. After 24 h, dehydrogenase activity was determined as micrograms of formazan per gram of soil and reported as a percentage of control activity (100%).

13.2.5.3 Plant Toxicology

To test the phytotoxicity of sediment on sorghum, the sediment extract was centrifuged (at 6000 rpm) and filtered with a No. 42 Whatman filter paper. The sediment extract was extracted by adding water to reach 85% moisture content. A diluted extract was made in distilled water and placed into six petri dishes with 10,000 seeds of sorghum in each. Each dilution was incubated at 27 °C for 72 h in the dark.

Equations (13.1–13.3) were used to calculate the GI based on the number of germinated seeds in the sample and the root elongation compared to the control:

$$\text{The relative seed germination percentage} = \frac{\text{Number of seeds germinated in the extract}}{\text{Number of seeds germinated in the control}} \times 100 \tag{13.1}$$

$$\text{Elongation of roots relative to root length in control (\%)} = \frac{\text{Root length in extract}}{\text{Root length in control}} \times 100 \tag{13.2}$$

$$\text{Germination index }(\%) = \frac{\text{GsLs}}{\text{GcLc}} \times 100 \tag{13.3}$$

Here, Gs and Gc are the average numbers of seeds that germinated in the sample and in the control replication, respectively, while Ls and Lc are the average amounts of root length in the sample and in the control replication.

13.2.5.4 Microbial Biomass (Fumigation and Extraction)

Microbial biomass carbon: ethanol-free chloroform was used. For each sample, two subsamples were made: one non-fumigated sample (10 g) for immediate extraction with 0.5 M K_2SO_4 and, in addition to the fumigated specimen (10 g), a non-fumigated subsample was placed for 3 days in a desiccator. 50 mL of 0.5 M K_2SO_4 was added to each subsample and then shaken for 30 min. After shaking, it was filtered through 0.5 M K_2SO_4 on pre-leached Whatman No. 1 filter paper, and the extract was stored in the freezer.

In a vacuum desiccator, 50 mg of the fumigated sample was placed into 50 mL glass beakers, each marked with a pencil. Sharpe operates in chloroform, so the beakers were placed inside a vacuum desiccator. Beakers were stacked in the desiccator by layering them with a vented plate. After placing boiling chips in a 50 mL scintillation vial and adding 30 mL of chloroform in the desiccator, the vial was evacuated and kept in darkness for 3 days (darkness prevents chloroform from breaking down). In each sample, 50 mL of K_2SO_4 was added, and it was shaken for 30 min. Then each sample was filtered through 1.25 mm Whatman No. 1 filter paper that had been pre-leached with 0.5 M K_2SO_4. A wet oxidation method was used to determine the total organic carbon in the extract, as described by Sánchez-Monedero et al. (1996).

13.2.5.5 Determination of the Rate at Which the Isolate Detoxifies Toxic Elements

To ensure that the sediment was free of organisms, 100 g of sediment was measured into nine different glassware containers and autoclaved at 121 °C for 30 min at a pressure of 15 lbs. Three mycelial discs of each of the fungal isolates were inoculated into the sterilized sediment along with nutrients. It was moistened at 60% and properly covered with a plug. For 12 weeks, the experiment was kept at 282 °C.

13.2.6 Analysis of Data

The ANOVA method was used to analyse the data obtained from the bioremediation experiments. The treatment means were separated according to the LSD method at a 5% probability level.

13.3 Results and Discussion

13.3.1 Physical and Chemical Analysis of the Sediment

Table 13.1 shows some analysis of the physical and chemical characteristics of the Asa River sediment used for the study. The sediment had a high level of organic carbon, organic matter, nitrogen, and cation exchangeable capacity. The result obtained in the study indicates that the sediment is acidic. Ogunwale and Azeez (2000) attributed the pH values of sediment to the nature of the parent materials on which the sediment is developed. The high organic matter content can be attributed to sewage, industrial wastes, and agricultural chemicals such as fertilizers, pesticides, and minerals, which are the primary causes of surface water pollution. It is widely recognized that rivers can become contaminated by traces of metal from numerous and diverse sources, which makes them rich in soil nutrients required for plant uptake (Adekola and Eletta 2007). The ECEC (64.20 Cmol/kg), the overall value of sodium, calcium, magnesium, potassium, and exchangeable acidity (0.65 Cmol/kg), present in the Asa River sediment was found to be high, which showed a high fertility status and its potential for agricultural use. However, anthropogenic activities, such as quarry sites and industrial effluents along the riverbank, still remain the principal cause of the increased amount of heavy metals that have been dumped into the water (Adekola et al. 2002), which have made the Asa River sediment a pool of heavy metals.

Table 13.1 Physicochemical properties of sediment collected from Asa River sediment

Parameter	Values
Particle size (%)	
Sand	75.96
Silt	11.28
Clay	12.76
Textural class	Sand
pH in H_2O	6.02
pH in KCl	5.14
Total organic carbon (%)	0.834
Total organic matter (%)	1.441
Total nitrogen (%)	0.37
Available phosphorus (P) (mg/kg)	23.7
Potassium (K) (Cmol/kg)	24.94
Sodium (Na) (%) (Cmol/kg)	23.83
Calcium (Ca) (Cmol/kg)	6.32
Magnesium (Mg) (Cmol/kg)	8.46
Exchangeable acidity (Cmol/kg)	0.65
Effective cation exchangeable capacity (ECEC) (Cmol/kg)	64.20

13.3.2 Microbial Analysis of Asa River Sediment and Organic Amendments

The pH of Asa River sediment, its organic content, and water are the main factors affecting the fungal population and diversity in the sediment, which is similar to the report made by Yu et al. (2007) that physical-chemical properties had a great impact on the fungal population. Fungi require organic carbon, nitrogen, phosphorus, and potassium. Mould development and sporulation, in addition to those of other microbes, are severely impeded in the absence of any of these (Saksena et al. 1995). According to reports, the monsoon (rainy) season, when soil moisture was noticeably high, was when the fungal population was at its highest level. According to Deka and Mishra (1984), the dispersion of mycoflora is significantly influenced by environmental parameters such as pH, moisture, temperature, organic carbon, organic nitrogen, and organic carbon. In the present study, 21 fungal species were observed (Fig. 13.1c). *Ascomycotina* and *Zygomycotina* had the highest number of fungal species observed. The report of the study shows that *Aspergillus niger* (15.4%), *Aspergillus flavus* (11.1%), *Aspergillus sydowii* (6.1%), *Aspergillus terreus* (4.7%), *Aspergillus glaucus (4.1%), Trichoderma harzianum (7.6%), Penicillium notatum, and Trichoderma viride* (4.5%) were the dominant species, and *Botryodiplodia theobromae* has the lowest occurrence (1.5%); they show vigorous growth and were found in large numbers. It was discovered that a variety of parameters, including temperature, humidity, vegetation, organic and inorganic materials, soil type, and texture, influence the frequency of mycoflora in various fields. Figure 13.1a depicts the proportion of fungus found in abattoir wastewater. There were 11 fungal species identified. *Microsporum nanum* had the highest rate of incidence (16.6%), whereas *Aspergillus niger* had the lowest rate (3.7%). Figure 13.1b depicts the frequency of occurrence of fungi identified from rice husk. A total of 14 fungus species were identified. *Aspergillus flavus* was the most common (14.6%), while *Stachybotrys chartarum* was the least common (2.2%).

Table 13.2 shows some important features of isolated fungal species based on their macroscopic and microscopic appearances. Figures 13.2, 13.3, 13.4, and 13.5a depict some of the characteristics of the potato dextrose agar (PDA) plate. Figures 13.2, 13.3, 13.4, and 13.5b show the conventional method's microscopic appearance at × 100. The morphology characterizations were done based on the colony's appearance, colony form, elevation, colony margin, and colour.

13.3.3 Bioremediation Experiment

13.3.3.1 Respiratory Activity in Microcosms

Figure 13.6a shows the rate at which the organisms present in each microcosm released CO_2 during the respiration process. Treatment A (the control pan) had the least value, probably because it was autoclaved at a very high temperature, leaving no room for organisms to survive at the commencement of the study, but at week 12, the value increased to 1.533, which may be attributed to exposure to

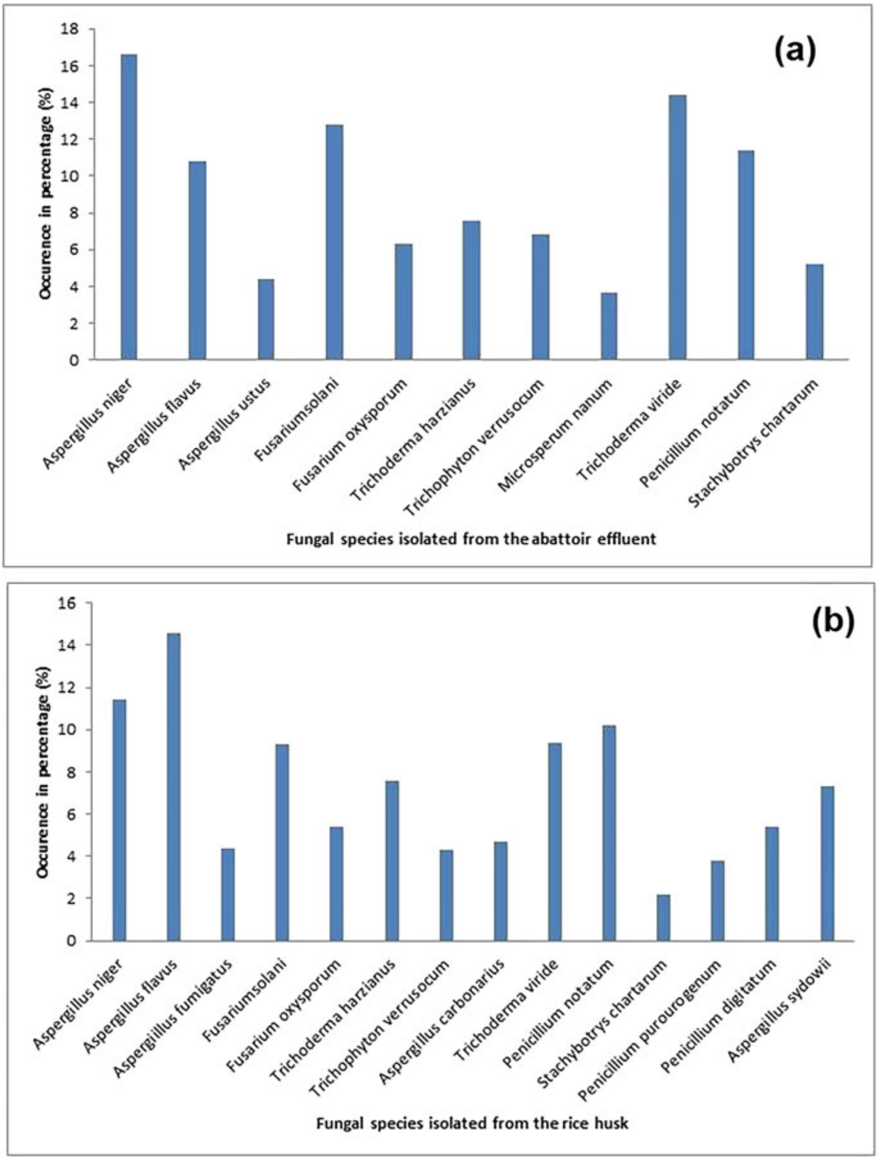

Fig. 13.1 Occurrence of fungi in (**a**) abattoir effluent, (**b**) rice husk, (**c**) Asa River sediment

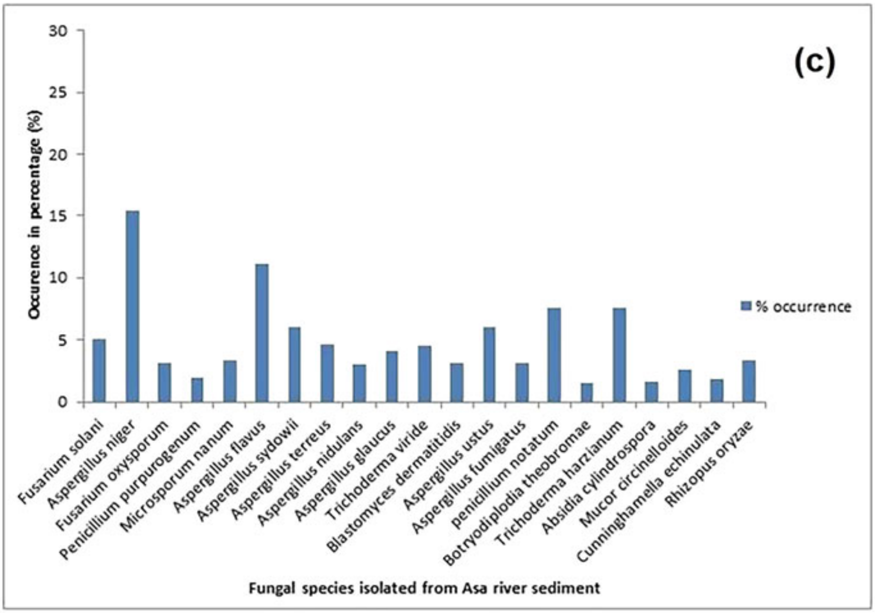

Fig. 13.1 (continued)

contamination from the air during the collection of sediment samples for analyses. The results of microbial activities in the different microcosms are shown in Fig. 13.6a. Treatments are shown comparing respiration rates in non-amended and modified sediment (amended) from the same location. Some trends can be observed: in almost all the treatments investigated, the respiration rate was higher in the modified sediment (biostimulation and bioaugmentation). This is probably due to increased organic nutrients from the microcosm, nutrient addition, or organic waste (rice husk and abattoir effluent) present in the pans. The reduction in CO_2 released thereafter could be a result of a reduction in microbial activity. The microbial activity might have dropped due to nutritional limitations. Engelberg-Kulka and Hazan (2003) demonstrated that bacteria and fungi cells that have begun the sporulation process postpone endospore production by eliminating their peers and feasting on the resources released as a result. They discovered that under nutritional stress, fungi such as *Aspergillus niger* exhibit cannibalistic behaviours. It was also observed that organisms in treatment 5 (nutrients with abattoir effluent) released more CO_2 than other treatments until the 10th week before dropping below treatments 6 and 4. The exception to this trend is the control, in which the respiration rate was 1.533 lower in the contaminated sediment. This may be due to the lack of aeration or addition of nutrients to reactivate the microbes present in the sediment. The action of the sediment microflora is indicated by basal respiration, which may be connected to the decomposition of the molecules in the sediment of the Asa River, which corresponds with the study by Bhattacharyya et al. (2001), where metabolic data

Table 13.2 Colony and microscopic morphology of fungal isolates

ID	Source	Colony morphology	Microscopic morphology	
A_1	Sediment	On PDA, the growth is rapid white aerial mycelia, which become tinged with purple colour and might be masked by cream to tan to orange sporodochia	Microconidia abundant, generally single celled, oval to kidney shaped, macroconidia abundant, only slightly sickled shaped, thin walled, and have attenuated apical cell	*Fusarium oxysporum*
A_2	Sediment	Colonies on PDA at 27 °C attained a diameter of 4–5 cm within 7 days, consisting of a compact white or yellow basal felt with a dense layer of dark brown to black conidiophores	Conidia heads, black, radiate, tending to split into columns with age. Conidiophore stipes smooth-walled hyaline but also in brown colour. Phialides borne on metulae, 7.0–9.5 × 3.5 μm, metulae brown often septate, 15–25 × 4.5–6.0 μm. Conidia globose to subglobose	*Aspergillus niger*
B_3	Abattoir effluents	Colonies with loose white to yellow mycelium rapidly becoming dark brown to black on the development of conidia	Conidial heads are large (3 mm by 15–20 μm in diameter), globose, dark brown, becoming radiate and tending to split into several loose columns with age. Conidial heads are biseriate with the phialides borne on brown, often septate	*Aspergillus niger*
A_3	Sediment	Growth rate: rapid, the texture is silky to coarsely fluffy, radial grooves, the colour is white and reverse is deep yellow. Variants are slow growing, heaped and folded, yellow surface, no reverse pigment, macroconidia absent; reverts to typical colony on rice grains	Long, rough, thick-walled macroconidia with asymmetrical knob on end few pyriform microconidia, lateral racquet hyphae, nodular bodies	*Microsporum canis*
B_4	Abattoir effluents	Growth rate is slow and its texture is waxy or glabrous, heaped or flat, thallus colour is white, grey or yellow and the reverse is colourless, variants, flat, downy, grey-white	Irregular hyphae with many terminal and intercalary chlamydospores. Chlamydospores are often in chains. The head of some hyphae is broad and club shaped, and occasionally divided. The occasional strains produce clavate to pyriform microconidia	*Trichophyton verrucosum*

(continued)

Table 13.2 (continued)

ID	Source	Colony morphology	Microscopic morphology	
			borne singly along the hyphae	
B_8	Rice husk	On potato dextrose agar, colonies are slow growing, small, button or disk shaped, white to cream coloured, with a suede-like to velvety surface, a raised centre, and flat periphery with some submerged growth. Reverse pigment may vary from non-pigmented to yellow	Irregular hyphae with many terminal and intercalary chlamydospores. Chlamydospores are often in chains. The head of some hyphae is broad and club shaped, and occasionally divided. The occasional strains produce clavate to pyriform microconidia borne singly along the hyphae	*Trichophyton verrucosum*
A_6	Sediment	Very rapid rate of growth, maturing in about 3 days. Surface is greenish-yellow to olive and may have a white border, usually consisting of dense felt yellow-green conidiophores. Conidial heads typically radiate, later splitting into several loose columns. Texture is often floccose, especially near the centre, and overall can be velvety to woolly. Unremarkable cream to tan to yellowish reverse	Conidiophores hyaline coarsely roughed, up to 1.0 mn (some isolates are up to 2.5 mm) in length. Phialides borne directly on the vesicle or metulae, 6–10 × 4.0–5.5 µm, metulae 6.5–10 × 3.5 µm. Conidia globose to subglobose	*Aspergillus flavus*
C_2	Rice husk	Colonies have fast-growing, suede-like to downy, white with yellowish green conidial heads. Colonies become greyish-pink to brown with age	Conidiophores are hyaline, smooth walled and bear terminal verticils of 3–5 metulae, each bearing 3–7 phialides. Conidia are globose to subglose, 2–3 µm in diameter, smooth walled and are produced in basipetal succession from the phialides	*Penicillium marneffei*
A_7	Sediment	Growth rate is moderate. Colour is influenced by media. It has a blue-green to dark green to greyish-turquoise. Colonies may have straw-coloured to reddish-brown shades with exudate. Reverse is maroon. Texture is lanose (woolly)	The long, smooth-walled stipes which bear the conidiophores are hyaline generally. The vesicles (7.0–17 µm wide) may appear sub-spherical or clavate. Conidiogenous structures are biseriate with metulae (2–3.5 µm × 4–6 µm) and	*Aspergillus sydowii*

(continued)

Table 13.2 (continued)

ID	Source	Colony morphology	Microscopic morphology	
			phialides (2–3 μm × 5–7 μm) in size. Conidia are spinose and are about 2.5–4.0 μm in diameter	
B_1	Abattoir effluents	Colonies growing rapidly, 4.5 cm in 4 days, aerial mycelium white, becoming purple with discrete orange sporidia present strains, reverse hyaline to dark purple	Conidiophores are short, single, lateral monophialides in the aerial mycelium, later arranged in densely branched. Macroconidia are fusiform and slightly curved. The phialides are short and mostly non-septate	*Fusarium oxysporum*
A_8	Sediment	Colonies on PDA appeared as rapidly growing powdery colonies with a characteristic buff or cinnamon-brown colour on the surface and a yellow to beige-brown colour on the reverse	Hyphae are septate and hyaline with conidial head formed of compact columnar and contain metulae, which supports the phialides (biseriate). The conidiophores are smooth walled, with length ranging from 50 to 320 μm long, and terminating in mostly globose vesicles; the conidia are globose, smooth and small with a size of 2–2.5 μm in diameter and the conidia are hyaline, globose, and sessile and are produced on submerge	*Aspergillus terreus*
A_{10}	Sediment	Growth is slow to moderate. Colony size expands rather slowly. Colony colouration is media dependent but is described as a dull to deep green to a greyish turquoise, with yellow to orange areas. The reverse is pale yellow to yellow	The conidia head radiates to loosely columnar; the conidiophores are smooth walled, 15–30 μm; the upper portion of the vesicle is covered by septate, phialides, and hyaline; the vesicles are globose to sub globose, uniseriate with a 3.5–6.5 μm	*Aspergillus glaucus*
B_6	Rice husk	Very rapid rate of growth, maturing in about 3 days. Surface is greenish-yellow to olive and may have a white border; it consists of dense felt yellow-green conidiophores. Conidial heads typically radiate, later splitting into several	Conidiophores hyaline coarsely roughed, up to 1.0 mn (some isolates is up 2.5 mm) in length. Phialides borne directly on the vesicle or metulae, 6–10 × 4.0–5.5 μm, metulae 6.5–10 × 3.5 μm.	*Aspergillus flavus*

(continued)

Table 13.2 (continued)

ID	Source	Colony morphology	Microscopic morphology	
		loose columns. Texture is often floccose, especially near the centre and overall can be velvety to woolly. Unremarkable cream to tan to yellowish reverse	Conidia globose to subglobose	
A_{11}	Sediment	It is a rapidly growing mould which matures in 3–5 days. Growth begins as fluffy white tufts, which then compact and appear woollier. Green tufts may develop within the colony due to the production of conidia. These often appear as concentric rings, typically starting at the edge of the colony. The reverse is typically a light tan to yellow or pale orange	Conidiophores hyaline, much branched, not verticillate; phialides single or in groups; conidia (phialospores) hyaline, one celled, ovoid, borne in small terminal clusters; usually easily recognized by its rapid growth and green patches or cushions of conidia	*Trichoderma harzianum*
C_7	*Rice husk*	The surface growth is velvety, downy, or powdery, showing various shades of green, most commonly a blue-green to a grey-green with a narrow white border. The colour typically darkens with age. The reverse is white to tan to pale yellowish. Colouration or shade can be dependent on the media on which the fungus is cultured upon	Hyphae are septate with smooth-walled conidiophores (usually less than 300 μm in length and 5–10 μm wide)	*Aspergillus fumigates*
B_5	Abattoir effluents	Colonies growing rapidly, 5–7 cm in 5 days, aerial mycelium white to cream, becoming bluish-brown when sporodochia are present	It possesses 3–5 septate, fusiform, cylindrical, moderately curved, a short blunt apical cell, 28–42 × 4–6 μm. Microconidia are usually abundant, cylindrical to oval, 1–2 celled and formed from long lateral phialides 8–15 × 3–4.8 μm, chlamydospores are hyaline, globose. Smooth to rough walled	*Fusarium solani*
A_{13}	Sediment	The surface growth is velvety, downy, or powdery, showing various	Hyphae are septate with smooth walled conidiophores (usually less	*Aspergillus fumigates*

(continued)

Table 13.2 (continued)

ID	Source	Colony morphology	Microscopic morphology	
		shades of green, most commonly a blue-green to a grey-green with a narrow white border. The colour typically darkens with age. The reverse is white to tan to pale yellowish. Colouration or shade can be dependent on the media on which the fungus is cultured upon	than 300 μm in length and 5–10 μm wide). Vesicles are subclavate in shape, roughly 20–30 μm in width. Phialides are flask shaped, uniseriate, compact, usually forming on the upper two-thirds of the vesicle and mature parallel to the axis of the conidiophore. Conidia are verrucose, (sub)spherical, and about 2–3.5 μm in diameter and develop in chains	
		Colonies are flat, spreading, and white to cream coloured, with a dense cottony surface which show some radial grooves. Colonies usually have a bright golden yellow to brownish yellow reverse pigment	Macroconidia are small typically spindle shaped with 5–10 cells, verrucose, thick walled and often have a terminal knob	*Microsporum canis*
A_{14}	Sediment	Colonies may show variation in surface colour from a yellowish brown to a drab olive with possible greys. They may show a lighter coloured outer edge, and droplets of purple exudate may appear on the surface of the maturing colony. The reverse is a yellowish brown colour. Texture was even and rather	It produces septate hyphae from which smooth-walled conidiophore stipes extend. Stipes are short (130–300 μm). Vesicles, subspherical in shape, also were rather small (7–15 μm diameter) from the vesicles, biseriate conidiogenous cells extend with the metulae being slightly shorter than the phialides. The conidiogenous cells produce round conidia (3.0–4.5 μm diameter) bearing a noticeably rough wall	*Aspergillus ustus*
B_6	Abattoir effluents	Colony grows fast on PDA, white-pinkish on surface and cream reverse	Conidiophores arising from a single or less often synnemata branched near the apex, penicillate, ending in phialides: conidia hyaline, one celled, mostly globose or ovoid, in dry basipetal chains	*Penicillium viride*

(continued)

Table 13.2 (continued)

ID	Source	Colony morphology	Microscopic morphology	
A_{17}	Sediment	The colony is flat, downy to cottony, covered by greyish, short, aerial hyphae. The reverse side is typically brown to black due to pigment production	It has a septate, dark hypha. Conidiophore is also septate and sometimes has a zigzag appearance. It bears simple or branched large conidia (8–16 × 23–50 μm), which have both transverse and longitudinal septations. These conidia are observed in acropetal chains and may produce germ tubes. They are ovoid to obclavate, darkly pigmented, muriform, and smooth. The end of the conidium nearest the conidiophore is round while it tapers towards the apex. This gives the typical beak or club-like appearance of the conidia	*Alternaria alternate*
A_{18}		Light yellow, moist appearance, red with cottony and orange-brown mycelium, with light brown exudates; it grows between 3 and 5 days on PDA	It has a long, thin with about 100 μm or more phialide; it has a single or pairs of chlamydospore; the microconidia is 8–16 × 2–4 μm with abundant, cylindrical, dorsal, and ventral surface parallel, 3–5 septa (35–55 × 4.5–6 μm)	*Fusarium solani*

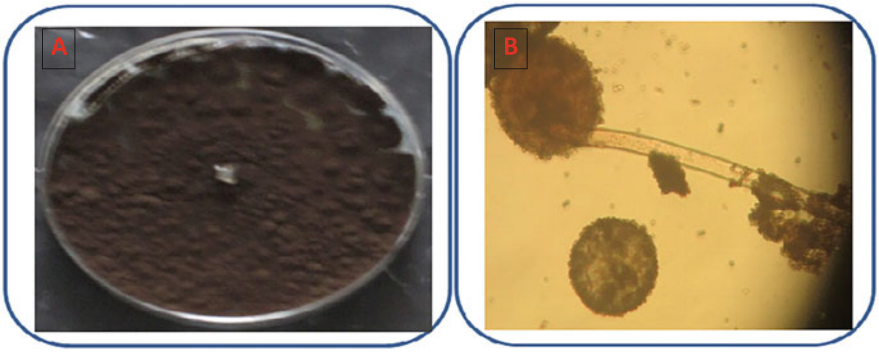

Fig. 13.2 (**a**) Colony morphology and (**b**) microscopic structure of *Aspergillus niger* ×100

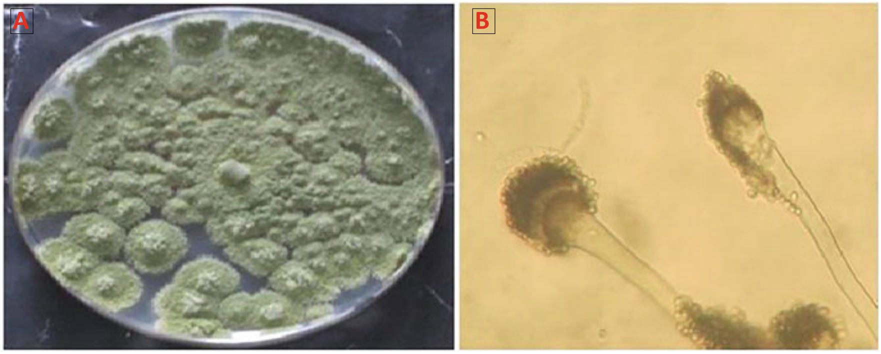

Fig. 13.3 (**a**) Colony morphology and (**b**) microscopic structure of *Aspergillus flavus* ×100

Fig. 13.4 (**a**) Colony morphology and (**b**) microscopic structure of *Fusarium oxysporum* ×100

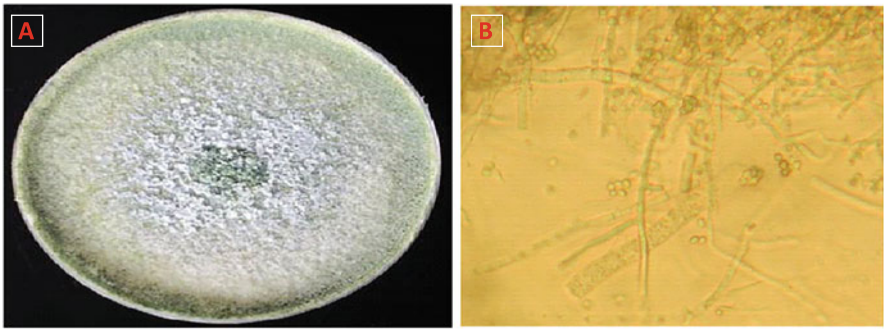

Fig. 13.5 (**a**) Colony morphology and (**b**) microscopic structure of *Trichoderma harzianum* ×100

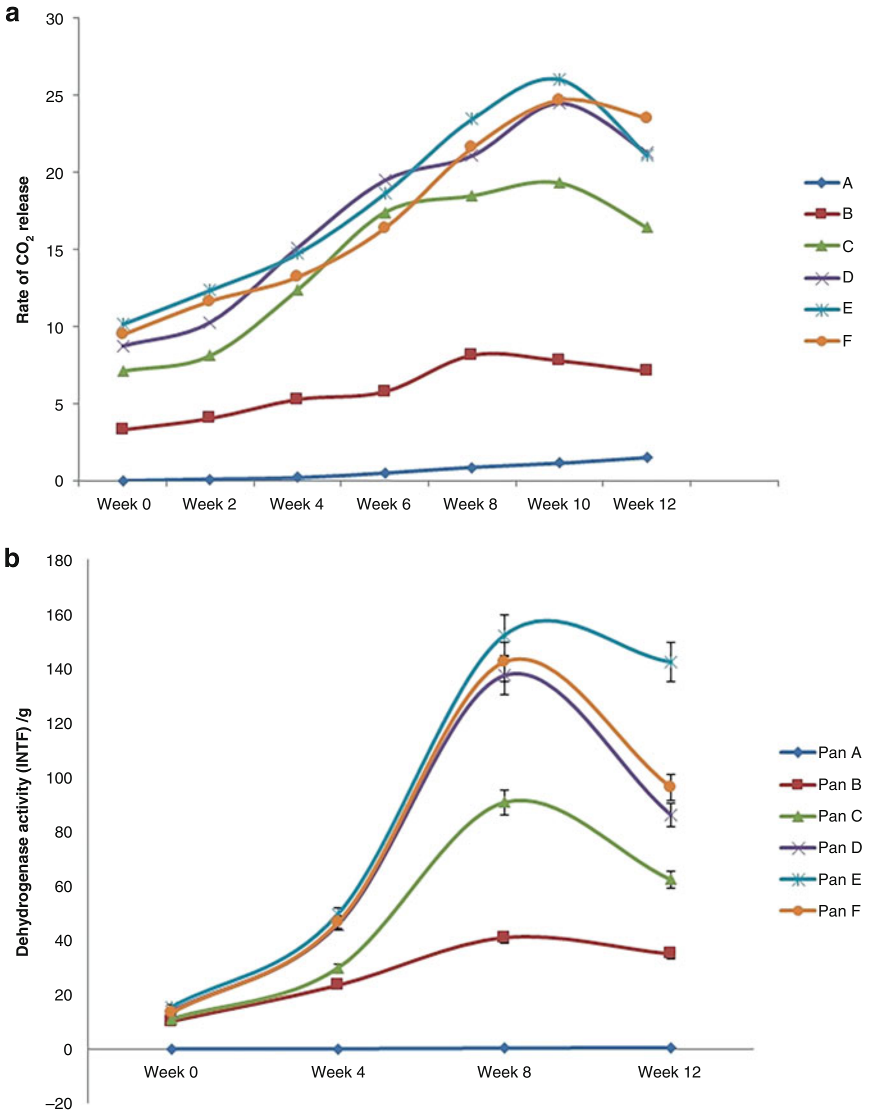

Fig. 13.6 Changes in (**a**) basal respiration with different treatments. (**b**) Dehydrogenase activity in different treatments. (**c**) Germination index (GI) of seeds with time within different treatments. (**d**) Microbial biomass with time within different treatments

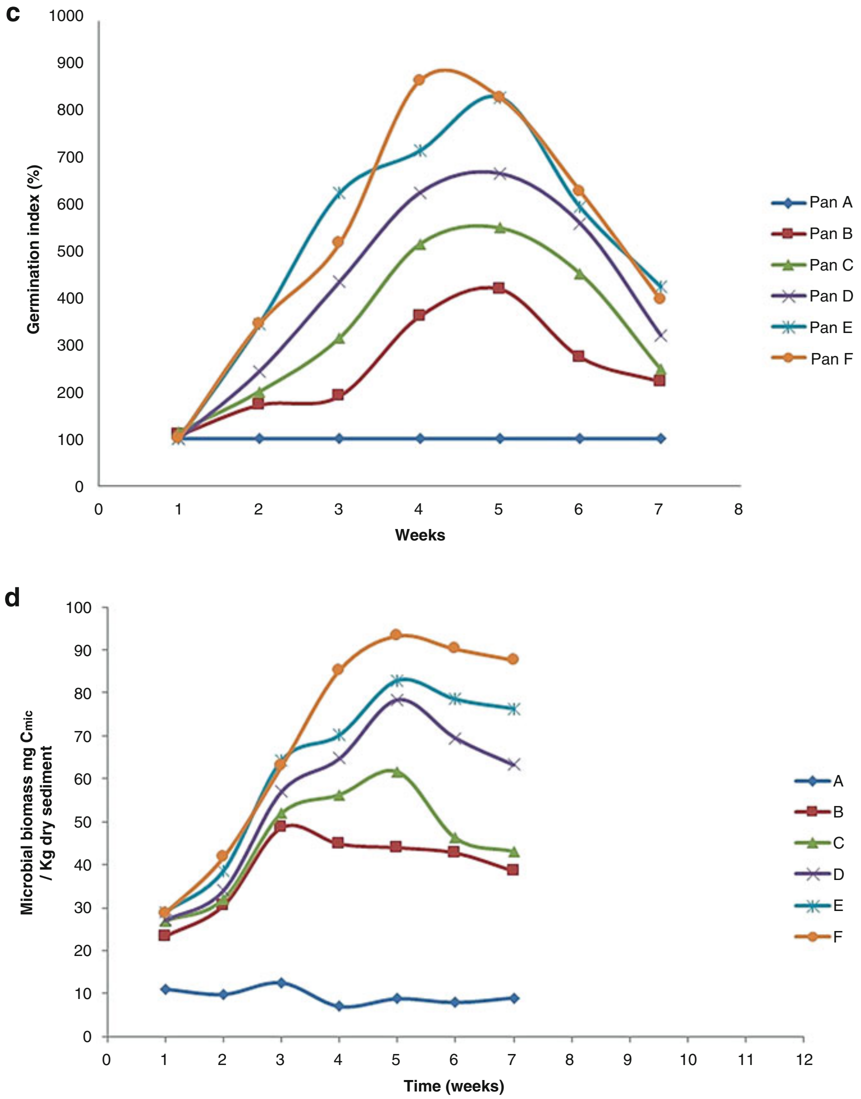

Fig. 13.6 (continued)

are used to estimate the amount and kind of substances that are amenable to mineralization as well as the biological growth in the sediment.

13.3.3.2 Dehydrogenase Activity (DHA)

The relative activity of dehydrogenase throughout treatment is seen in Fig. 13.6b. Treatment 5 (nutrient and abattoir effluent) had the largest microbial activity, as shown by the elevated dehydrogenase activity as a result of sediment moisture content; DHA is increased when the moisture is high, and water availability in the abattoir effluent strongly affects soil microbial activity and composition (Chander and Brookes 1991). This could be a major reason for the increase in microbial numbers (Bhattacharyya et al. 2001). Thus, the organic amendment increases the organic matter content, which directly increases the enzyme activity. By week 8, the incorporation of rice husk and an improved microbial community had raised the dehydrogenase activity from 15.4 to 152.4 μg INTF/gm dw. In treatment 6, which had nutrients and rice husk, the dehydrogenase activity increased from 13.5 to 142.57 μg INTF/gm dw by week 8. Surprisingly, the quality of the OM in the soil is more significant than its quantity since OM impacts the energy source for microbial development and the manufacture of enzymes (Aoyama and Nagumo 1997). The addition of an enriched microbial consortium in treatment 4 also had a great effect. Biostimulation with nutrient addition increased dehydrogenase activity, but at a lesser rate when compared to pan with a microbial consortium. The activity of the enzyme was enhanced by biostimulation with aeration alone (treatment 2), with a small rise in dehydrogenase activity.

DHA levels in all treatment units were observed to decrease after 8 weeks, most likely as a result of the degradation of labile organics. Bioaugmentation (pans D, E, and F) had a higher rate of dehydrogenase activity than the treatments with biostimulation (B and C) and control. The nutrients (energy) in pans D, E, and F revive the microbes present in them for optimum dehydrogenase activity. In this regard, Aoyama and Nagumo (1997), Nweke et al. (2006), and Nweke et al. (2007) established that little modification of the sediment increases the energetic metabolism, which increases the enzymes' activities.

13.3.3.3 Phytotoxicity Assay

Table 13.3 shows the results of sorghum seeds that germinated after 24, 48, and 72 h. It was observed that the germination average on all amended treatments is higher than that of the non-amended treatment (control). Figure 13.6c demonstrates that after the addition of an organic amendment and an enriched colony of microorganisms, the phytotoxicity degree in the sediment has been significantly lowered (treatments 5 and 6). This was soon followed by treatment 4, and a comparably lesser drop in phytotoxicity was found in treatment 3, which boosted indigenous microbial activity through the incorporation of oxygen and supplements. Treatment 2 got biostimulation with aeration only, which resulted in a slight rise in its germination index. Controls exhibited poor GI values that did not alter over treatment, but they also had low germination percent and root length when compared to treatments 5 and 6, where the microorganisms received nutrition for their energy metabolism.

The observations were obvious after week 12, when the amendments had decomposed. Trace element levels were shown to have a considerable ($p < 0.05$) phytotoxic impact on the germination index (Fig. 13.6c). The phytotoxicity of germination and root length improved considerably with a decrease in toxic element concentrations. The results of this finding indicated that heavy metals at levels above the required amount had significant phytotoxicity on sorghum seed germination

Table 13.3 Effects of different treatments on germination rates of seeds

	A (week 0)	A (week 12)	B (week 0)	B (week 12)	C (week 0)	C (week 12)	D (week 0)	D (week 12)	E (week 0)	E (week 2)	F (week 0)	F (week 12)
24 h	0 of 10	1 of 10	1 of 10	2 of 10	1 of 10	3 of 10	0 of 10	3 of 10	0 of 10	2 of 10	0 of 10	3 of 10
48 h	2 of 10	3 of 10	2 of 10	6 of 10	3 of 10	5 of 10	0 of 10	6 of 10	0 of 10	7 of 10	1 of 10	6 of 10
72 h	2 of 10	5 of 10	2 of 10	7 of 10	3 of 10	7 of 10	2 of 10	8 of 10	1 of 10	10 of 10	2 of 10	9 of 10
Average after 72 h (%)	20	50	20	70	30	70	20	80	10	100	20	90

characteristics. Toxic materials' detrimental effect on shoot and root length is directly related to their toxicity on the sorghum germination index. This study's results are in line with those of Radha et al. (2010) and Shaikh et al. (2013), who found that the phytotoxicity of toxic metals on GI was reduced at lower doses and rose at higher doses.

All of the pollutants contained in the treatments significantly ($p < 0.05$) impacted the GI of sorghum. Root lengths and germination rates were both negatively impacted by elevated heavy metal concentrations, and a significant drop was mostly seen at week 12 when concentrations were compared to the control treatment (Table 13.3). Excess salt deposition in the cell wall may reduce germination rates and root lengths by adversely altering metabolic functions and limiting cell wall flexibility (Naseer 2001). Along with causing chromosomal abnormalities and aberrant mitosis, heavy metals may also interfere with cell division, which would impede root growth (Bhattacharyya et al. 2001). According to other studies on the bioassay tests (Kapanen and Itävaara 2001), the results showed the same differences between the control, where the GI was lower, and the amended sediment (bioaugmentation and biostimulation), where the GI was highest.

13.3.3.4 Microbial Biomass

The microbial biomass carbon was determined after week 12. The result as seen in Fig. 13.6d showed that treatment A (sterile sediment) fluctuated at weeks 6, 8, 10, and 12 most likely due to fluctuations in microbes generated by microbial succession. Organic wastes have the effect of the treatment increasing the C_{mic} values, which are significantly higher than those of biostimulation. Beyond week 8, when the microbial biomass was seen to diminish more slowly than in treatment 3, the effects of the microbial consortium and organic wastes were clearly obvious in treatments 4, 5, and 6.

13.3.4 Chemical Analysis of Microcosm

Figure 13.7a–i shows the chemical analysis of different microcosms. A significant decrease in the heavy metal concentration was observed in different treatment units (B, C, D, E, and F). During the 12 weeks of incubation, treatment E (bioaugmentation with abattoir wastewater) demonstrated the ability to eliminate the pollutant the most. However, some of the loss could have resulted from volatilization, as shown in control samples.

In all the figures:
Pan A—control
Pan B—simple aeration
Pan C—biostimulation
Pan D—bioaugmentation (consortium)
Pan E—bioaugmentation (abattoir effluent)
Pan F—bioaugmentation (rice husk)

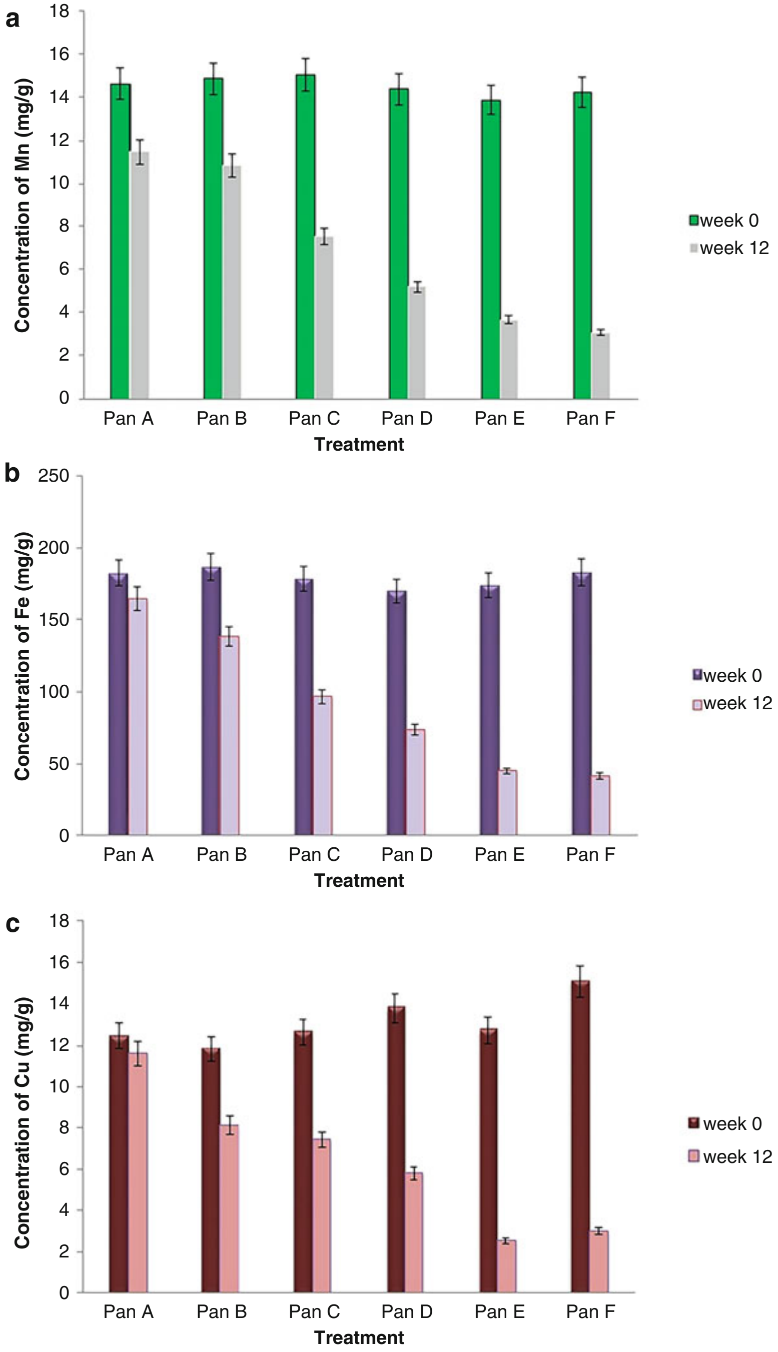

Fig. 13.7 Rate of degradation of (**a**) manganese, (**b**) iron, (**c**) copper, (**d**) zinc, (**e**) cobalt, (**f**) chromium, (**g**) cadmium, (**h**) nickel, and (**i**) lead in different treatments

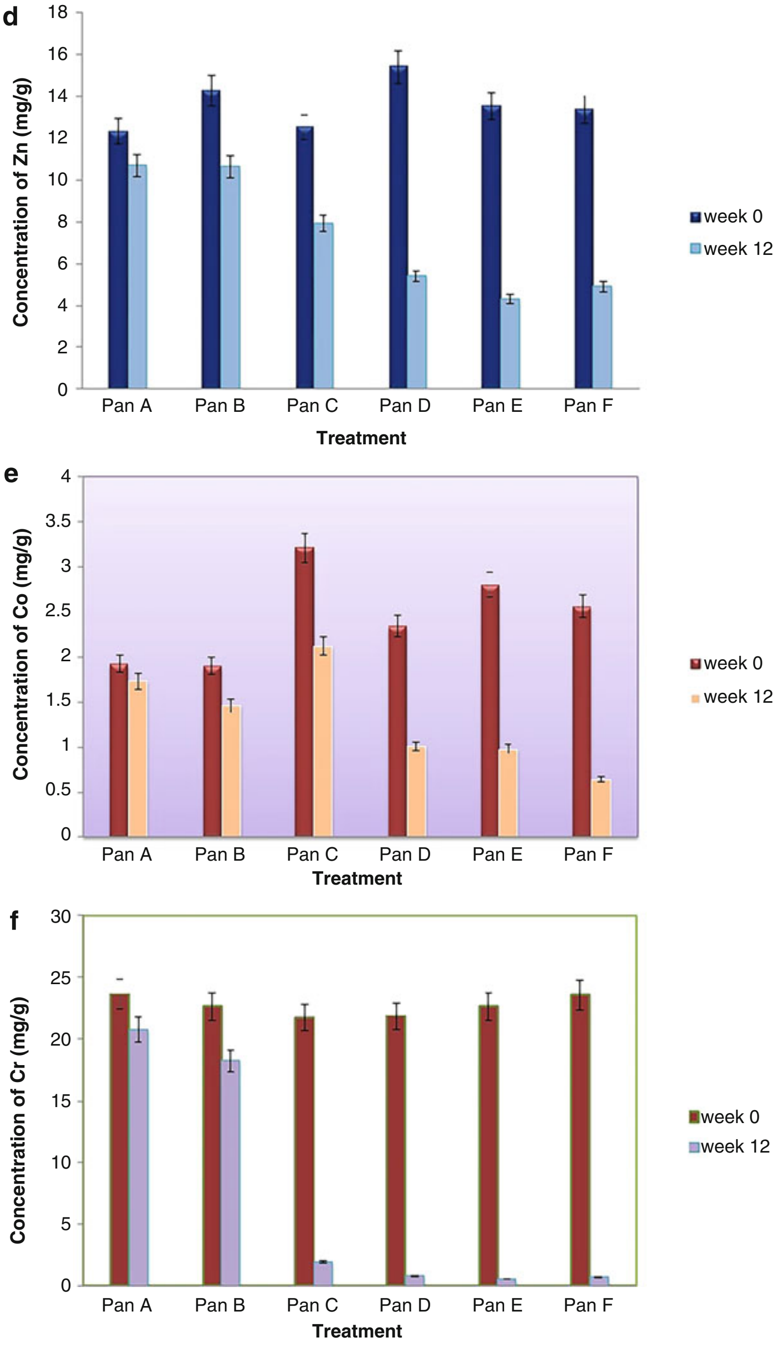

Fig. 13.7 (continued)

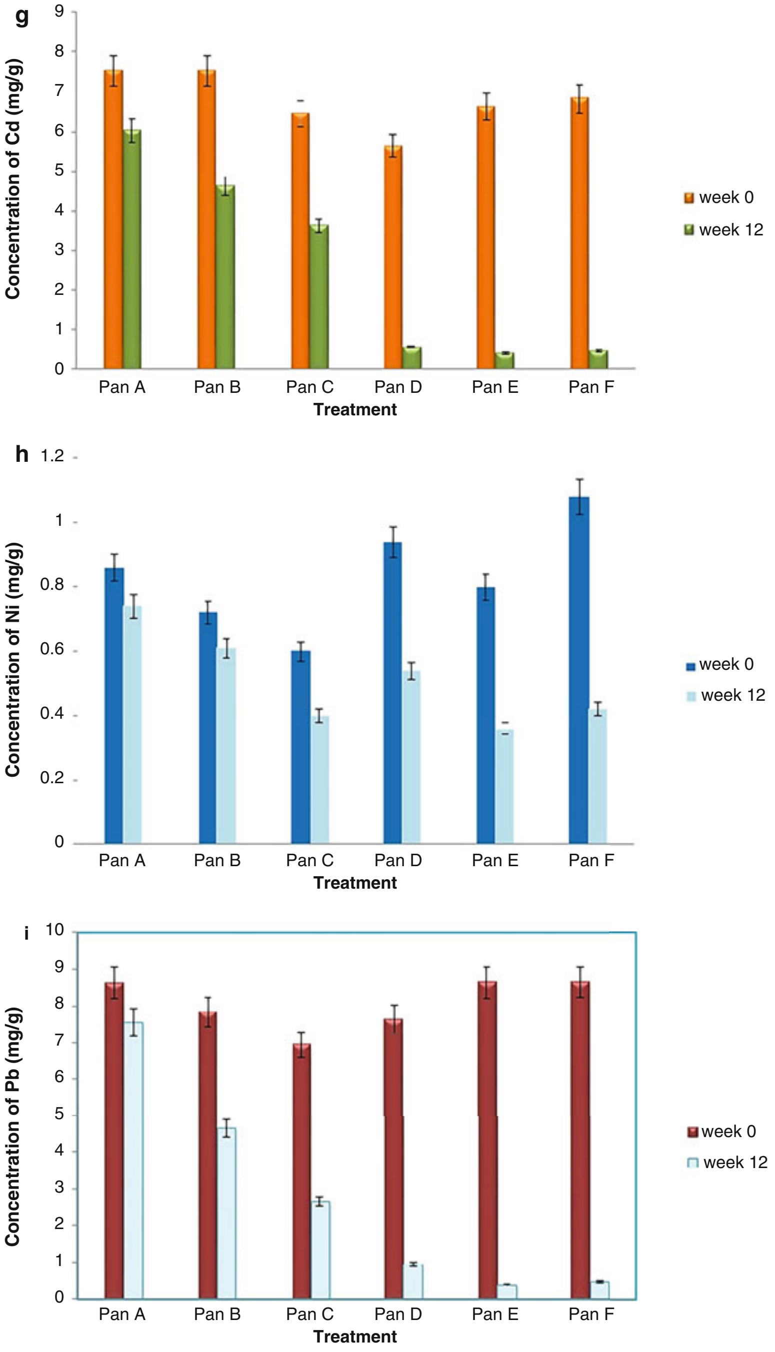

Fig. 13.7 (continued)

13.3.5 Effect of Some Fungal Isolates on the Toxic Elements in Asa River Sediment

Microorganisms isolated from Asa River sediment with substantial metal levels and organic waste show a strong resistance to these components. This resistance may be owing to some abiotic conditions or to the microorganism's biochemical and genetic responses. Romero et al. (1999) observed that numerous microbes have been evaluated for their heavy metal adsorption ability, but those isolated from the Asa River sediment, where these pollutants are prevalent, are of particular relevance in this study. Fungi possess a very-well-known heavy metal sorption capacity. The result showed that some fungal species are commonly connected with substrates that have high concentrations of heavy metals and can even be regarded as heavy metal hyperaccumulators, as previously described by Gadd (1997).

The *Fusarium* sp. showed good tolerance level behind *Aspergillus niger* of sediment samples. There was at least one isolate from each of the two major groups of fungi. Figure 13.8(a–i) illustrates *Aspergillus* sp. with varying degrees of metal tolerance, which was investigated in this study. The isolates from river sediment show that some fungi (*Aspergillus* sp., *Penicillium*, etc.) from heavy metal-contaminated river sediment have higher resistance to heavy metals than others and might be used to mitigate these metals from solutions. Gadd (2007) remarked that due to their intracellular metal sorption nature and resistance to metals, filamentous fungi are more fitted for this function than other microbes. Heavy metals may be amassed by various fungi by a variety of processes, such as polypeptide binding.

Before inoculating samples with various fungal isolates, the sediment contained a high concentration of toxic elements. Figure 13.8a–i shows the differences in the value of heavy metals present before and after 12 weeks of inoculation. *Aspergillus* spp. was found to be among the most prevalent in the heavy metal-polluted sediment, which was similar to the results obtained by Ahmad et al. (2005) and Nweke et al. (2006). Various *Aspergillus* spp. such as *A. niger*, *A. fumigatus*, and *A. flavus* have been engaged in the sorption of heavy metals. Nweke et al. (2007) and Tunali et al. (2006) also observed similar results in their studies. Gadd (2007) investigated the elimination of hazardous elements by *Aspergillus* sp. from untreated wastewater. According to Nweke and Okpokwasili (2013), Cd, Cu, and Ni were the metals to which *Aspergillus* strains were most tolerant. As a result, *A. tamarii, A. flavus, A. niger,* and *A. terreus* were chosen to be studied in the current investigation. *Aspergillus niger* had a higher degradation for most of the heavy elements present in the sediment, except nickel, where *Fusarium solani* had the highest degradation. It was also observed that all the fungi significantly decreased the metal level when compared with the control.

The sediment had a high content of toxic element before inoculating samples with different fungal isolates. Figure 13.8(a–i) shows the differences in the value of heavy metals present before and after 12 weeks of inoculation with varying fungal isolates. *Aspergillus niger* had a higher degradation for most of the heavy elements, except nickel, where *Fusarium solani* had the highest degradation. It was also observed that

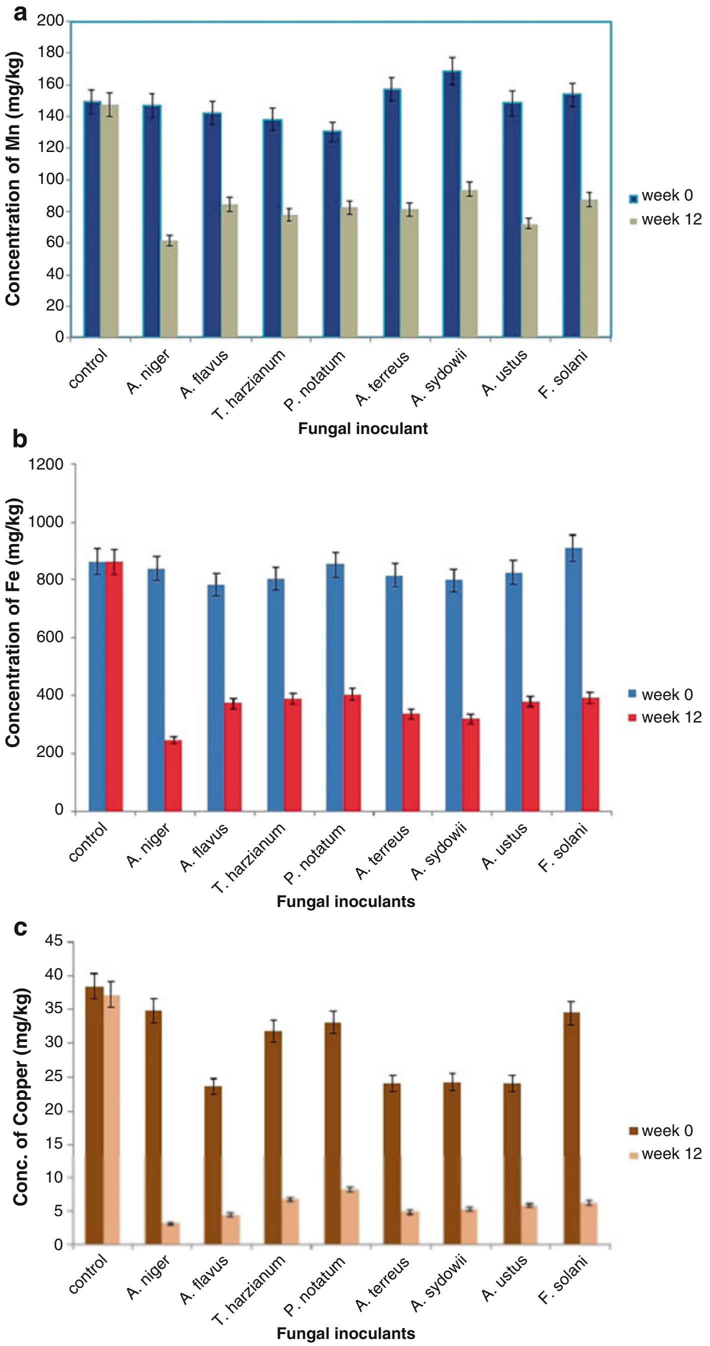

Fig. 13.8 Effect of fungal inoculants on (**a**) manganese, (**b**) iron, (**c**) copper, (**d**) zinc, (**e**) cobalt, (**f**) chromium, (**g**) cadmium, (**h**) lead, and (**i**) nickel levels in Asa River sediment

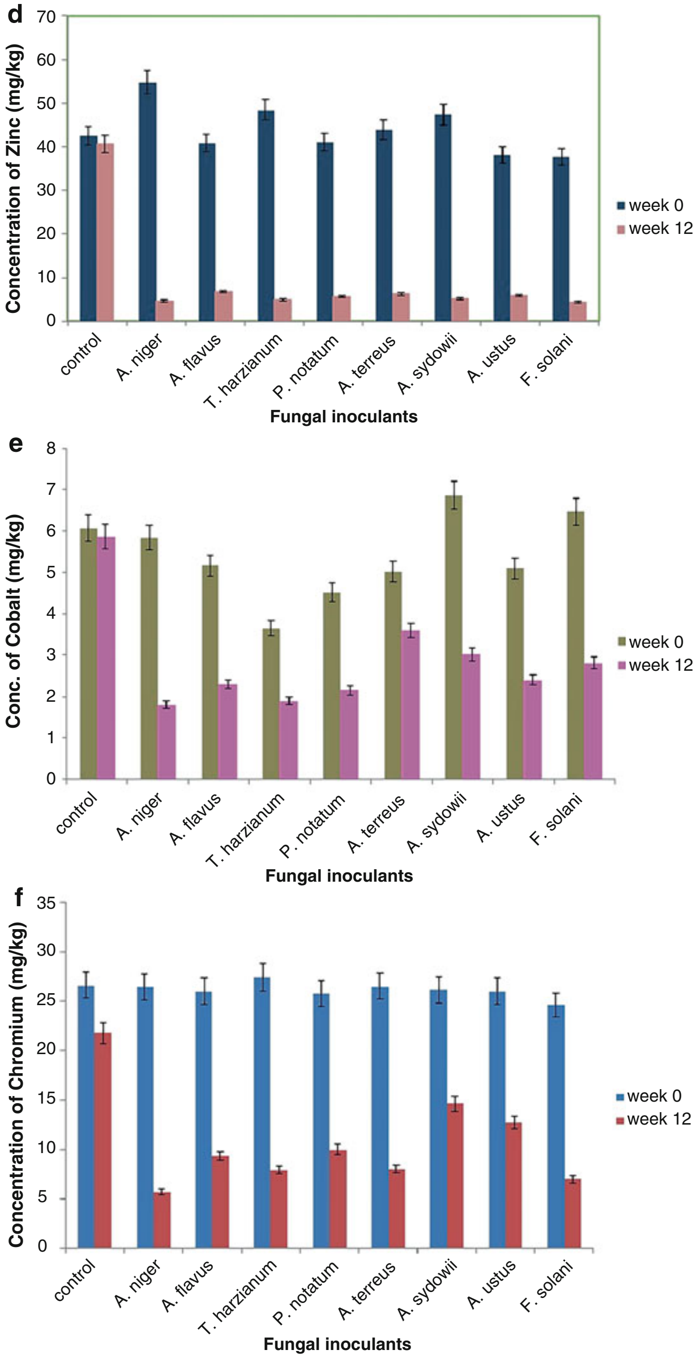

Fig. 13.8 (continued)

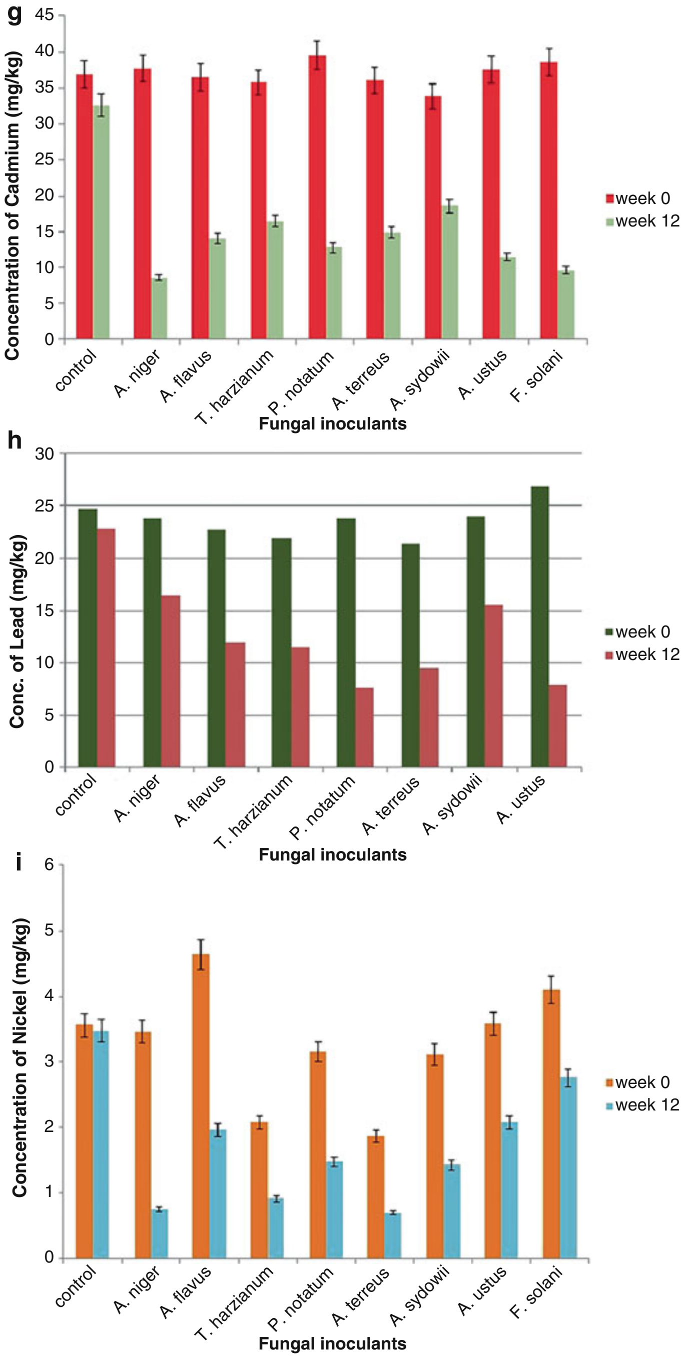

Fig. 13.8 (continued)

all the fungi species led to a significant decrease in heavy metal content when compared with the control.

Figure 13.8a indicates that Mn is degraded in the following order*: A. niger* > *A. ustus* > *A. terreus* > *A. sydowii* > *T. harzianum* > *F. solani* > *A. flavus* > *P. notatum.*

Figure 13.8b indicates that Fe is degraded in the following order*: A. niger* > *A. sydowii* > *A. terreus* > *F. solani* > *A. ustus* > *P. notatum* > *A. flavus* > *T. harzianum.*

Figure 13.8c indicates that Cu is degraded in the following order*: A. niger* > *F. solani* > *A. flavus* > *A. terreus* > *T. harzianum* > *A. sydowii* > *A. ustus* > *P. notatum.*

Figure 13.8d indicates that Zn is degraded in the following order*: A. niger* > *T. harzianum* > *F. solani* > *A. sydowii* > *A. ustus* > *P. notatum* > *A. terreus A. flavus.*

Figure 13.8e indicates that Co is degraded in the following order: *F. solani* > *A. flavus* > *P. notatum* > *T. harzianum* > *A. sydowii* > *A. niger* > *A. ustus* > *A. terreus.*

Figure 13.8f indicates that Cr is degraded in the following order: *A. niger* > *F. solani* > *T. harzianum* > *A. terreus* > *A. flavus* > *P. notatum* > *A. ustus* > *A. sydowii.*

Figure 13.8g indicates that Cd is degraded in the following order: *A. niger* > *F. solani* > *A. ustus* > *P. notatum* > *A. flavus* > *A. terreus* > *T. harzianum* > *A. sydowii.*

Figure 13.8h indicates that Pb is degraded in the following order: *A. ustus* > *P. notatum* > *A. terreus* > *T. harzianum* > *A. flavus* > *F. solani* > *A. niger* > *A. sydowii.*

Figure 13.8i indicates that Ni is degraded in the following order Ni*: A. niger* > *A. sydowii* > *A. terreus* > *A. flavus* > *T. harzianum* > *P. notatum* > *A. ustus* > *F. solani.*

13.4 Conclusion

This work evaluated the use of agricultural wastes (rice husk and abattoir effluent) to bio-remediate the sediment of the Asa River. The physicochemical and heavy metal analyses revealed high concentrations of organic carbon, organic matter, and heavy metal concentrations, among others, in the river sediment. It was observed that higher concentrations of the metals were very phytotoxic ($p < 0.05$) and prevented crop germination. This showed that human activities such as sewage disposal, industrial effluents, and chemicals from agricultural practices are the major causes of the river's sediment and low soil fertility. A total of 21 fungi were isolated from the samples and the agricultural wastes, and they all successfully degraded the heavy metal concentrations, with *Aspergillus niger* being the most effective. This study presents bioremediation as a low-cost and environmentally benign technique for remediating Asa River sediment.

Statements and Declarations

Conflict of Interest The authors declare that there are no conflicts of interest.

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Human and Animal Rights This chapter does not contain any studies involving human or animal subjects.

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Potential Application of Biochar for Efficient Restoration of Crude Oil-Contaminated Sites

14

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Abstract

Crude oil contamination is a serious matter as it contributes majorly towards environmental pollution all across the globe. The ever-increasing urbanization and industrialization have increased the demand for fossil fuel, which is the driving energy source. The different activities of oil industry lead to emancipation of a huge volume of hydrocarbon in the environment, which has adverse effect towards the ecosystem. Bioremediation is one of the most widely accepted technologies for remediation of crude oil-contaminated sites as it is cost effective and eco-friendly in nature, but it has limitations due to its slow rate as hydrocarbons are hydrophobic in nature. Upgradation of the bioremediation process by incorporating stimulating agents can be beneficial. Biochars are wonder bio-based components, which are drawing attention in the present day, as they can be used as biostimulant to enhance the efficiency of biodegradation process due to its attractive properties. The notion of this chapter is to discuss the importance and role of biochar in the remediation of hydrocarbon-contaminated sites.

Keywords

Crude oil · Environmental pollution · Bioremediation · Biostimulant · Biochar

14.1 Introduction

The rapidly growing urbanization and the ever-increasing demand for fossil fuel in order to meet the energy requirement lead to massive crude oil exploration. Although during the COVID-19 pandemic, the demand for crude oil decreased to 91 million barrels per day from 99.7 million barrels, it again increased to 96.5 million barrels in 2021, and this is expected to rise further as the pandemic condition has gradually improved. The demand for petroleum is increasing day by day. The various activities in oil fields and refineries and the transportation of oil cause the accidental liberation of a huge amount of crude oil into the environment. Crude oil contamination is of global concern as it leads to the destruction of soil structure and alters its physico-chemical properties, and also imposes adverse effect towards plant growth and existing life forms. The major constituents of petroleum hydrocarbon are carbon, hydrogen, and oxygen, although in some cases sulphur and nitrogen are also present. Either straight-chain or ring-shaped aliphatic hydrocarbons, aromatic hydrocarbons, and polyaromatic hydrocarbons or PAHs (consisting of two or more benzene rings) are present in petroleum hydrocarbons that are highly poisonous in nature due to their carcinogenic and mutagenic properties (Zhang et al. 2019). Further, the transfer of hydrocarbons across the food chain can also lead to hazardous effect on humans. Thus, considering the negative impact of crude oil pollution, restoration and mitigation of crude oil-contaminated sites are of utmost necessity for a sustainable ecosystem. Several treatment techniques are utilized for rehabilitation of crude oil-contaminated soil, such as solvent washing, electrochemical techniques, precipitation, coagulation, incineration, flocculation, and adsorption; however, such techniques emancipate toxic products and gases that pollute the environment (Ali et al. 2020). Bioremediation is considered to be the most efficient, clean, and cost-effective method. Some microorganisms possess the ability to take up and utilize hydrocarbon for their metabolism and degrade them to simpler forms, and even certain plants can accumulate and convert hydrocarbon to their intermediate forms. For instance, bacterial genera such as *Bacillus*, *Rhodococcus, Burkholderia, Pseudomonas, Arthrobacter, Acinetobacter, Alteromonas, Mycobacterium, Kocuria, Enterobacter, Marinobacter, Streptococcus, Staphylococcus,* and *Achromobacter* are known to degrade hydrocarbon components from polluted sites (Varjani and Gnansounou 2017; Xu et al. 2018). Bioremediation usually comprises two approaches: (1) bioaugmentation and (2) biostimulation (Wu et al. 2016a, b). In bioaugmentation, biological organisms are introduced in a contaminated environment for initiating the remediation approach, whereas in biostimulation, external nutrient and media are added for triggering or accelerating the degradation to be mediated by the indigenous microflora or vegetation. Although bioremediation is a widely acceptable technology, it has certain limitations. As hydrocarbon compounds are hydrophobic in nature, they are not easily bioavailable in nature, due to which the rate of bioremediation is slow (Makkar and Rockne 2003). Many studies have found that the combined approach of biostimulation and bioaugmentation leads to a better outcome of remediation experiments. The activity of indigenous soil flora or plants is enhanced by supplementation of biostimulants. A wide range of agricultural by-products such as peanut peel, rice straw, and biomasses can be applied as stimulating agents for enhancing the activity of the microorganisms dwelling in a contaminated site (Xue et al. 2019). New techniques and ideas for the development of advanced bioremediation are being incorporated to achieve better outcomes. Recently, biochar has been gaining importance as it has shown to improve soil quality and enhance microbial activity that performs the desirable degradation of hydrocarbons, as they use them for their metabolism and convert them to simple forms. Biochar is nothing but the carbon-rich material that is obtained by pyrolysis of organic matter. The biochar possesses a number of attractive properties such as high porosity, better adsorption, nutrient absorption ability, and enhanced stability as compared to other biological wastes (Ali et al. 2019). Biochar promotes microbial growth; it enhances the metabolism of microbes and increases its tolerance towards toxic pollutants in the environment (Xue et al. 2019). It improves soil fertility and soil enzyme activity that play a major role in determining the fate of remediation approaches (Wang et al. 2015; Zhang et al. 2019). Thus, amendment of biochar in hydrocarbon-contaminated sites can be promising in resolving the quandary caused by the crude oil pollution. In this chapter, we shall discuss about biochar and its role in triggering bioremediation of hydrocarbon-contaminated soils.

14.2 Negative Impact of Petroleum Hydrocarbon

Crude oil has an adverse effect on the soil quality. It alters the physicochemical properties of the soil, as a result of which the vegetation in oil-polluted sites is adversely affected (Devatha et al. 2019). The crops cultivated in crude oil-contaminated sites show poor growth and yield, as the crude oil hampers its normal metabolism and uptake of nutrients from the soil. Certain components of crude oil, such as PAHs, can enter mammalian body including humans through different routes including inhalation, dermal contact, ingestion of contaminated food stuff, and smoking of tobacco cigarettes (Dong et al. 2012; Beyer et al. 2010). Contamination of water bodies by crude oil spillage affects aquatic organisms including fishes, planktons, microalgae, etc., and the sunlight- or UV-induced photooxidation of PAHs enhances their toxic effects (Björn 2015). The International Agency for Research on Cancer has classified certain PAHs as possible carcinogen against human. The Environment Protection Act (EPA) has classified seven PAHs, namely, benzo(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)-fluoranthene, dibenz(ah)anthracene, indeno(1,2,3-cd)pyrene, and chrysene, as possible carcinogens for humans (EPA 2008). Usually, the PAHs trigger alteration of genetic makeup of an organism, which ultimately causes carcinogenic diseases (Luch 2005). Crude oil components also affect immunity as revealed from studies on rodents although the detailed mechanism of action is not known clearly. PAHs are even suspected to impose teratogenic effects as several studies observed birth defects and depletion in the weight of neonatal mice populations that were served with doses of PAHs during pregnancy period (Dejmek et al. 2000).

Crude oil pollution also affects plant growth. They also interpreted that the total chlorophyll and carotenoid contents also decreased due to crude oil contamination. Crude oil contamination leads to a decrease in chlorophyll content in *Cyperus brevifolius* (Rottb). It was also found that the plant biomass was significantly reduced, and structural deformation in leaves and tissues was observed due to crude oil contamination (Patowary et al. 2017). The rice plant parts including the grains were found to accumulate hydrocarbon compounds, and it can be assumed that consumption of such adulterated cereals can lead to health issues. Our findings also suggest that it is necessary to investigate the quality of the soil before the land is utilized for other purposes, especially cultivation or animal rearing.

14.3 What Is Biochar?

Biochar is nothing but the carbon-rich product obtained by the thermal conversion of biomasses in low or absence of oxygen, i.e. pyrolysis. Biochar can be produced from different kinds of biomass, domestic or kitchen waste, and it can lead to better solution for waste management. Usually, a temperature of more than 350 °C is necessary for the conversion of the biomass to the biochar, although the temperature requirement may vary based upon the composition of the biomass utilized. The carbons present in the biochar are randomly arranged in aromatic rings, and the intensity of aromatization actually determines the stability of the biochar (Wiedemeier et al. 2015). Further, the stability of the biochar also depends on the biomass and the temperature applied for its preparation. Biochar can serve as a cost-effective approach for waste management that can be widely applied to remediate contaminated environment. Amendment of biochar as a soil conditioner can lead to improvement of soil health and promote the growth of plants in contaminated or problem soil.

14.3.1 Properties of Biochar

Biochar possesses a wide number attracting properties that make it a suitable candidate for application in remediation purposes. It has a high surface area and negative charge and is recalcitrant in nature. It has a high adsorption capacity compared to other sources and also has high porosity. The high adsorption capacity of the biochar allows adsorption of the contaminants from the contaminated environment and prevents their leaching into the groundwater (Downie et al. 2009; Yang et al. 2016). The pores in the biochar are created during the thermochemical decomposition of the biomass, and based upon the size of the pore size (internal diameter), biochars are classified into three types: macropores (>50 nm), mesopores (2–50 nm), and micropores (<2 nm) (Mukherjee et al. 2011) (Fig. 14.1). The properties of biochar can be classified into three groups:

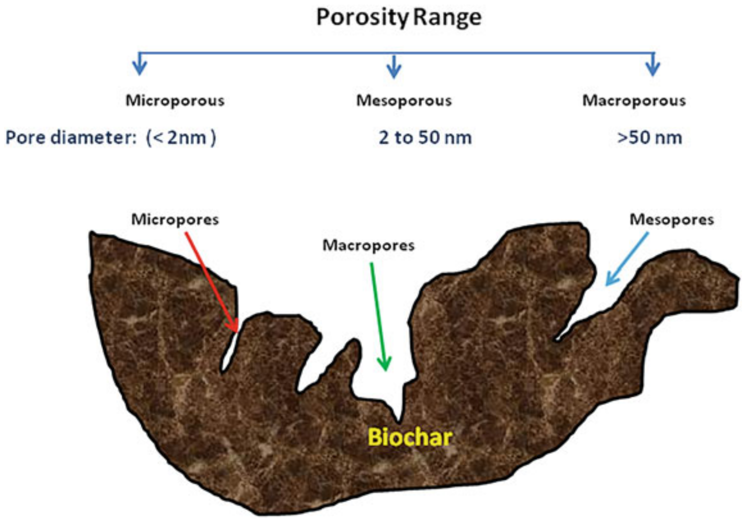

Fig. 14.1 Schematic representation of porous structure of the biochar mentioning its porosity range

14.3.1.1 Physical Properties

The physical properties of biochar mainly include its density, pore structure, hydrophobicity, and surface area. Biochar generally has low bulk density, and its porosity largely depends on the pyrolysis temperature used to convert the biomass. As the temperature increases, the porosity of biochar increases. For instance, the porosity of biochar obtained from woodchips increases from 50% to 70% as the pyrolysis temperature increases from 300 to 850 °C (Somerville and Jahanshahi 2015). Water-holding capacity of the biochar is dependent on the porosity of the biochar; the higher the porosity, the more the water-retaining capacity of it. The functional groups of the biochar also have an impact on the hydrophobicity. The increased pyrolysis temperature reduces the functional group present at the surface of the biochar, and this reduces the affinity of the biochar towards water (Pimchuai et al. 2010).

14.3.1.2 Chemical Properties

The chemical properties of biochar include pH, ionic exchange capacity, and composition. The increasing pyrolysis temperature enhances the pH and cationic exchange capacity of the biochar. The elemental composition of biochar also depends upon the pyrolysis temperature, as the composition undergoes various changes in forms and properties. The major elements present in the biochar are C, H, O, and N, and some amount of S, P, Si, Cu, Fe, Zn, and Mn in meagre amount, although the type of biomass utilized for biochar preparation determines its composition (Wu et al. 2016a, b). Thus, these minerals in the biochar aid in plant growth promotion and enhance microbial population that triggers the remediation of contaminated environment. The C is the backbone of the biochar and usually exists in carbonate and bicarbonate forms; H is the main building block, and it plays a major role in the sorption of molecules. During pyrolysis, the peptide bonds present in the biomass convert to N-heteroaromatic carbon compounds (Lian and Xing 2017).

14.3.1.3 Surface Functionality

The surface of the biochar mediates its activity and interaction with other components. The surface charge, functional groups on the surface, and structure-related functionality contribute to the activity of the biochar. With increasing pyrolysis temperature, the surface radicals on the biochar also change. The free radicals play an important role in mediating the degradation of organic contaminants from the environment as they can react with hydrogen peroxide and persulfate (Xiao et al. 2018).

The biochar properties vary on account of different biomass used and the temperature at which it is prepared. Further different pyrolysis conditions such as pressure and gas also influence the biochar characteristic properties (Sohi et al. 2010; Shackley and Sohi 2010). Various sophisticated technologies such as scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), Brunauer-Emmett-Teller (BET), and gas pycnometry can be used for the elucidation of physical structure and characteristic features of biochar. The chemical properties can be determined by Fourier transform infrared spectroscopy (FTIR); proximate analysis to determine the ash, moisture, fixed carbon, volatile matter, etc. can be done by CHNS analyser; and to determine the aromaticity of the biochar, magnetic resonance spectroscopy (NMR) can be used. Mainly, the surface area and the porosity are two factors that determine the adsorption capacity of biochar.

14.4 Factors Affecting the Quality of Biochar

The quality of biochar is a vital property that signifies its activity. The two main factors that contribute majorly to the quality of biochar produced are the biomass used for the biochar preparation and the condition in which the biochar is prepared. The temperature utilized to produce biochar determines the surface area of the biochar, and it has been observed that the higher the temperature applied, the more the surface area of the biochar formed.

14.4.1 Biomass Utilized for Biochar Preparation

The composition of biomass utilized for biochar produced determines its type and properties. The plant-based biomass usually consists of lignin, cellulose, and hemicelluloses, and depending upon the sources, the amount of these three constituents varies accordingly (Saini et al. 2015). The cellulose and hemicelluloses are easily volatile than lignin, and thus lignin requires a higher temperature for pyrolysis. Different agricultural by-products and plant materials are being involved for biochar production.

14.4.2 Condition Used for Biochar Preparation

The temperature that is used for biochar preparation determines the properties of the biochar formed. The aromaticity and the carbon content of the biochar increased on increasing heating and pyrolysis temperature, whereas the yield and surface functional properties got reduced. The biochar produced at high temperature has more pronounced surface area, as the pores blocked in unpyrolyzed organic matter are opened up at high heating temperature (Zahed et al. 2021). The heating principle used for biochar preparation, that is, the conventional heating involving muffle furnace or advanced heating approaches by microwave heating, also contributes to the quality of the biochar.

14.5 Benefit of Biochar Amendment in Remediation of Petroleum-Contaminated Soil

The versatile properties of biochar make them a suitable biostimulating agent for remediation of pollutants from the environment. Application of biochar in environmental remediation can serve for waste management, as biochar itself is prepared from biomass waste of different types and origin. Figure 14.2 has shown the mechanism by which biochar aids in the remediation of environmental polluted sites and leads to waste management. As biochar has high porosity, it can adsorb the pollutants and immobilize them, and on the other hand, biochar, as it is rich in nutrient components, leads to improvement of soil quality and enhances microbial activity and soil enzyme activity that mediate the remediation of contaminants from the polluted environment. The water-holding capacity of soil is enhanced by biochar incorporation, as a result of which more moisture is retained by the soil that aids vegetation to grow well in affected soils. It adsorbs contaminants from the environment, and this reduces the level of contaminants present, and the growth of microorganisms is enhanced. Biochar can adsorb both hydrophobic and hydrophilic compounds by electronic interactions (Trinh et al. 2017). The biochar promotes the redox reactions for degradation of organic pollutants due to the presence of graphite

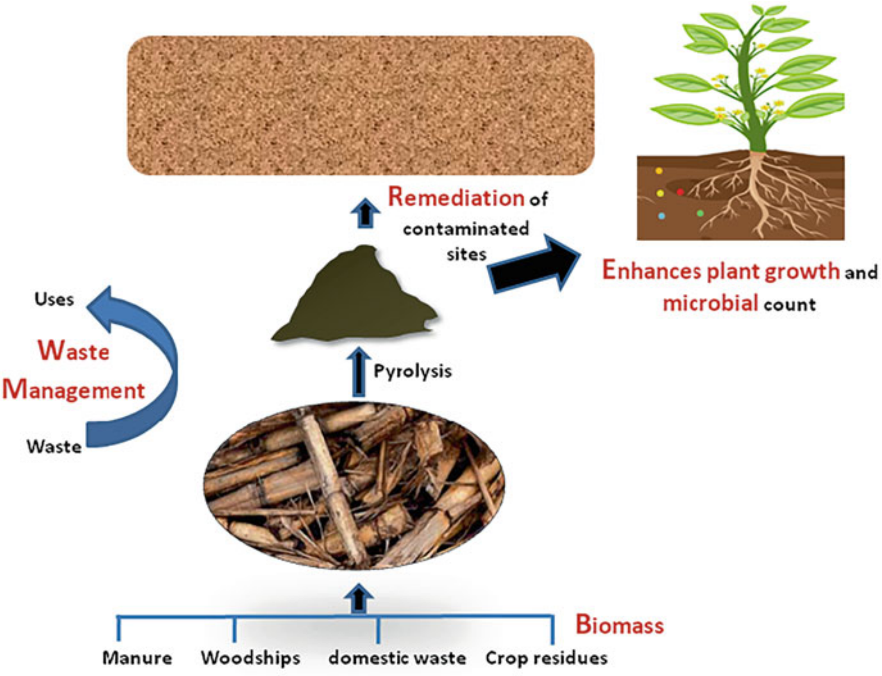

Fig. 14.2 The role of biochar in the remediation of environmental contamination recycling of wastes

and quinine structures that can accept and donate electrons (Yu et al. 2019). The biochar incorporation moderates the various parameters that are vital for determining the fate of bioremediation of hydrocarbon-polluted environment. Table 14.1 sums up the different parameters that play an important role in mediating bioremediation and mentions the ways by which biochar moderates the parameter for efficient bioremediation to occur. The activity of indigenous soil microflora is triggered by biochar amendment, which brings about the desired degradation of petroleum wastes. Thus, biochar amendment actually promotes plant growth and increases microbial population in contaminated sites, and it provides an aesthetic condition for them to flourish and minimizes the toxicity of contaminants (Fig. 14.3). The microbes and the plants and mutual interactions actually bring about the desired remediation of the pollutant from the environment. There are several studies which have reported on the beneficial role of biochar in the remediation of petroleum oil-contaminated environment. Table 14.2 sums up the research works where biochar has been applied for the restoration of crude oil-contaminated sites.

14.6 Impact of Biochar on Soil Microorganisms

The biochar plays an important role in the microbial community of a particular area. Biochar also changes the soil bacteria-to-fungal ratio and also soil enzyme activity that plays a major role in the remediation of contaminants from the environment (Ahmad et al. 2016; Nielsen et al. 2014). Several factors that are responsible for the impact of biochar on microbes are as follows:

14.6.1 Nutrient Supplement for the Microbes

The biochar can serve as nutrient sources for the soil microbes, as biochars are known to be rich in several nutrients such as Na, K, Mg, N, and P, and the attracting properties of biochar such as large surface area, high pore volume, and negative surface charges make the nutrients to be better adsorbed (Chathurika et al. 2016). The composition of nutrients present in biochar depends on the biomaterial used for its preparation and also the procedure adopted for its preparation. Biochar facilitates cation exchange capacity that results in higher nutrient retention and also prevents nutrient loss due to leaching, and this favours microbial activity (Lehmann 2007). Biochar also increases the availability of rhizobacteria that transform S and P present in the soil to its bioavailable form, and such a phenomenon enhances several groups of microbial growth. The carbon in the biochar can also serve as carbon sources for the microbes to carry out its metabolic activities, although the aromaticity of the biochar can sometimes hinder its proper usability. Application of biochar promotes the formation of macroaggregates, which favours the fungal growth rather than bacterial growth, which may be due to the hyphal networks in fungi that facilitates nutrient translocation (Ascough et al. 2010).

Table 14.1 Summary of different parameters necessary for bioremediation and the action of biochar in regulating such parameters

Sl. No.	Parameters	Effect in remediation	Action of biochar in regulating ambient condition	References
1.	Soil pH and oxygen availability	The pH and oxygen availability are important factors that have impact on the activity of the microbes and plants that brings about the remediation of the polluted sites	Biochar helps in regulation of soil pH and also helps to maintain aerobic condition in the soil due to its porous nature	Yu et al. (2019)
2.	Temperature	An optimum temperature (30–40 °C) is necessary for the microbial action for mediating the degradation of the oily components	–	Thamer et al. (2013)
3.	Oxidation and reduction potentiality	The electron donors or acceptors and their ratios determine the pathway of the degradation	Biochar due to its surface functionality alters the ionic property of the soil	Yu et al. (2019)
4.	Water content	Moisture content in the soil is important for the vitality of the soil. It promotes plant growth and also enhances the soil microbial activity	The increased porosity of the biochar leads to enhanced water-holding capacity of the soil	Basso et al. (2013)
5.	Nutrient availability	Nutrients are important for the microbes and plants for their growth and metabolism	Biochar amendment provides nutritional components in the soil that promotes microbial and also plant growth that ultimately leads to better degradation of the contaminants	Nikolopoulou et al. (2013); Yu et al. 2019
6.	Type of pollutant	The composition and type of hydrocarbon (for instance, aliphatic chain is more easily degradable than aromatic rings) and saturated and unsaturated hydrocarbon chains determine the efficiency	–	Semple et al. (2004)

(continued)

Table 14.1 (continued)

Sl. No.	Parameters	Effect in remediation	Action of biochar in regulating ambient condition	References
		of the remediation process		
7.	Presence of co-contaminant in the site	Co-contaminants can affect and alter the properties of the principal contaminants and hence change its degradation scope	Biochar with high adsorption capacity leads to the adsorption of many components present in the soil	–
8.	Microbial community	The microbial community present in the contamination site determines the fate of degradation of oily contaminants	Biochar enhances the activity of microbes and also increases its population	Zhu et al. (2017)
9.	Soil enzyme activity	The soil enzyme plays an important role in mediating the degradation of petroleum hydrocarbons from the soil	Biochar enhances the activity of the soil enzymes	Zimmerman and Ahn (2010)

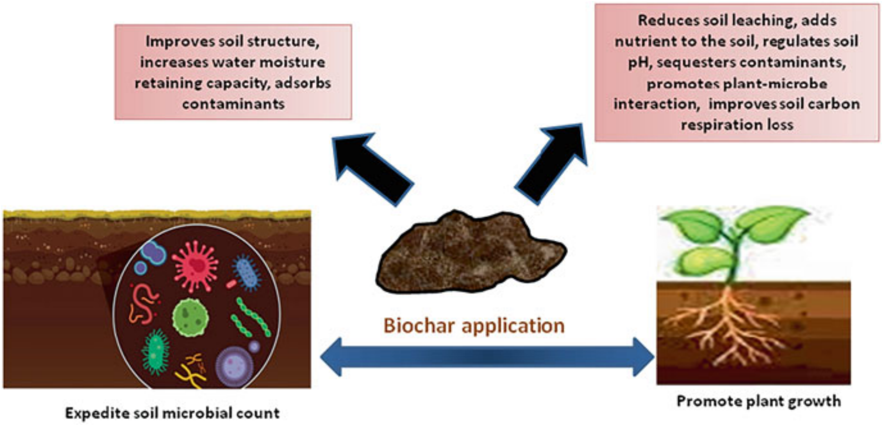

Fig. 14.3 The role of biochar in promoting plant growth and enhancing microbial count

Table 14.2 Application of biochar for remediation of crude oil-contaminated environment

Sl. No.	Biomass used for biochar preparation	Application type	Outcome/findings	References
1.	–	Chitosan-biochar composite was applied to immobilize microbial agent (*Pseudomonas aeruginosa* and *Bacillus licheniformis*) for remediating crude oil-contaminated soil	The remediation of the oily components increased drastically. The microbial count in the soil was also found to be increased	Liu et al. (2023)
2.	Coconut shell	Biochar and graphite carbon nitride were applied for treatment of crude oil-contaminated soil	The removal rates of nC_{13}–nC_{35} were above 90%. Both adsorption and photocatalysis phenomena actually enhanced the removal of the hydrocarbon	Lin et al. (2022)
3.	Rice, sewage sludge, petroleum coke	Rhamnolipid-modified biochar was applied for treatment of crude oil-contaminated soil	Biochar amendment was found to be effective in regard to degradation of TPHs and increased microbial diversity	Zhen et al. (2021)
5.	Sugarcane fibre	Artificial crude oil contamination (1%) in microcosm study (Erlenmeyer flask), where biochar was applied in combination with biosurfactant and nitrogen source	80.9% remediation was achieved	Wei et al. (2020)
6.	Sugarcane leaves	Remediation of wetland soil was carried out at microcosm scale. Biochar +biosurfactant mixture was applied	Biochar amendment reduces ecotoxicity of oil in the contaminated environment and thereby enhances the activity of plants and microbes for mediating the remediation	Wei et al. (2020)
7.	Sugarcane bagasse	Biochar, *Enterobacteria* MN17, was added in artificial diesel-contaminated soil where mung bean has been sowed	It was found that biochar amendment significantly enhanced petroleum hydrocarbon (PHC) removal and enhanced the growth of mung bean	Ali et al. (2020)
8.	Spent mushroom substrate	Petroleum-degrading bacteria were immobilized on biochar and applied for treatment of total petroleum hydrocarbon (TPH)-contaminated soil	The immobilization of bacteria on the biochar enhances its activity, and better remediation was obtained in contrast to the bacteria alone	Zhang et al. (2019)

(continued)

Table 14.2 (continued)

Sl. No.	Biomass used for biochar preparation	Application type	Outcome/findings	References
9.	Green garden waste	Biochar+compost +bacterial consortium was applied in ryegrass-planted area contaminated with crude oil	Highest degradation of TPH (85%) was obtained in the soil where the soil was amended by all of the three components. The organic amendment enhanced ryegrass growth and also bacterial count in the rhizosphere area	Hussain et al. (2018)
10.	Bulrush straw	Biochar and nutrients (N and P) were supplemented in oil-contaminated soil at laboratory scale	It was observed that the combination of biochar and nutrients has a beneficial effect on the removal of TPH	Wang et al. (2017)
11.	Wheat straws	Ryegrass was used as a phytoremediation candidate for treatment of crude oil-contaminated soil, and biochar was amended in the soil	Biochar amendment was not found to be effective for phytoremediation of crude oil-contaminated oil by ryegrass	Han et al. (2016)
12.	Rice straw	Biochar was amended in petroleum-contaminated soil in a microcosm-scale study	It was observed that biochar amendment had a positive effect on the degradation of TPHs. Additionally, it was found that the amendment of biochar at later phase of the study showed more better outcome than the biochar added at the beginning of the study	Qin et al. (2013)

14.6.2 Modification of Microbial Habitat by Biochar

Biochar aids in improving soil physical properties, and the porosity of biochar can lead to the reduction of soil density and enhance soil aeration, which promotes microbial growth. The amendment of biochar in soil allows more retention of water and prevents moisture loss in the dry season, and this helps in maintaining a stable microbial population. Biochar also serves as a potential liming agent to neutralize the soil pH.

14.6.3 Reduction of Toxicity Impact Imposed by Soil Contaminants

The amelioration of biochar in soil allows better adaptability of microbes in contaminated environment. The biochar leads to immobilization of the soil contaminants as it sequesters them in their porous structures, and this alleviates the associated risks caused by the contaminants (Zielinska and Oleszczuk 2016; Seneviratne et al. 2017). The microbial mortality is reduced in contaminated environment on introduction of biochar (Koltowski et al. 2017). The interaction of the microbes and biochar also plays a major role in reducing the toxic effect by the contaminants.

14.6.4 Influence in Microbial Communication

The biochar is responsible for modification of microbial cell communication as it adsorbs the signalling molecules that mediate microbial communications. It has been reported that biochar leads to hydrolysis of AHL (N-acyl homoserine lactone), which is the main signalling molecule responsible for gene regulation in most of the bacterial population (Masiello et al. 2013; Gao et al. 2016). Biochar can also affect microbe-plant interactions. It has been found that biochar application reduces the action of plant pathogens that cause various plant diseases. Such an action of biochar can be due to increased interactions of plant roots and plant growth-promoting rhizobacteria (PGPR) and even arbuscular mycorrhizal fungi, or negative impacts of biochar on the plant pathogens (Graber et al. 2010). Thus, in-depth study in this particular area can be fruitful to develop some biopesticides from the biochar.

14.6.5 Alteration of Soil Enzyme Activity

Soil enzyme activity is a vital phenomenon that determines the fate of remediation of pollutants from the environment. It is indeed an indicator of biological changes imposed by pollutants in a particular environment or soil quality (Bandick and Dick 1999). Biochar adsorbs soil enzymes, and they also block their active sites as a result of which they cannot appropriately bind to their substrate. Biochar also alters enzyme activity by changing soil pH, and it has been reported that the biochar components might also act as allosteric regulators of enzymes (Bailey et al. 2011).

14.7 Biochar for Plant Growth Promotion

The biochar helps in plant growth promotion in problem soil that is contaminated with different kinds of pollutants. The quality of soil actually determines the fate of plant growth in a particular area. Due to its organic nature (60–80%), attractive properties, and attractive functionality, biochar plays an important role in improving the quality of soil. Amendment of biochar increases the soil bulk density, increases soil porosity, and enhances root biomass and water-holding capacity of soil, i.e. the ability to retain moisture, which helps in plant growth (Zhang et al. 2012; Xiang et al. 2017). The strength of roots is necessary for the growth of plants, and biochar allows better establishment of roots. The biochar also leads to regulation of soil pH, which is another vital characteristic important for plant growth and sustainability. The release of industrial wastes, chemicals, leads to alteration of soil pH, and this affects the growth of plants in contaminated sites (Amin and Eissa 2017).

The deprivation of nutrient components in the soil disrupts the plant growth in a variety of ways, starting from cessation of roots, disruption of cell membranes, and reduced metabolism, ultimately leading to death of plants (Hodges and Constable 2010). Biochar also adds nutrient to the soil. It improves growth of plants in lesser fertile soil, by adding nutrient components, improving better utilization of soil substrates by plants, and enhancing rhizospheric activity (Alloway 2013; Maru et al. 2015). The application of biochar has also been recognized to reduce salt stress and improve plant growth in salt-affected soil. The biochar might adsorb or entrap Na from the soil and also provide nutrients to the plants to grow properly and combat with the stressed situation (Dahlawi et al. 2018). Thus, amendment of biochar in contaminated soil can be a state-of-the-art technology to improve the quality of the soil that ultimately leads to the rehabilitation of contaminated sites.

14.8 Techniques Adopted for Application of Biochar

There are various ways in which biochars are applied for the treatment of a contaminated environment (Sizmur et al. 2016). Biochar can be applied in sophisticated and controlled laboratory-scale microcosm level to field scale. Various experimental approaches that can be used for biochar application are as follows:

14.8.1 Batch Sorption Studies

Here, biochar is blended with an artificially contaminated environment under standard condition, and the amount of contaminants removed by the biochar is estimated. Usually, a known concentration of contaminants is applied so that the amount removed by the biochar application can be calculated easily.

14.8.2 Biochar-Soil Incubation

In this approach, the biochar is mixed with contaminated soil, and then the mixer is chemically extracted to measure the bioavailability of the contaminants. This method is more advantageous, as it offers information on both desorption and adsorption of the contaminant. Here also, the conditions are properly controlled so that the findings can be replicated.

14.8.3 Bioassays

In this method, a biological organism is included in addition to the amendment of biochar in a contaminated site. The uptake, toxicity towards the organism, and changes in the concentration of the contaminant are assessed. Bioassays provide more efficient outcomes and provide information on desorption and adsorption of contaminants, uptake of contaminants by the organism, and transport of contaminants.

14.8.4 Field Experiments

The biochar is applied to specific contaminated site/plot, and the effect of biochar can be estimated by the change in soil properties and observing the viability of plants in the site. This approach provides the ultimate or realistic effect of biochar on a particular contaminated environment.

14.9 Conclusion and Future Perspective

Petroleum is the most important source of energy that contributes majorly to meet the energy demand of the growing population, in spite of increasing emphasis being given on the use of renewable and clean sources of energy. The various activities of the petroleum industry starting from exploration and excavation to refining leads to the release of a huge amount of oil in the environment that leads to environmental pollution. The crude contamination has a negative impact on the environment, as it changes soil properties and deliberate toxic effect on life forms. Crude oil contamination is a global problem that has been drawing much more attention in the recent years. Thus, to resolve such quandary due to the oil pollution, effective treatment technology is needed to be adopted for rehabilitation of the oil-polluted sites. Advanced bioremediation can be an efficient and cost-effective and clean technology to restore crude oil-contaminated sites. Biochar, as discussed in the chapter, can be a suitable organic substrate that can be used as a biostimulant for enhancing the remediation of oil-polluted sites. The attractive physical properties of biochar such as high porosity and pronounced water-holding capacity and the nutritional value make the biochar a potent adjuvant that enhances the microbial as well as phytoremediation efficiency of plants. However, limited studies have been conducted on the application of biochar in environmental remediation experiments; thus, more studies including field trial studies in the future are needed to validate the action of biochar in mediating remediation of contaminated sites. Detailed investigation on the action of biochar, its synergistic effect with microbes and plants, and ionic interaction of biochar and biological entities is necessary for proper understanding of the phenomena by which biochar enhances the bioremediation of the contaminated sites. Utilization of biochar in remediation study can also lead to increasing biowaste management. Molecular approaches, next-generation sequencing, and other biotechnological tools can aid in providing useful information on the impact of biochar on the microorganisms. Further, metagenomic studies can reveal information on biochar-microbe interactions and effect on microbial community structure in a contaminated environment. Further, intertwining nanostructures and biochar component can actually enhance the effect of nanoparticles in mediating desirable removal studies, as the adsorption capacity might get enhanced on account of such initiatives. Biochar has also been known to sequester the C-emission in the environment and hence play a vital role in managing climate change as a result of global warming; thus, in-depth study in this particular area of research can be fruitful in developing new techniques for environmental management. In contrast to the positive effect of biochar, the negative impact incurred by biochar on the environment is also needed to be investigated. Detailed ecotoxicity studies of biochar can provide such kind of information, which is actually very essential for long-term and wide-scale application of biochar for environmental restoration. Further, minimization of cost and energy for biochar production is another challenging criterion that is also needed to be focused for increasing the opportunities of commercial application of biochar.

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Biodegradation of Low-Density Polyethylenes (LDPE) Using Microbial Consortia

15

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Abstract

Low-density polyethylene (LDPE) is a synthetic plastic used globally in quantities ranging from 57 million tonnes per year. The increasing accumulation rate and non-biodegradability are wreaking havoc on the organism and the environment. The biodegradation method can be used in a more environmentally friendly way to eliminate plastics from the soil. The microbial population is primarily involved in biodegradation because it is capable of secreting specific enzymes that cleave higher molecular weight molecules in LDPE, increasing the rate of biodegradation and eliminating them from the environment. This chapter focuses on the steps involved in the biodegradation process, like biodeterioration, biofragmentation, bioassimilation, and mineralization. Several other factors have contributed to the process's speeding up. The exposure circumstances (abiotic—moisture, pH, temperature, nutrients; biotic—microbe exposure) on LDPE, as well as polymer characteristics (molecular weight, hydrophobicity, size, shape, functional groups, additives) of an LDPE, have a significant impact in this regard. Nanoparticles (SPION, NBT, fullerene-60) and other pretreatments (UV treatment, prooxidants, photocatalysis) are promising techniques for combining with bacteria to increase biodegradation results.

Keywords

LDPE · Hydrophobic · Enzyme · Nanoparticles · Microbes · Microplastics

15.1 Introduction

Plastic is one of the most harmful and persistent pollutants. The word “plastics” comes from the Greek word “plastikos,” a material that can be molded into any shape (Ghosh et al. 2013). Chewing gums, shellac, rubber, and nitrocellulose were some of the naturally occurring compounds that inspired the creation of synthetic plastics because of their similarity to plastic in appearance and behavior (Millet et al. 2018). The first known use of polymers dates back to approximately 1600 BC when the ancient Mesoamericans prepared balls, figures, and bands out of natural rubber, which was the beginning of the polymer uses in the society (Hosler et al. 1999). Nowadays, the polymer industry synthesizes two types of plastics that can be differentiated based on their tendency to biodegrade: nonbiodegradable plastics and degradable plastics (Ahmed et al. 2018).

Plastics that are not biodegradable are made of a combination of molecules derived from fossil fuels and compounds derived from biological sources. However, the majority of synthetically created nonbiodegradable plastics are fossil based. These polymers are formed from hydrocarbon and petroleum and have a very high molecular weight due to long chains of hydrocarbon monomer units (Ghosh et al.

2013). Polyethylene terephthalate (PET), polyester, polyvinyl alcohol, polypropylene (PP), polyethylene (PE), nylon, polyethylene succinate, and polycaprolactone are examples of fossil-based polymers (PCL). In addition, some polymer mixes, such as starch and polyvinyl chloride (PVC), are commonly utilized in commercial and industrial applications today (Ahmed et al. 2018). This synthetic plastic is being used on such a vast scale that around 380 million tonnes of plastics are manufactured worldwide yearly. However, less than 20% of that amount is routinely recycled, contributing significantly to global trash and environmental damage (Zhao et al. 2022). Since having good utility in daily life, scientists are now developing friendly biodegradable plastics. Polyhydroxyalkanoate (PHA), polylactic acid, and polylactide (PLA) are examples of bio-based polymers. The use of biodegradable plastics in specific applications, such as packaging, agriculture, and the health industry, is the most creative and environmentally safe solution to address issues linked to the disposal of plastic waste created from various sources. If used, bio- and fossil-based biodegradable polymers efficiently break down in the environment, within cells, or in well-maintained industrial settings (Ahmed et al. 2018).

This chapter discusses biodegradation processes of polyethylene (PE) such as biodeterioration, biofragmentation, bioassimilation, and mineralization. PE is, generally, the fossil-based polymer that was first discovered by two research chemists, Reginald Gibson and Eric Fawcett, in March 1933 at ICI's Winnington Laboratory in the UK, which was first synthesized as a low-density polyethylene (LDPE). PE is considered the second most used resin class, while polypropylene (PP) remains the first. According to the average density of the resin, PE has been classified into different grades: linear low-density polyethylene (LLDPE), 0.925 g cm^{-3}; low-density polyethylene (LDPE), 0.930–0.935 g cm^{-3}; medium-density polyethylene (MDPE), 0.93–0.945 g cm^{-3}; and high-density polyethylene (HDPE), 0.945–0.965 g cm^{-3}(Andrady and Neal 2009).

LDPE, however, is very dispersive everywhere in the environment, from a single plastic bag to beautiful colorful straws. They are accumulating in the environment at a very high speed over time due to poor waste maintenance and littering by humankind (Sharma et al. 2016). The way of exposure in nature is becoming a threat to the environment and living organisms as well. Long-term exposure to the soil leads to decrease in soil fertility, microbial ecology, and many other health problems. Additionally, the ocean's plastic increase is six times that of the existing phytoplankton, which adversely affects the marine ecosystem. Humans also face many health problems regarding this (Ahmed et al. 2018). Therefore, eliminating these persistent pollutants from nature is very important to restore the ecosystem, which can be done in various ways.

Remediation of LDPE and other plastics involves photo-, chemical, thermal, and biological degradation (Muthukumar and Veerappapillai 2015). The traditional mechanical, chemical, and thermal degradation (Komal et al. 2018; Mumtaz et al. 2009) procedures typically employed to address these pollutants have limited efficacy and are also expensive. Therefore, developing methods for treating hazardous wastes has much potential to benefit from biotechnology. The use of bioprocesses to treat hazardous wastes is a technology that shows promise because it is both affordable and capable of eliminating the danger and mineralizing it. In addition, the process by which organic/inorganic material is broken down into nutrients that other species can utilize is known as biodegradation. These intrinsic biodegradation process can diminish or eliminate certain environmental pollutants (Eskander and Saleh 2017).

LDPE sheets can undergo both biotic and abiotic degradation. The biotic ones consist of biodegradation and bio-oxidation. On the other hand, abiotic ones are photo- and oxidative degradation (Mumtaz et al. 2010). In order to accelerate the bioremediation process, pretreatments are anticipated to be a crucial component of plastics' biodegradation as part of a circular economy strategy. Furthermore, oxidation and surface modifications on the plastics speed up biodegradation and increase biogas production (Mat Yasin et al. 2022).

Without ignoring the involvement of abiotic forces, biodegradation is thought to occur through following stages: biodeterioration (Zhang et al. 2022), biofragmentation, bioassimilation, and mineralization (Kumar Sen and Raut 2015; Remya et al. 2022). In a study, it was anticipated that *Bacillus* sp. strain BP4 showing similarity of 99.72% with *Bacillus anthracis* strain X11 and strain BP6 showing a similarity of 99.93% with *Bacillus paramycoides* strain 8929 were seen to release enzymes that can break down LDPE plastic into monomers, which are then taken up by bacterial cells and undergo natural decomposition, serving as a carbon source for bacterial development. Bacterial extracellular enzymes break down complicated polymers to create smaller oligomers, dimers, and monomers. These carbon- and energy-rich short-chain molecules can be mined to create CO_2, H_2O, or CH_4 as the final by-product (Fibriarti et al. 2021). Fungal genera such as *Acremonium, Cladosporium, Debaryomyces, Emericellopsis, Eupenicillium, Fusarium, Mucor, Paecilomyces, Penicillium, Pullularia, Rhodosporidium, Verticillium, Aspergillus, Aureobasidium, Chaetomium, Cryptococcus, Rhizopus, Thermoascus, Penicillium roqueforti,* and *Tritirachium album* and bacterial genera such as *Brevibacillus, Streptomyces, Amycolatopsis, Clostridium*, *Schlegelella,* and *Pseudomonas* have been known to degrade various types of plastics (Ghosh et al. 2013).

In addition to microbial consortia, nanoparticles are being investigated for their potential to speed up biodegradation. According to specific theories, nanoparticles, which typically vary in size from 1 to 100 nm, have more surface area per unit weight than larger particles, making them more receptive to other molecules. These particles may improve biodegradation by speeding up microbial growth and magnifying the synthesis of hydrolytic enzymes (Cada et al. 2019). Some potentially used nanoparticles in LDPE biodegradation include nanobarium titanate, fullerene-60 nanoparticles, supermagnetic iron oxide nanoparticles, and doped and undoped TiO2 with LDPE (Bhatia et al. 2013).

15.2 Chemical Composition of LDPE and Its Impact on Organisms

PE is made up of a linear saturated C-C backbone (− [CH2-CH2] n−) (Zhang et al. 2022). Using gas chromatography and mass spectroscopy (GC-MS) to analyze the chemical makeup of LDPE films, researchers discovered the presence of alkanes, aromatic hydrocarbons, chlorocarbons, saturated fatty acids, unsaturated fatty acids, and other unidentified compounds (Kyaw et al. 2012). Low-density polyethylene (LDPE) is a strong and malleable polymer with long branches that do not pack tightly into crystallites (Jordan et al. 2016). It has reduced intermolecular tensions, lowered tensile strength, and more resilience. Due to its side branches, it has fewer crystalline and closely packed molecules. This could result in a reduced density of LDPE. Carbon and hydrogen are two components found in LDPE. Excellent resistance to dilute and concentrated acids, alcohols, bases, and esters; good resistance to aldehydes, ketones, and vegetable oils; poor resistance to aliphatic and aromatic hydrocarbons, mineral oils, and oxidizing agents; and not advised for use with halogenated hydrocarbons are some of its other characteristics (R. Pramila 2011). LDPE with a thickness greater than 5 mm sometimes breaks and gets converted into microplastics later. Microplastics are bits of plastic less than 5 mm in size that can potentially break apart when entering the marine environment. The term “microplastics (MP)” typically refers to particles with a size between 50 nm and 5 mm. Because they are used in more significant quantities and have smaller particle sizes, this plastic group is thought to generate more pollution overall (Hahladakis et al. 2018). Microplastics could grow in all natural resources derived from the oceans, such as salt if plastic debris is not removed from water bodies such as rivers and oceans.

More than 90% of the brands of salt that were randomly sampled did contain microplastics, with Asia being the primary source. Salt eaters are particularly vulnerable to this microplastic issue, which also harms the food chain and marine biota (Novarini et al. 2021). Over 800 animal species were found to have been contaminated with plastic through ingestion or entanglement, according to a 2016 UN report. This number is 69% more than a 1977 review, which estimated only 247 infected species. 220 of these 800 species have been discovered to consume microplastic waste naturally (Murray and Cowie 2011; Smith et al. 2018). Due to microplastics in products, foods, and the air, exposure can occur through ingestion, inhalation, and skin contact. Microplastic exposure can potentially generate particle toxicity in all biological systems, oxidative stress, inflammatory lesions, and enhanced absorption or translocation. The immune system’s failure to eliminate artificial particles may cause persistent inflammation and raise the risk of neoplasia. Additionally, pathogenic organisms, pollutants that have been adsorbed, and elements of microplastics may be released (Prata et al. 2020). Due to their small size, aquatic organism at the lower trophic levels, such as plankton and filter feeders, may unintentionally consume microplastics. The most significant concentrations of MPs will be found in organisms at higher trophic levels, including mollusks, where these compounds can accumulate along the food chain (Sarma et al. 2022).

Hazardous seafood items that finally make it to human consumers may arise from such bioaccumulation of MPs, which may contain hazardous chemicals (Cole et al. 2011; Katyal et al. 2020; Revel et al. 2018). After ingesting the microplastics, the staghorn coral (*Acropora formosa*) experienced bleaching and necrosis, which coincided with the release of zooxanthellae. The overall findings supported the hypothesis that coral health is impacted by MPs produced by LDPE (Syakti et al. 2019).

Many of the chemicals that are frequently used to create plastics are harmful. The endocrine disruptors bisphenol A (BPA), phthalates, and some of the brominated flame retardants used to produce home goods and food packaging LDPE have been shown to be harmful to humans if consumed or inhaled (Ingale et al. 2021) (Campanale et al. 2020). BPA is a well-known endocrine disruptor; studies in the lab have shown that it binds to estrogen receptors and has estrogenic effects. Although BPA has been found to have a lower affinity for nuclear estrogen receptors relative to 17-beta-estradiol (E2), its estrogenic potency is equal to E2 for responses mediated by nonnuclear estrogen receptors (Rochester 2013). During formative phases, it can harm the thyroid gland, the brain, and the reproductive system. Most recently, it has also been connected to the emergence of human cancer (Chouhan et al. 2013). Phthalates and their by-products have been scrutinized over the past few decades, especially in products marketed to children or pregnant women (Giuliani et al. 2020). Phthalates cause cryptorchidism, hypospadias, a decline in adult sperm count, a reduction in testosterone, and a drop in Insl3 production (Lottrup et al. 2006). Humans from fetal life to adulthood are exposed when brominated flame retardants (BFRs) leak from consumer products. Fish, mainly farmed fish, and crude fish oil intended for human consumption, may contain significant BFRs, and infants and toddlers who regularly consume these items may consume more than is safe. This suggests that fish and fish oil pose a risk to human health. Additionally, exposure to other sources of this intake is included (breast milk, other food, and house dust) (Lyche et al. 2015).

15.3 Factors Affecting the Biodegradation Rate

Plastics' characteristics and biodegradability are related. Plastics' chemical and physical characteristics impact how they degrade biologically—the characteristics of the surface (surface area, hydrophilic, and hydrophobic traits). The first-order structures of polymers—chemical structure, molecular weight, and molecular weight distribution—as well as the high-order structures of those same polymers—glass transition temperature, melting temperature, modulus of elasticity, crystallinity, and crystal structure—all play significant roles in the biodegradation processes (Tokiwa et al. 2009). One of the elements influencing the biodegradation of plastics is molecular weight. Biodegradation is favored by low molecular weight. Enzymatic degradability is significantly influenced by a polymer's melting temperature (Tm). In general, polyester biodegradability tends to decrease with increasing melting points. With passing time, enzymatic degradability reduces. The degradability of the polymer was reduced by higher order structure characteristics, including crystallinity and modulus of elasticity (Kale et al. 2014). Many elements, including temperature, moisture, oxygen, sunlight, stress, living things, and pollutants, can cause a polymer to degrade (Muthukumar and Veerappapillai 2015; Shah et al. 2008). Some of the main factors of biodegradation are discussed below:

15.4 Exposure Conditions

15.4.1 Abiotic Factors

15.4.1.1 Moisture

Moisture aids in bacterial polymer breakdown since bacteria require water to grow and multiply, so moisture can have various consequences on biodegradation. For quick microbial action, polymer degradation speed is increased in the presence of enough moisture (Ahmed et al. 2018). In an experiment, the amount of banana starch was used to determine how much moisture the LDPE sheets would absorb. The films with 20% banana starch absorbed up to 4.5% moisture (Aht-Ong and Charoenkongthum 2022). Sago starch-filled linear low-density polyethylene (LLDPE) composites appear to be hydrolyzed enzymatically using surface starch granules; embedded granules are difficult to access due to the matrix's weak moisture absorption or transmission properties. As a result, composites absorbed more moisture as the starch concentration and immersion time rose (Danjaji et al. 2002).

15.4.2 pH and Temperature

pH, as well as temperature, plays a significant role in promoting the biodegradation process. An optimum range is essential for a microbe to thrive and perform its metabolic processes. Therefore, the investigation of pH fluctuations is utilized to confirm any metabolic activity of the bacterial isolates in supplemented media because metabolism demonstrated by microbial cells may substantially support the evidence of breakdown (Hussein et al. 2015). For example, researchers experimented at temperatures ranging across 25, 30, and 35 °C and pH levels of 5, 7, and 9. The most significant amount of LDPE was removed at pH 7 and 30 °C. With a tolerance of 2–7% for 30 days, mixed cultures of *Thiobacillus* sp. and *Clostridium* sp. were able to degrade LDPE plastic gravimetrically (Islami et al. 2019).

15.4.3 Nutrients

Plasticizers and other additives added to plastics provide nutrition for the growth of microbes (Mohanan et al. 2020). By providing optimum enhancers, additives like various carbon sources, the substrate's nutrition increases instantly and promotes biodegradation. For example, under minimal nutritional circumstances, LDPE and sucrose were used as carbon sources to observe LDPE deterioration. Weight loss of up to 30% was achieved by *Aspergillus niger* and *Aspergillus terreus* (Sáenz et al. 2019).

15.4.4 Biotic Factors

15.4.4.1 Microbes

Exposing LDPE to microbes starts to degrade by producing enzymes and biosurfactants. Therefore, these two factors are essential to balance to achieve the best results. Enzyme adsorption on the polymer surface and hydro-peroxidation/ hydrolysis of the bonds are the two stages of the enzymatic degradation process. The sources of enzymes that break down plastic include microorganisms from various environments and the intestines of some invertebrates. Therefore, to depolymerize waste petro-plastics into polymer monomers for recycling or converting waste plastics into higher value bioproducts, such as biodegradable polymers via mineralization, microbial and enzymatic degradation of waste petro-plastics is a promising strategy (Mohanan et al. 2020).

Biosurfactants can be used as facilitators for the biodegradation process of LDPE. In a biodegradation study, isolated soil bacteria, *Bacillus subtilis* and *Pseudomonas aeruginosa*, were combined with pure cultures of the organisms to produce biosurfactants. The high biosurfactant concentration produced under static circumstances at 25 °C was 0.84 mg/mL. During a 30-day incubation period, adding biosurfactants boosted the biodegradation effectiveness by at least 1.2% compared to employing the bacteria alone (Nnaji et al. 2021).

15.5 Polymer Characteristics

15.5.1 Molecular Weight

Microorganisms play a crucial role in assimilating carboxylic acids and low-molecular-weight polyethylene chains from the high-molecular-weight compounds in the biotic environment. The lack of carboxylic acids in the biotic samples further supports the assimilation of the low-molecular-weight compounds. This could also be enhanced with starch and prooxidant for excellent output. Thus, it is confirmed that biodegradation acceleration is better if the molecular weight of a polymer is low (Albertsson et al. 1998).

15.5.2 Hydrophobicity

Surface hydrophobicity, associated with bacterial solid adhesion on the polymer surface, is thought to affect the rate at which organic materials degrade under composting conditions. Hydrophobicity and hard segment formation are believed to help polyethylenes fend off enzymatic and hydrolytic breakdown (Kim and Kim 1998). High levels of LDPE biodegradation are produced by bacteria that maintain increased cell surface hydrophobicity (Das and Kumar 2013).

15.5.3 Shape and Size

The degradation process is significantly influenced by the polymer's characteristics, such as its size and form. For example, compared to polymers with a limited surface area, those with an enormous surface area can deteriorate more quickly (Ahmed et al. 2018; Kijchavengkul and Auras 2008).

15.5.4 Functional Groups

Functional groups on the surface of PE are hypothesized to be significant because oxidized groups improve hydrophilicity, which leads to efficient microbial adhesion to the PE surface and promotes biodegradation (Albertsson et al. 1995; Ghatge et al. 2020; Tribedi and Sil 2013).

In an experiment, photooxidation of LDPE was expedited by prooxidant treatment prior to UV exposure. This caused functional groups to be formed in the polyethylene film, which led to biodegradation since *Aspergillus oryzae* consumed the carbonyl and carboxylic groups, which is shown by a decrease in carbonyl peak intensity (Konduri et al. 2011).

15.5.5 Additives

The capacity to degrade LDPE is impacted by non-polymeric impurities such as colors (waste or debris of catalysts employed for the polymerization and additive conversion products) or filler. According to specific reports, as the amount of lignocellulosic filler in a sample grows, the thermal stability decreases, followed by an increase in the ash content. The primary determinants of the composite system's heat stability are the thermoplastic polymer and lignocellulosic filler's dispersion and interfacial adhesion (Ahmed et al. 2018). Prooxidant additives potentially answer the polyethylene film litter contaminating the environment. Prooxidants speed up photo- and thermo-oxidation, leading to polymer chain cleavage and an apparent increase in the product's susceptibility to biodegradation (Koutny et al. 2006).

15.6 Different Types of Pretreatments

By breaking down macromolecules on the substrate, oxygen causes oxidation degradation. This results in modifications to the chemical structure and a decrease in molecular weight, which alters the polymer's brittleness, cross-linking, and temperature of disintegration (Artham et al. 2009; Jawaid and Khan 2018). PE degradation in the environment is accelerated by the combined effects of photo- and thermo-oxidative degradation and biological activity (i.e., microorganisms). Alkanes, alkenes, ketones, aldehydes, alcohols, carboxylic acids, keto acids, dicarboxylic acids, lactones, and esters are just a few of the compounds that are liberated when PE is thermo- and photooxidized. When PE is blended with additives, autooxidation is typically enhanced, the polymer's molecular weight is decreased, and microorganisms more easily degrade the low-molecular-weight components. Unfortunately, the biodegradability with microorganisms on the PE side of the blends is still relatively poor, despite all these efforts to improve the biodegradation of PE blends (Tokiwa et al. 2009).

The development of oxidized functional macromolecules was one of the significant impacts of abiotic aging on LLDPE/LDPE film, which was more pronounced in natural weathering settings than thermal aging. Additionally, as evidenced by elevated carbonyl peaks in the ATR-FTIR spectra, the enrichment cultures may have been able to raise the oxidation level of the naturally worn film. Additionally, the reduction in water contact angle (WCA) that arises from biotic aging is evidence of the degeneration of the surface property of LLDPE/LDPE film (Jaiswal et al. 2022).

15.6.1 Treatment with Prooxidants

Prooxidant additives potentially answer the polyethylene film litter contaminating the environment. Prooxidants speed up photo- and thermo-oxidation, leading to polymer chain cleavage and an apparent increase in the product's susceptibility to biodegradation (Konduri et al. 2011). Manganese, iron, cobalt (Fontanella et al. 2010), manganese stearate (Konduri et al. 2011), calcium, and iron stearates are some of the potential prooxidants that enhance LDPE degradation by rapidly forming biofilms on the surfaces of the polymer after microbial treatment onto it (Abrusci et al. 2011). A multistep process begins as soon as bacteria adhere to a surface and produce a complex adherent microbial population known as a "biofilm." Surface adherence is necessary for bacteria to arrange themselves positively in their environment (Das and Kumar 2013). Polyethylene can be made sensitive to microbial breakdown by including starch and a prooxidant. To create biodegradable polyethylene, they are employed. The starch enhances the hydrophilic properties of polyethylene, enabling amylase enzymes to catalyze the reaction. Microbes easily break down this component. Degradation is preceded by photodegradation and chemical degradation when a prooxidant is added to polyethylene (Muthukumar and Veerappapillai 2015). In the presence of three well-defined enriched microbial strains, *Bacillus pumilus*, *Bacillus halodenitrificans*, and *Bacillus cereus*, in basal salt medium, the degradation of abiotically aged low-density polyethylene (LDPE) films containing trace amounts of a representative prooxidant (cobalt stearate) was investigated. According to GC-MS analyses, the abiotic treatment created unoxidized low-molecular-weight hydrocarbons and extractable oxygenated molecules (A. C. Albertsson et al. 1995; Roy et al. 2008).

15.6.2 Thermo-UV Pretreatment (Photooxidation)

UV radiation from the sun is a plentiful source, and polymer waste discharged in the open is subject to this photoinitiation process. Radiation is formed as a result of photooxidation, which is governed by the intensity of the light. As a result of these radicals diffusing throughout the polymer and producing new radicals, the polymer becomes more reactive. The polymer's average molecular weight is reduced due to this processing. Carboxylic groups and other functions like esters, ketones, alcohols, and double bonds are often used to end cleaved chains. A crucial part of the photoinitiation process that results in the homolytic cleavage of the chain is played by peroxides and hydroperoxides, which absorb UV light with weak UV absorption in the wavelength range of 290–400 nm (Chr Albertsson et al. 1993; Arkatkar et al. 2009).

When exposed to environmental and mechanical stressors, the plastic becomes brittle and weakened due to photooxidation and fragments. For example, weakened plastics are broken down in the ocean by wave action, swelling-deswelling, abrasion with sand, and contact with marine creatures (Andrady et al. 2022). In addition, the chemical structure of LDPE film is impacted by weathering conditions, particularly solar irradiation in the 290–400 nm wavelength region, which influences its mechanical and physical properties (Briassoulis et al. 2004).

Pretreatments like UV radiation and chopping can also speed up the breakdown of LDPE plastic. The plastic will be broken up into smaller pieces during pretreatment, hastening biodegradation. Other tests, such as an examination of changes in the plastic surface and an analysis of changes in biochemical components, are required to evaluate the biodegradation of plastics in addition to reducing the weight of the plastic (Fibriarti et al. 2021). UV irradiation accelerated *B. borstelensis* biodegradation (measured as dry weight loss) compared to nonirradiated HDPE samples. It was discovered that 60 h of ultraviolet exposure before the bacterium's incubation improved the biodegradation of LDPE by about 39%. Additionally, a 25% drop in the dry weight of *B. borstelensis* strain 707 on nonirradiated LDPE demonstrated that it could thrive there (Hadad et al. 2005).

15.6.3 Photocatalysis

A photocatalyst semiconductor accelerates the reaction rate by its presence (Ameta et al. 2018). TiO_2 is a photocatalyst that absorbs UV radiation while being environmentally benign. Consequently, UV radiation is effectively absorbed by polymer films that include TiO_2. In photocatalysis mediated by TiO_2, photons of the right energy are absorbed, resulting in the creation of electrons and holes that encourage the formation of free radicals, which then causes the polymer to oxidize and degrade (Ghatge et al. 2020; Zan et al. 2004).

The LDPE films containing nano-sized rutile-TiO_2 and nano-sized anatase-TiO_2 (1% w/w) decreased the film tensile strength by 32% and 55%, respectively, during shortwave UV irradiation for 72 h. On the other hand, only 7–10% less commercial TiO_2 in the form of micron-sized particles affects the film's tensile strength (Shawaphun et al. 2010).

15.7 Nanoparticles as an Enhancer for LDPE Degradation

Nanoparticles possess distinctive potentiality in polymer degradation by enhancing the degradation process by influencing the growth of suitable microorganisms and being great catalysts for the degradation or transformation process (David et al. 2021). According to a literature assessment, these particles could accelerate biodegradation by speeding up microbial growth and boosting the generation of exoenzymes, hydrolytic enzymes, acids, and organic acids (Ali et al. 2020). Several nanoparticles improve biodegradability, mechanical and physiochemical stability, and growth cycle. By creating claylike nanocomposites with an extremely high surface area-to-volume ratio using nanoparticles, nanoclays are created. When used as fillers, nanoparticles promote the material's characteristics and deterioration (Chrissafis et al. 2007; Pandey et al. 2015). With the substantial buildup of plastic garbage and ineffective strategies to control it, LDPE degradation has become a significant problem to be resolved. Specific applications of microbial decomposition have been demonstrated to be successful. The researchers have therefore discovered the ability of microbial degradation to be enhanced by nanoparticles, which has been given in Table 15.1. It has been demonstrated that LDPE can be broken down by nanobarium titanate, fullerene-60, and supermagnetic iron oxide nanoparticles (SPIONs) with increased microbial activity. While doping helps to shift the absorption range, enabling photocatalytic degradation to occur in the presence of visible light, undoped TiO_2 and doped TiO_2 nanoparticles have been embedded in the LDPE matrix to enhance degradation by the known photocatalytic activity of TiO2 that occurs in the presence of UV light (Bhatia et al. 2013). Significant alterations, such as a reduction of the lag phase and an extension of the exponential and stationary growth phases, respectively, might be used to identify the pro-bacterial effects of the nanoparticles, which ultimately boosts the biodegradation efficiency (Kapri et al. 2009).

Table 15.1 Different nanoparticles and their microbial effects in plastic biodegradation

Nanoparticles	Size	Characterization techniques	Consortium effects	Detection method of degradation	Degradation observations	References
Superparamagnetic iron oxide nanoparticles (SPIONs)	10.6 nm	XRD, FT-IR spectra, simultaneous TG-DTG-DTA, vibrational sample magnetometry (VSM), and transmission electron microscopy (TEM)	Enhancement of *Microbacterium* sp., *Pseudomonas putida*, and *Bacterium* Te68R	λ-Max shifts, Fourier transform infrared spectroscopy (FT-IR), and simultaneous thermogravimetric-differential thermogravimetry-differential thermal analysis (TG-DTG-DTA)	Improvement in the exponential phase durability by 36 h	Kapri et al. (2010)
SiO_2	20 nm	–	Enhancement of *Bacillus* sp. strain V8 and *Pseudomonas* sp. strain C-25	Spectroscopy, FT-IR analysis and their synergistic effect on *Vigna mungo* growth and germination	C–H stretching, O–H stretching, and $C \equiv H$ stretching	Pathak and Navneet (2017)
Iron-doped ZnO (Fe-ZnO) nanoparticle	–	Myriad characterization techniques	Inactivation of *Escherichia coli*	Fourier transform infrared (FTIR) analysis, field-emission scanning electron microscopy (FESEM)	Formation of pores at the interface between polymer matrix and Fe-ZnO	Lam et al. (2021)
Iron oxide nanoparticles (IONPs)	10–20 nm	–	Enhancement of *Bacillus pseudofirmus* and *Bacillus agaradhaerens*	FTIR, UV-Vis spectrophotometer, and SEM analysis	Reduction in polymer weight of 18.3 ± 0.3%	Cada et al. (2019)
Magnetic iron oxide nanoparticles (Fe_3O_4)	8 nm	Transmission electron microscopy (TEM) and dynamic light scattering (DLS)	Inhibitory effect on the growth of *Escherichia coli*	Colony-forming unit (CFU) count	The production of free radicals and reactive oxygen species (ROS)	Chatterjee et al. (2011)

(continued)

Table 15.1 (continued)

Nanoparticles	Size	Characterization techniques	Consortium effects	Detection method of degradation	Degradation observations	References
Silver nanoparticles (AgNPs)	20–80 μg/mL	Nanoparticle tracking analysis (NTA)	Accelerated the growth of *Cupriavidus necator* H16 (DSM 428, syn. *Ralstonia eutropha*)	–	Shows partial growth inhibition and extended lag phases	Schacht et al. (2013)

15.7.1 Superparamagnetic Iron Oxide Nanoparticles (SPIONs)

Due to their exceptional magnetic characteristics, chemical stability, and biocompatibility, superparamagnetic iron oxide nanoparticles (SPIONs) have recently been used widely in LDPE biodegradation. However, different physicochemical and synthetic parameters impact SPIONs' magnetic characteristics (Kandasamy and Maity 2015). With a size range of 10.6–37.8 nm, superparamagnetic iron oxide nanoparticles (SPIONs) were created and studied using XRD, FT-IR spectra, simultaneous TG-DTG-DTA, vibrational sample magnetometry (VSM), and transmission electron microscopy (TEM). In minimal broth Davis medium without iron and dextrose, the impact of SPION size variants on the growth profile of the low-density polyethylene (LDPE)-degrading microbial consortium composed of *Microbacterium* sp., *Pseudomonas putida*, and *Bacterium* Te68R was observed. These nanoparticles accelerated bacterial growth and increased exponential phase durability by 36 h. Changes in the lag phase and cumulative effects of sonication on growth profiling were also documented. FT-IR, simultaneous thermogravimetric-differential thermogravimetry-differential thermal analysis, λ-max shifts, and SPION of size 10.6 nm all showed that the SPION considerably increased the biodegradation efficiency of the consortium (TG-DTG-DTA). This work emphasizes the importance of interactions between bacteria and nanoparticles, which can significantly affect metabolic processes like biodegradation (Kapri et al. 2010).

15.7.2 Nanobarium Titanate (NBT)

In order to change the growth profiles of the low-density polyethylene (LDPE)-degrading consortia, nanobarium titanate (NBT) supplementation in the minimum broth is mainly investigated. Studies on in vitro biodegradation showed that LDPE dissolved more readily in the presence of NBT than in the absence of it. The breakdown and creation of bonds in the polymer backbone were confirmed (Kapri et al. 2009). This is because NBT was created with little broth and can regulate the growth of bacteria that break down low-density polyethylene (LDPE). Decreasing the delay step period and increasing the fixed and phase spread impact the time delay, increasing phase, and stationary phase. NBT supports the rapid evolution of bacterial consortiums by providing nutrients, which enables the consortia to digest plastic pollution (Remya et al. 2022).

15.7.3 Fullerene-60

Fullerene had no detrimental effects on the consortia growth at a concentration of 0.01% (w/v) in minimum broth devoid of dextrose. At greater concentrations (0.25%, 0.5%, and 1%), fullerene was discovered to be harmful to bacterial development. Although adding 0.01% fullerene to biodegradation experiments containing

5 mg/mL LDPE drastically reduced growth curves, further examination of the degraded products showed that biodegradation had increased (Sah 2010). λ-Max shifts to 209, 220, and 223 nm for 2, 3, and 4 days, respectively, due to the polymeric shape change are brought on by the absence of fullerene-60 NPs. On the other hand, fullerene-60 max in fullerene samples increased from 209 to 224.97 nm on day 1, indicating a greater degradation rate (Remya et al. 2022).

15.8 Steps Involved in Biodegradation Process of a Typical LDPE

There have been several identified microbes that can grow on polyethylene. The impacts of these microorganisms on the physiochemical characteristics of this polymer, such as changes in crystallinity, molecular weight, sample topography, and functional groups on the surface, have been documented. Plastics can deteriorate chemically, thermally, visually, or biologically. Any physical (such as sample weight loss or tensile strength) or chemical (such as carbon dioxide generation) changes in the substance hint at biological degradation caused by microbes (Muthukumar and Veerappapillai 2015). A list of potential microorganisms involved in LDPE biodegradation, based on successful research, is briefly cited in Table 15.2. Numerous studies have shown that polyethylene is biodegradable and deteriorates over time. It is crucial to realize that biodegradation is rarely 100% effective, meaning that the polymer will rarely degrade to 100%. Even if the destruction of plastics by microbes is not conceivable, it has been seen in multiple trials that there is a 98% drop in mechanical qualities (Nowak et al. 2011). This is because a small amount of the polymer was incorporated into the microbial biomass, humus, or other natural products (Shah et al. 2008). Given the chemical similarity between polyethylene and olefins, it has been proposed that the metabolic pathways for the degradation of hydrocarbons can be used once the size of polyethylene molecules decreases to an acceptable range for enzyme action. Nevertheless, it is recognized that both enzymatic and abiotic factors (such as UV light) can mediate the initial oxidation of polyethylene chains (typically from 10 to 50 carbons) (Restrepo-Flórez et al. 2014). It is essential to look into the population and distribution of bacteria that break down polymers in different ecosystems. The main mechanisms involved in the microbial degradation of plastics typically entail the adhesion of microbes to the material's surface, followed by the colonization of the exposed surface. Enzymes bind to the polymer substrate in the first step of the enzymatic breakdown of plastics by hydrolysis before catalyzing the hydrolytic cleavage. The breakdown of polymers through enzymes results in low-molecular-weight oligomers, dimers, and monomers, which are then mineralized to produce CO_2 and H_2O (Alshehrei 2017; Tokiwa et al. 2009). For example, in a study, *Aspergillus clavatus* JASK1 growing on LDPE surface showed changes in the surface causing the material to undergo minor cracks, physical weakness, and wrinkles after 90 days of incubation (Fig. 15.1). The biodegradation process is generally described in four main processes: biodeterioration, biofragmentation, bioassimilation, and mineralization.

Table 15.2 Potential microorganisms, their characterization, incubation settings, detection methods, and rate of LDPE biodegradation

Scientific name/strain		Characterization of microbial isolates	LDPE incubation (duration and temperature)	Detection methods of degradation	Rate of degradation	References
Bacteria	*Pseudomonas*, *Bacillus cereus* strain A5,a (MG645264), *Brevibacillus borstelensis* strain B2,2 (MG645267), *Cellulosimicrobium*, *Lysinibacillus*	16S rDNA sequences	16 weeks at 37 °C	Fourier transform infrared spectroscopy (FTIR) and GC-MS	35.72 ± 4.01% and 20.28 ± 2.30% by (MG645264) and (MG645267), respectively	Muhonja et al. (2018)
	Pseudomonas aeruginosa ISJ14 (accession no. MG554742)	16S rDNA sequences	60 days at 37 °C on 180 rpm	Field emission scanning electron microscopy (Fe-SEM) and Fourier transform infrared spectrophotometry (FTIR)	Bushnell Haas broth (BHM) (8.70%) and minimal salt medium (MSM) (6.5%)	Gupta and Devi (2020)
	Acinetobacter pittii (IRN19)	16S rRNA sequence	4 weeks	FT-IR spectroscopy, scanning electron microscopy	26.8 ± 3.04% gravimetric weight	Montazer et al. (2018)
	Pseudomonas spp.	Standard microbiology protocols	37 °C in pH 9.0 for 120 days	Zone of clearance method, computational docking studies	35–40% of plastic weight reduction	Skariyachan et al. (2015)
	Brevibacillus parabrevis (JQ304812)	16S rRNA gene sequences	37 °C	UV-VIS spectrophotometer, Sturm test analysis	0.7042 g/L of CO_2 evolution	Pramila (2012)
	Acinetobacter baumannii (JQ304813, JQ294033)				1.0603 g/L of CO_2 evolution	
	Pseudomonas citronellolis (JQ304811)				0.5706 g/L of CO_2 evolution	

(continued)

Table 15.2 (continued)

Scientific name/strain		Characterization of microbial isolates	LDPE incubation (duration and temperature)	Detection methods of degradation	Rate of degradation	References
Fungi	*Aspergillus niger*, *Fusarium* sp.	Lactophenol cotton blue (LPCB) staining, colony morphology, and microscopic examination	37°*C* for 30 days	Light microscope	0.1%	Kumar et al. (2013)
	Aspergillus oryzae strain A5, 1 (MG779508)	18S rDNA sequences	16 weeks at 28 °C	Fourier transform infrared spectroscopy (FTIR) and GC-MS	36.4 ± 5.53%	Muhonja et al. (2018)
	Mucor circinelloides	Slide culture technique	1 week to 28 days at room temperature	Colonization studies, SEM, and Sturm test analysis	5.9 g/L of CO_2 evolution	Pramila and Vijaya Ramesh (2011)
	Aspergillus flavus				4.4 g/L of CO_2 evolution	
	Trichoderma viride (RH03)	Polymerase chain reaction and DNA sequencing	(26 ± 2 °C) for 45 days	Analyses of electron micrograph	5.13%	Munir et al. (2018)
	Aspergillus nomius (RH06)				6.63%	

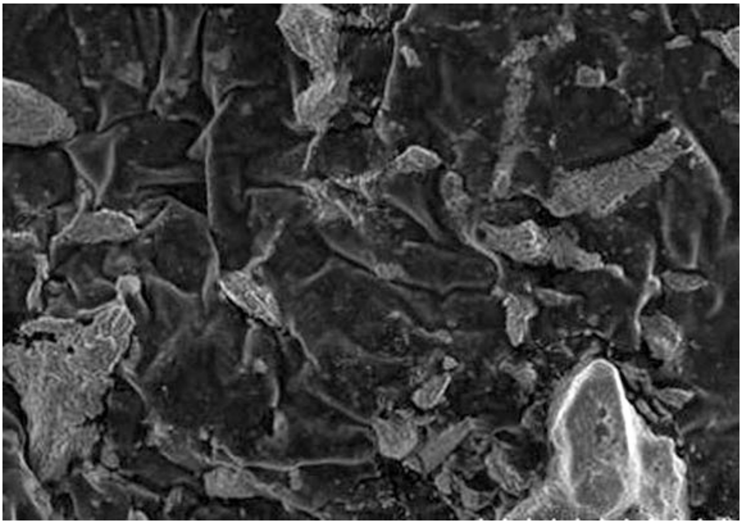

Fig. 15.1 After 90 days of incubation, scanning electron microscopy of *Aspergillus clavatus* JASK1 growing on the surface of LDPE films reveals the presence of physically weak, tiny fractures and wrinkles on the surface of LDPE films (Source: Open access: Gajendiran et al. 2016)

15.8.1 Biodeterioration

Biodeterioration is described as carbonyl groups created by oxidative enzymes secreted by microbes or brought on by abiotic factors, such as exposure to sunshine (ultraviolet). The quantity of carbonyl groups is decreased by further oxidation, which produces carboxylic acids (Mohanan et al. 2020). For the bacteria to carry out the breakdown process, they use enzymes such as monooxygenase, dioxygenase, and dehydrogenase. The first phase in biodegradation is microbial oxidation caused by the enzymes involved. Additionally, UV radiation causes photocatalytic oxidation, which speeds up the biodegradation process in soil (Bhatia et al. 2014). Polystyrene (PS) is resistant to biodegradation in natural conditions because it shares the same C-C backbone as PE. Therefore, a mix of biotic and abiotic forces is a workable strategy for disintegrating PS polymers. The primary or side-chain cleavage can initiate degradation, leading to various degradation pathways (Zhang et al. 2022).

15.8.2 Biofragmentation

Biofragmentation, mediated by enzymes released by microorganisms, involves hydrolysis or fragmentation of the polymer carbon chains and release of intermediate products (Mohanan et al. 2020). In an experiment, extracellular lipase—one of the primary enzymes responsible for polymer degradation—was discovered. According to computational docking studies, the plastics' polyethylene glycol and polystyrene content may interact well with microbial lipase, forming stable binding and interacting forces that may be one of the causes of the degradative mechanisms (Skariyachan et al. 2015).

15.8.3 Bioassimilation

In the bioassimilation step, hydrolyzed molecules transport and integrate into the microbial metabolism that occurs in the cytoplasm (Miller et al. 2009; Mohanan et al. 2020). The initial breakdown of the polymer into oligomers with 10–50 carbon atoms that can be incorporated into the cell for additional metabolism in microbes explains bioassimilation in LDPE (Ghatge et al. 2020).

15.8.4 Mineralization

Mineralization is the transfer of hydrolysis products inside the cell wall, and the intracellular conversion of hydrolysis products into microbial biomass with a corresponding release of carbon dioxide and water expelled out of the cell is an example of this process (Ammala et al. 2011). The release of carbon dioxide or oxygen consumption is the final indicator of aerobic biodegradation (de Villalobos et al. 2022). Phenols, alcohols, ketones, and other minor compounds formed in the degraded LDPE indicated that the branched plastic had broken down (Jayaprakash and Palempalli 2019).

15.9 Conclusion and Future Perspectives

According to the literature review, plastic materials are unavoidable to suit our daily demands. Plastics are in ever-increasing demand and application. This procedure must be favorably associated with waste management, litter reduction, and using biobased and fossil-based biodegradable materials in specific applications for long-term environmental safety. The simplicity with which microbial treatment approaches can be used for polluted materials makes them more effective than many other conventional methods and offers significant cost savings in cleanup and disposal. From the perspective of creating new materials, biodegradable plastic is a creative way to address the issue of disposing of plastic. According to studies, nanoparticles can improve the capacity of microbes to degrade materials. The degradation of LDPE with enhanced microbial activity has been described for nanobarium titanate (NBT), fullerene-60, and supermagnetic iron oxide nanoparticle (SPION). Since it deals with the growth profiles of microorganisms, nanoparticles are a new subject in the development of research connected to biodegradation.

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Biodegradation Aspects of Endocrine-Disrupting Chemicals in Soil

16

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Abstract

Endocrine disruptors (EDs) are chemical substances of natural (phytoestrogens) or artificial (pesticides, flame retardants, polycyclic aromatic hydrocarbons, dioxins, etc.) origin, which can hamper the normal functioning of the endocrine system in organisms and thus induce various adverse effects, including decreased sperm quality, hormone-sensitive cancers, teratogenic defects, genomic mutations, etc. The sources of the exposure of the organisms to EDs are mainly water and food, but also air and soil. Thus, the need to eliminate them from the environment is of great importance to reduce their threat to living organisms. Biological processes offer a potential solution for the effective and eco-friendly removal of EDs from the soil through biodegradation, which involves different metabolic pathways. This chapter provides an overview of the recent advances in using microorganisms and their catabolic enzymes to partially or totally degrade and counter the toxicity of some of the most currently encountered EDs in the soil.

Keywords

Biodegradation · Endocrine disruptors · Microorganisms · Mineralization · Soil · Toxicity

16.1 Introduction

Increasing and diversifying anthropic activities worldwide have generated levels of pollution never reached before. Despite tremendous financial efforts aiming to reduce the impacts of pollutants on the different ecosystems on Earth, their threat remains very serious.

Endocrine-disrupting chemicals, also called endocrine disruptors (EDs), are a group of polluting compounds found in daily used products. People are exposed to EDs mainly through cosmetics, furniture, food packaging, and food contaminated with toxic compounds such as pesticides and dioxins. EDs consist of a wide range of diverse natural and artificial chemicals, including phytoestrogens, dioxins, pesticides, flame retardants, polycyclic aromatic hydrocarbons, pharmaceuticals, metals, etc., which are potentially related to a variety of diseases of different degrees of severity that go from obesity to reproductive disorders and certain cancers (Yang et al. 2020) whose economical costs are huge. These compounds act on the endocrine system by interfering with its normal functioning through different mechanisms of action, including hormone antagonism, hormone mimicry, and disruption of the normal interaction between the hormones and their receptors (Kumar et al. 2020; Marlatt et al. 2022).

Soil pollution is a worldwide problem that profoundly affects the physicochemical and biological qualities of the soil itself, food that grows on it, water, and air. EDs are responsible for a large proportion of soil pollution through agricultural activities and industrial and urban waste disposal. Because of the threat related to ED pollution in the environment, it is urgent to find a solution to prevent and reduce their toxic effects efficiently and cost-effectively. One of the remediating solutions in vogue today is bioremediation, which emerges as an efficient and eco-friendly process using prokaryotic or eukaryotic microorganisms or plants to degrade/neutralize either organic or inorganic pollutants (Salah-Tazdaït and Tazdaït 2022). The concentration of contaminants in the different environmental media deeply influences their microbial biodegradation. The biodegradation of a given contaminant can occur only from a particular concentration called minimum substrate concentration (S_{min}). In this case, the contaminant would serve as a growth substrate (Becker and Seagren 2010). In the case of inorganic pollutants such as heavy metals, and depending on the microbial species, the microorganisms involved in their bioremediation act mainly by two mechanisms: (1) biosorption through either complexation or ion exchange mediated by different functional groups (phosphoryl, carbonyl, etc.) present on the cell surface and (2) bioreduction, which is a metabolically dependent mechanism involving specific enzymes that reduce the solubility of toxic metals by lowering their redox state, thus preventing their dispersion in the environment. The microbial mechanisms involved in the biodegradation of organic pollutants include mineralization and biotransformation. Mineralization refers to a series of metabolic reactions that leads to the complete degradation of organic pollutants yielding simple mineral compounds (H_2O, CO_2, NH_3, SO_4^{2-}, etc.) without generating any toxic intermediate (Tazdaït et al. 2013; Kaur and Goyal 2019). In this case, the degraded pollutant, called primary substrate, serves as a nutrient (carbon, nitrogen, sulfur, phosphorus) and/or energy source, thus supporting biomass production. Biotransformation is a process that occurs in pure cultures during which the contaminant undergoes minor chemical modifications and does not serve as a growth substrate. It is thus called a secondary substrate. This process requires the presence of simple (glucose, acetate, glycerol, citrate, etc.) or complex (whey, syrup date, molasses, etc.) growth substrates and generates metabolites that have the same or even more toxicity than the parent contaminant (Tazdaït et al. 2015; Salah-Tazdaït et al. 2018; Tazdaït and Salah 2021). Thus, it is important to pay much attention to the biodegradation reactions that take place during the bioremediation process by identifying the end metabolites of the contaminants and ensuring their harmlessness.

There are a number of research and review articles that have focused on the identification and characterization of microbial strains or their catabolic enzymes capable of partially or completely degrading various classes of EDs and their potential application in the bioremediation of ED-contaminated environmental media (Wu et al. 2011; Chen et al. 2015; Eltoukhy et al. 2020; Moreira et al. 2021; Li et al. 2022; Werkneh et al. 2022).

This chapter provides an overview on the ability and efficiency of microbial species to interact with and degrade some EDs of great concern present in the soil.

16.2 Endocrine Disruptors (EDs): General Considerations

There are wide varieties of endocrine disruptors, with more than a hundred identified to date and about 500 suspected. They are traditionally grouped into families according to their uses. The major groups of endocrine disruptors are pesticides, pharmaceutical products, natural hormones, combustion products, dietary antioxidants, plasticizers, detergents, and flame retardants.

These endocrine disruptors are found in human, animal, or industrial waste. Substances from different sources are therefore mixed in the media, which induce polyexposure of living organisms in contact with their environment.

Generally, the sources of contamination are grouped as follows:

- Outside air
- Indoor air and dust
- Waters
  - Feed
- Household objects and clothes, toys
  - Cosmetic products
- Maintenance products
  - Medical material
  - Pharmaceutical products

Contamination of the population has been widely proven in numerous studies. There is variability depending on individual eating habits. For example, the levels of organophosphate pesticides, such as malathion and chlorpyrifos, found in children fed a traditional diet are significant. However, they decrease to undetectable levels in children fed an “organic” diet.

Food seems to be the primary source of contamination for certain pesticides such as malathion.

Children ingest more pesticides than adults relative to the body weight. Indeed, a child consumes six times more fruits, two times more vegetables, and three to five times more cereals than an adult. Food is, therefore, a significant source of contamination by a large number of pesticides, and there is variability in exposure depending on the eating habits of populations. In addition, some pesticides can accumulate in the body. They are thus found in the blood of individuals at levels known to cause abnormalities in humans and animals.

It should be noted that the contamination persists in foods prepared from fresh produce. Pesticide residues are even found in baby foods prepared from fruits. Pesticides are not found only in plant foods. Thus, milk, eggs, and meat contain traces of persistent pesticides, such as organochlorine pesticides, which have been used illegally for many years (De Coster and van Larebeke 2012; Akash et al. 2021).

16.2.1 Physical and Chemical Characteristics of EDs and Their Sources

Around a hundred substances have been identified as endocrine disruptors, including natural substances:

16.2.1.1 Natural or Synthetic Hormones

Natural hormones include estrogen, progesterone, and testosterone, naturally present in the body of humans and animals, but also phytoestrogens produced by certain plants such as alfalfa and soybeans. Synthetic hormones are designed to act specifically on the endocrine system and modulate it. These are oral contraceptives, hormone replacement therapy, and animal feed additives. Phytoestrogens are hormones naturally present in certain plants; they have an activity similar to that of estrogens once present in the human organism. These compounds are similar in structure and/or action to mammalian estrogens. The main source of phytoestrogens for humans is food. Four classes of phytoestrogens exist: they are isoflavonoids, lignans, stilbenes, and coumestans. For humans, these are xenoestrogens. The human body rapidly absorbs and excretes these substances, which do not accumulate in the tissues. However, high consumption of foods containing these substances induces a non-negligible exposure (Sweeney et al. 2015; Kumar et al. 2020; Guarnotta et al. 2022).

16.2.1.2 Pesticides

The term pesticide refers to substances used to prevent, control, or eliminate undesirable organisms (plants, animals, or bacteria). Pesticides do not only refer to products for agricultural use but also concern domestic and urban uses. These are numerous substances (more than 40,000 existing compounds) and diverse in their chemical formulas and modes of action. The modes of action are classified into four groups:

- Action on the invertebrates: insecticides, molluscicides, and nematicides
- Action on the vertebrates: rodenticides, avicides, piscicides, and repellents
- Action on the plants: herbicides, growth regulators, defoliants, and desiccants
- Action on the microorganisms: disinfectants and bactericides, fungicides, and algaecides

In the context of their professional practice, farmers are a population particularly exposed to pesticides. If the human population is exposed, it is not the only one. There is also the problem of the impacts of these substances on animal species, which leads to a decline in biodiversity. Over 120 pesticides have now been identified as having endocrine-disrupting properties (McKinlay et al. 2008; Jabłońska-Trypuć et al. 2017; Ghosh et al. 2022).

Several pesticides that are now generally prohibited (DDT, chlordane, methoxychlor) are still present in the environment, as they are very persistent. Part of the pesticides used are dispersed in the environment compartments (air, soil, and water).

Various complex mechanisms are involved in these dispersal phenomena, the main ones being transfer, retention in soils, and physical or biological degradation. Therefore, soil constitutes a storage compartment for pesticides, a compartment from which they can return to the air or the aquatic environment. Many uncertainties remain as to pesticide fate in the soil because it varies from one pesticide to another (physicochemical properties, biodegradability, adjuvants of commercial formulations), but also according to the composition of the soil itself. However, there is a risk of accumulation in soils and sediments and subsequent release from these two poorly understood phenomena. Likewise, their persistence (or remanence) in these environments is probable. Their half-life in the soil varies from 20 to 100 days, but for some pesticides studied, the residual quantity of pesticide after 1 year is greater than 10% of the initial amount. Organochlorine pesticides are particularly persistent; soil pollution by the chlordecone used in the West Indies from 1972 to 1993 could last for several centuries. Therefore, soil and sediments constitute a reservoir, liable to contaminate other compartments of the environment, such as water and air (Ali et al. 2017; Combarnous 2017; Leemans et al. 2019).

16.2.1.3 Combustion Products: Dioxins and Furans

Dioxins are derivatives of benzene, an aromatic hydrocarbon, which form two families of compounds: polychlorinated dibenzo-para-dioxins (PCDD) and polychlorinated dibenzo-furans (PCDF). There are 75 members of the PCDD family—including 2,3,7,8-TCDD, known as Seveso dioxin—and 135 members of the PCDF family.

These compounds have never been produced intentionally; they are released into the environment during natural or thermal processes (any combustion in the presence of hydrogen, oxygen, carbon, and chlorine generates dioxins) related to human activities. Today, it is mainly industrial activities that produce dioxins: incineration of domestic waste and metallurgy.

Efforts to reduce dioxin emissions have led to a significant reduction in human exposure. Still, their presence in the environment (particularly in sediments and soil), resulting from past activities, persists and leads to food chain contamination. Food is the major source of human exposure. PCDDs and PCDFs are strongly absorbed into the air, water, and soil particles and are persistent in the environment. These compounds are not very volatile, which makes their dispersion in gaseous form negligible, even if their dispersion by air is possible in the event of absorption of these compounds in particles. Dioxins are also hydrophobic and therefore poorly soluble in water. Their lipophilicity allows these organochlorine compounds to cross cell membranes and accumulate in living organisms, particularly in fatty tissue. They are poorly biodegradable and are classified as persistent organic pollutants (POPs) (Fernández-González et al. 2015; González and Domingo 2021).

16.2.1.4 Plasticizers and Plastics: Phthalates and Bisphenol A

Artificial plastics cover an extensive range of polymeric materials and are composed of a polymer, which is added as plasticizers, additives, and adjuvants. Their number has increased considerably, as well as their uses, due to their interesting properties (transparency, shock resistance). Phthalates are therefore widely produced and can be released into the environment by products containing them, during their industrial production, use, and disposal. Bisphenol A (BPA) is an aromatic organic chemical compound derived from the reaction of phenol and acetone, used in the plastics industry (Filardi et al. 2020; Martínez-Ibarra et al. 2021).

16.2.1.5 Flame Retardants (PCB and PBDE)

Polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) are persistent organic pollutants (POPs), such as organochlorine pesticides, dioxins, and furans. Polychlorinated biphenyls (PCBs) are a family of 209 chlorinated organic compounds produced by the chemical industry. No natural source of PCB is known. They are used as flame retardants (paints, plastics, adhesives, lubricants, sealants, heat transfer fluids, capacitors, transformers, vacuum pumps, and gas transition turbines) or as insulators in very-high-voltage environments. PCBs are thermally stable and only decompose at temperatures above 1000 °C. PCBs persist in soils. They are incorporated into living organisms and accumulate throughout the food chain, particularly in animal and mammal organs or fatty tissues. PBDEs are brominated chemical compounds used as plastic and textile flame retardants in a wide variety of consumer goods. Generally, the less brominated PBDEs (1–5 bromine atoms) are considered potentially more dangerous to health. PBDEs are volatile and easily airborne. They are poorly soluble in water but have a high affinity for organic matter. They are also fat soluble. They are resistant to acids and bases, as well as to light and heat, and redox compounds (Dishaw et al. 2014; Eskenazi et al. 2017).

16.2.1.6 Detergents: Nonylphenol

The term nonylphenol encompasses a large number of isomers, with the molecular formula $C_6H_4(OH)C_9H_{19}$. It is a phenol substituted with a 9-carbon alkyl group. The alkyl group can theoretically be linear or branched in various ways and located at the ortho, meta, or para position. In practice, four nonylphenols correspond to a mixture of NPs substituted in the para position on the phenol and represent 80% of the nonylphenols in commercial mixtures. Other isomers are present as impurities. Nonylphenols are nonionic surfactants used in detergents, pesticides, biocides, cosmetics, and pharmaceuticals. They have estrogenic activity, which can cause reproduction problems in aquatic organisms, but their toxicity to humans has not been determined (De Coster and van Larebeke 2012).

16.2.2 Toxicity of EDs

Endocrine disruptors are suspected to be responsible for several disorders observed in humans. Thus, they can cause reproductive disorders, hormone-dependent cancers, or metabolic and developmental disorders.

16.2.2.1 Reproductive Disorders

The three main health effects mentioned in the context of exposure to EDs in humans are generally:

- Deterioration of reproductive functions, which is manifested by a reduction in the quality of sperm and causes fertility problems
- Disruption of the development of the male fetus leading to a malformation of the urogenital tract: non-descent of the testicles (cryptorchidism) or abnormal positioning of the opening of the urethra (hypospadias)
- Testicular germ cell cancer

In women, many dysfunctions of the reproductive system are suspected to be due to exposure to EDs. They can:

- Cause precocious puberty
- Disturb the duration of the cycle
- Cause polycystic ovary syndrome
- Induce spontaneous abortions
- Lead to fetal death, premature delivery, or low birth weight
- Cause endometriosis (Costa et al. 2014; Laws et al. 2021)

16.2.2.2 Metabolic and Developmental Disorders

Neurological dysfunctions could be explained by endocrine dysfunction, particularly involving thyroid hormones, due to their established role in development in general, development of the brain and the cerebellum, and development of the retina and the cochlea. Normal neurological development can also rely on estrogen and androgen hormones because steroid receptors are present in the brain. This toxicity is observed in particular at the level of:

- Cognition, learning, and memory
- Neurodevelopmental disorders such as autism, attention deficit disorder, mental retardation, or cerebral palsy
- Reduced motor functions, memory loss, and subtle behavioral changes
- Movement disorders (hypotonia, hyporeflexia, motor development), general slowness, and significant intelligence quotient deficits
- Sensory deficits (ototoxicity and visual defect) (Frye et al. 2012)

16.3 Biochemical Mechanisms for the Microbial Degradation of EDs

Following regular application and/or high concentration of different pollutants, soil bacteria have acquired and/or developed the ability to metabolize and use them as a nutrient source in an environment where nutrients are scarce. Thus, bacteria can mineralize these molecules either via a single strain or by organizing themselves into bacterial consortia. This adaptation of bacteria to xenobiotic molecules takes place via different events:

- Induction or derepression of specific enzymes that were absent (or present at a low level) in the population before exposure to the contaminant.
- Selection of new metabolic capacities following genetic rearrangements involving mutation events: The short generation times and the high plasticity of their genomes allow bacteria to generate new genes at relatively high frequencies. This plasticity is also linked to homologous recombination events at the origin of DNA rearrangements and increased genetic content.
- Acquisition of this genetic information by horizontal gene transfer: Thus, the genes involved in the degradation of xenobiotic molecules are often associated with transposition elements and insertion sequences. They are also frequently located on plasmids.
- Increase in the number of organisms capable of catalyzing the reaction (s) involved.

Thanks to these adaptation processes, the bacteria best able to resist or degrade xenobiotic molecules will be selected. They will gradually represent a more significant fraction of the total microbial population than before the presence of the xenobiotic.

The degradative enzymes involved in the degradation of pesticides can possess a broad specificity making possible cross-acclimatization of bacteria. That is to say that the degradation of a molecule in soil may be due to the prior application of another pesticide belonging to the same chemical group. Moreover, the strong homology between certain pollutants and secondary plant metabolites (exudates), which are metabolized by soil bacteria, seems to have an essential role in developing enzymes degrading organic pollutants.

Although no longer in contact with the molecule, soil bacteria can retain the ability to degrade it thanks to:

1. The formation of spores or other forms of resistance that allows them to survive for long periods in less-than-optimal conditions
2. The low concentrations of pesticides, which slowly desorb from the soil, constituting a continuous substrate source for degrading bacteria
3. The presence of other genes on the plasmid involved in the degradation, which under another selection pressure allows the conservation of the plasmid
4. The fact that the bacteria involved are maintained at a sufficiently large population level thanks to the use of other nutrient sources.

16.3.1 Natural and Synthetic Hormones

Several studies have addressed natural and synthetic hormones' aerobic and anaerobic biodegradation. Estrogens are a group of naturally occurring steroid hormones, including estrone (E1), 17-estradiol (E2), and estriol (E3). 17α-Ethynylestradiol (EE2) is a synthetic estrogen. Certain bacteria, isolated from soil, sand, sea, compost, or activated sludge, have proven to be capable of degrading natural or synthetic hormones. For example, *Novosphingobium tardaugens*, *Nocardia* sp., and *Sphingomonas* sp. can transform 17-estradiol (E2) in estrone (E1) by dehydrogenation of ring D in carbon 17. This reaction is performed by 3β, 17β-hydroxysteroid dehydrogenase. E1 can be transformed to 4-hydroxy estrone (4-OHE1) by E1 4-hydrolase. In *Novosphingobium tardaugens* NBRC 16725, a succession of reactions makes it possible to obtain the 3aα-H-4α(3′-propanoate)-7a-β-methylhexahydro-1,5-indanedione (HIP), which will also be degraded thereafter (Yu et al. 2013; Chen et al. 2018; Ibero et al. 2020). However, the synthetic estrogen 17α-ethynylestradiol (EE2) is transformed into estrone (E1) by the bacteria *Sphingobacterium* sp. JCR 5 (Haiyan et al. 2007). Also, *Phoma* sp. UHH 5-1-03 is a fungus able to adsorb large amounts of the synthetic hormone EE2 on chitin and chitosan present in their surface (Olicón-Hernández et al. 2017).

Lignans are a class of phytoestrogens found in flax, composed of over 95% of secoisolariciresinol diglucoside (SDG). The deglycosylation of SDG can be catalyzed by *Bacteroides distasonis*, *Bacteroides fragilis*, *Bacteroides ovatus*, *Clostridium cocleatum,* and *Clostridium saccharogumia*. The demethylation of its aglycone can be catalyzed by *Butyribacterium methylotrophicum*, *Eubacterium callanderi, Eubacterium limosum*, *Blautia producta*, and *Peptostreptococcus productus* (Ionescu et al. 2021).

16.3.2 Pesticides

Pesticide degradation pathways depend on the pesticide itself and the microorganisms involved in its degradation. For example, the degradation of atrazine (herbicide belonging to the chemical family of triazines) in the soil is due to the adaptation of certain soil bacteria, which use this pesticide as carbon and/or nitrogen sources. These degrading bacteria and the degradation pathways involved have been widely studied. Thus, many bacteria have been isolated, and degradation pathways have been elucidated, involving different functional genes. *Bacillus licheniformis* and *Bacillus megaterium* are aerobic atrazine-degrading bacteria. Methanogenic bacteria can degrade atrazine under anaerobic conditions. Atrazine is first converted to hydroxyatrazine by atrazine chlorohydrolase. The latter is produced from the *atzA* and *trzN* genes. The hydroxyatrazine obtained is transformed into N-isopropylammelide by hydroxide chloroatrazine ethylaminohydrolase. This enzyme is produced from the *atzB* gene. N-isopropylammelide is transformed into cyanuric acid by N-isopropylammelide isopropylaminohydrolase. This enzyme is encoded by *atzC* gene. Cyanuric acid aminohydrolase will convert cyanuric acid into carboxybiuret. Cyanuric acid aminohydrolase is produced from the *atzD* and *trzD* genes. The carboxy biuret will be transformed into dicarboxyurea by 1-carboxybiuret hydrolase. This last enzyme is produced from the *atzEG* gene. By an unclear mechanism, the dicarboxyurea will be transformed into allophanate.

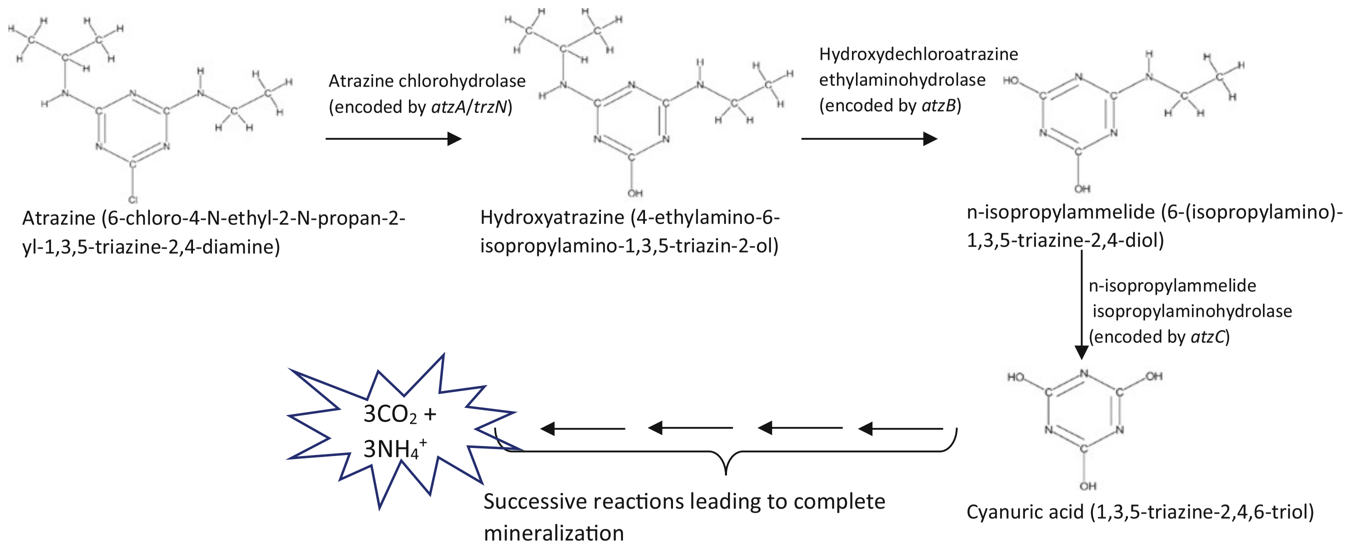

Fig. 16.1 Atrazine degradation pathway

Finally, allophanate is converted into carbon dioxide and ammonium by allophanate hydrolase produced from the *atzF* gene (Fig. 16.1) (Ghosh and Philip 2004; Solomon et al. 2013; Billet et al. 2019; Zhu et al. 2019; Espín et al. 2020).

Fungi have special properties allowing them to detoxify soil polluted with pesticides. These strategies include nonenzymatic processes such as biosorption and the synthesis and secretion of surfactants capable of reducing surface tensions and allowing the increase of interactions between molecules (Olicón-Hernández et al. 2017).

16.3.3 Combustion Products: Dioxins and Furans

In the case of aerobic biodegradation of dioxins (PCDD) and furans (PCDF), the reaction mechanism, named angular deoxygenation, is based on selective dioxygenation by dioxygenases capable of degrading dioxins by simultaneously hydrolyzing the carbon bearing an ether bond and an adjacent unsubstituted carbon (angular carbon) using oxygen as an electron acceptor. For example, the bacterial biodegradation of dibenzo-*p*-dioxin by the angular dioxygenase system successively generates 1,10a-dihydroxy-1-hydrodibenzo-*p*-dioxin and 2,2′,3-trihydroxydiphenyl ether. The latter will be transformed into 2-hydroxy-6-oxo-6-(2-hydroxyphenoxy)-hexa-2,4-dienoate (HOHPDA) by 2,2′,3-trihydroxybiphenyl dioxygenase. The product of this last reaction will serve as a substrate for 2-hydroxy-6-oxo-6-phenylhexa-2,4-dienoate hydrolase and generate catechol and 2-hydroxymuconate. In anaerobic conditions, *Dehalococcoides* can degrade dioxins. However, in aerobic conditions, *Sphingomonas*, *Pseudomonas,* and *Burkholderia* can degrade dioxins (Chang 2008; Saibu et al. 2020; Nguyen et al. 2021).

Dioxins can also be degraded by fungi. In this case, the first degradation reaction is breaking ether bonds at the ring level, forming a hemiacetal (Nakamiya et al. 2005).

Furans metabolization in fungi proceeds by reduction of furans to the less toxic furfuryl alcohol, and a furoic acid is obtained after oxidation. Also, 2-oxoglutarate and tricarboxylic acid are obtained after several enzymatic steps (Zanellati et al. 2021).

16.3.4 Plasticizers and Plastics: Phthalates and Bisphenol A

The biodegradation of phthalates by aerobic bacteria has demonstrated the existence of several biodegradation pathways depending on the bacteria studied and the type of phthalate. As an example, the biodegradation of dimethyl phthalate (DMP) will successively generate monomethyl phthalate (MMP), phthalic acid (PA), dihydroxyphthalic acid, catechol, muconic acid semialdehyde, muconic acid, succinic acid, and acetic acid (Wu et al. 2007; Tang et al. 2017).

In anaerobic conditions, *Thauera chlorobenzoica*, *Aromatoleum aromaticum, and Aromatoleum evansii* can biodegrade phthalates (Boll et al. 2020).

Fungal degradation of dibutyl phthalates (DBPs) produces phthalic acid anhydride (PAA), diethyl phthalate (DEP), monobutyl phthalate (MBuP), a-hydroxyphenylacetic acid, o-hydroxyphenylacetic acid, and benzyl alcohol (Luo et al. 2012).

The biodegradation mechanisms of bisphenol A by bacteria are divided into two pathways. The first, so-called major route would represent 85% of the biodegradation of bisphenol A. This pathway consists of the first oxidation of bisphenol A and then a metabolization leading to the production of 4-hydroxybenzaldehyde (4-HBAL) and 4-hydroxyacetophenone (4-HAP). 4-HBAL then undergoes oxidation to become 4-hydroxybenzoic acid (4-HBA). 4-HBA and 4-HAP can be metabolized by bacteria and transformed into CO_2 and biomass. The second pathway, characterized as "minority" with 15% biodegradation, begins with the metabolization of bisphenol A to give 2,2-bis(4-hydroxyphenyl) propan-1-ol. This compound will also be able to either oxidize by transforming into 2,2-bis (4-hydroxyphenyl) propanoic acid (10%) or metabolize into 2,3-bis (4-hydroxyphenyl) propan-1,2-diol (90%). The propanediol chain of the latter can be separated to give either HBA or 4-hydroxyphenacyl alcohol (Eltoukhy et al. 2020; Wang et al. 2020). Aerobic degradation of bisphenol A can be done by *Achromobacter xylosoxidans* (Zhang et al. 2007). Under anaerobic conditions, *Bacillus* sp., a facultative anaerobic bacterium, can biodegrade bisphenol A (Hardegen et al. 2021).

Fungi can adsorb large amounts of bisphenol A on their surfaces thanks to the particular composition of the wall, rich in chitosan or chitin (Olicón-Hernández et al. 2017).

16.3.5 Flame Retardants: PCB and PBDE

Several bacteria are known to degrade PCBs under aerobic conditions. Degradation most often takes place by double oxygenation on the less chlorinated part of the biphenyl nucleus by the enzyme 2,3-biphenyl dioxygenase and then by 2,3-dihydroxy-biphenyl dioxygenase. This step results in the cracking of the target phenolic ring. The formation of chlorobenzoic acid and 2-ketopenta-4-enoic acid is then observed. Chlorobenzoic acid will then undergo a similar attack (dioxygenation). 2-Keto-penta-4-enoic acid is transformed into acetaldehyde and pyruvic acid, which are involved in cell metabolism (for example: synthesis of acetyl-CoA). The chlorine will be discharged as Cl^- (Jing et al. 2018; Bako et al. 2021).

Fungi can degrade PCBs through laccases, manganese-dependent peroxidase, aryl-alcohol oxidase, and cytochrome P450 (Šrédlová et al. 2021).

Under aerobic conditions, *Pseudomonas stutzeri*, *Bacillus* sp., and *Sphingomonas* sp. can biodegrade certain PBDEs into smaller congeners. However, under anaerobic conditions, *Sulfurospirillum multivorans, Dehalococcoides ethenogenes, Anaeromyxobacter, Bacillus, Brevibacillus, Burkholderia, Clostridium,* *Mycobacterium, Pseudomonas, Rhodobacter, Sedimentibacter, and Shewanella* can degrade deca-brominated diphenyl ether (DBDE) (Sahu et al. 2021).

Fungal biodegradation of PBDEs, by *Trametes versicolor*, implies the intracellular enzyme cytochrome P450 and produces hydroxylated PBDEs with different degrees of bromination, 4-bromocatechol, and 2-hydroxymuconic acid (Vilaplana et al. 2012).

16.3.6 Detergents: Nonylphenol

In aerobic conditions, there are two ways of biotransformation of 4-NP (nonylphenol) according to the substitution of carbon in α of the cycle. In the first case, the alkyl chain has a quaternary carbon at the α of the cycle. Biodegradation begins with an ipso-substitution of a hydrogen atom by an OH group on carbon 4 of the phenol ring. This ipso-substitution leads to a rearrangement of the distribution of electrons. The rearrangement leads to the detachment of the alkyl chain, which becomes a carbocation. This detachment is only possible if the carbon at α of the cycle is quaternary, allowing the substituents (CH_3 or C_2H_5) to compensate for creating the positive charge. The carbocation then reacts with a water molecule to give quaternary alcohol. On the other hand, the phenol ring undergoes rearomatization giving the final product hydroquinone (benzene-1,4-diol). In the second case, the hydrogen on carbon 4 of the phenol ring is replaced by an OH group by ipso-substitution. Then, a rearrangement of the electrons will lead to the migration of the alkyl chain to the neighboring carbon. In this case, the alkyl chain cannot detach because the carbocation that would be formed would not be stable enough. This instability comes from the fact that the alkyl chain does not contain a quaternary carbon in the α of the cycle. A final rearomatization of the molecule will give the final product of this biotransformation of 2-nonyl-benzene-1,4-diol or 2-nonyl-hydroquinone (Gabriel et al. 2008).

Anaerobic degradation of nonylphenol can be achieved, by a sulfate-reducing bacteria, isolated from soil relatively close to *Bacillus niacini* (Chang et al. 2007).

Fungal degradation of nonylphenol by *Trametes versicolor* shows complete mineralization (Mallerman et al. 2019).

16.4 ED-Degrading Microorganisms in the Soil

Despite being greatly affected by all sorts of pollution, soils have an excellent potential to neutralize and attenuate the adverse effects of pollutants. The richness of soils in microorganisms provides an extraordinary natural reservoir from which microbial strains capable of efficiently degrading virtually every organic pollutant, including EDs, could be isolated, characterized, and used as decontaminating agents. Thus, an important body of studies dealing with isolating and characterizing ED-degrading microorganisms from different soils is available. Some examples of newly isolated microbial strains from soils are exposed below. In a study by

Eltoukhy et al. (2020), an isolate of *Pseudomonas putida* strain YC-AE1 was isolated from soil samples collected in the vicinity of an area polluted by electronic wastes by selective culture technique. The bacterial strain exhibited a high level of tolerance against high BPA concentrations (bisphenol A) (up to 1000 mg/L) and reached complete removal of the pollutant within 72 h for initial concentrations ranging from 50 to 500 mg/L in liquid medium under aerobic conditions. On the other hand, it was evidenced that the strain was also capable of degrading six other organic pollutants (bisphenol F, bisphenol S, bisphenol B, diethylhexyl phthalate, diethyl phthalate, and dibutyl phthalate) among which bisphenol F and B were the best degraded with removal percents of 67% and 60%, respectively. Besides, the authors proposed two metabolic pathways, both suggesting that *Pseudomonas putida* YC-AE1 could degrade BPA by mineralizing it and using it as a growth substrate. In another study, two species of the genus *Bacillus*, namely *Bacillus thuringiensis* and *Bacillus cereus*, isolated from agricultural soil, were tested separately or in a consortium for their ability to degrade a mixture of three phthalic acid esters (diethyl phthalate, dibutyl phthalate, dimethyl phthalate, and dipropyl phthalate) in liquid medium. When tested separately, the two strains showed better degradative performances against diethyl, dibutyl, and dimethyl phthalate at 50 mg/L. Of the two strains, *Bacillus thuringiensis* was the best in removing the four toxic compounds, with a maximum degradation rate of 76% observed for dimethyl phthalate. Besides, the authors noted that *Bacillus thuringiensis* reached a maximum degradation rate of 96% for dimethyl phthalate within 80 h for an initial concentration of the contaminant mixture of 400 mg/L (Surhio et al. 2017). In their study, Gao et al. (2014) showed that a strain of *Stenotrophomonas maltophilia* isolated from soil contaminated by high levels of toxic compounds (heavy metals, polycyclic aromatic hydrocarbons, organotins, etc.) collected at Guiyu in Guangdong Province (China) effectively degraded the pesticide triphenyltin. The pesticide is first adsorbed on the strain and then transported into the cell compartment, where it is degraded, yielding diphenyltin and monophenyltin. A removal efficiency of 86.2% was obtained with triphenyltin tested at 0.5 mg/L and 0.3 g/L inoculum concentration within an incubation period of 10 days. The biodegradation of another endocrine disruptor herbicide, namely alachlor (2-chloro-N-(2,6-diethylphenyl)-N-(methoxymethyl)acetamide), has recently been reported by using four soil-isolated strains (*Aspergillus niger*, *Aspergillus flavus*, *Penicillium chrysogenum*, and *Xanthomonas axonopodis*). Among the three fungal strains, *Aspergillus niger* exhibited the best biodegradation potential (72.6%) within 35 days for an initial alachlor concentration of 10 mg/L. *Xanthomonas axonopodis* gave a better biodegradation percent of 82.1% after the same incubation period. It should be mentioned here that none of the microbial strains tested achieved mineralization of alachlor, but acted by a biotransformation process, which resulted in the formation of different metabolites such as N-(2,6-diethylphenyl)-methyleneamine; 7-ethyl-N-methylindole; 1-chloroacetyl, 2,3-dihydro-7-ethylindole; and chloroacetate, chiefly through hydrolysis and oxidation (Ahmad 2020). As another example of a pesticide with hormone-disrupting activities, diazinon at a high concentration (775 mg/L) was shown to be co-metabolically degraded in the presence of glucose (2.25 g/L) by *Candida pseudolambica* isolated from a soil contaminated with pesticides collected in Babol (Iran). The yeast strain was capable of a removal rate of 69.6% attained within 24 h only. However, the strain achieved a degradation rate of 34% in the presence of diazinon (500 mg/L) as the sole source of carbon (Ebadi et al. 2022). In a study by Janicki et al. (2016), the soil filamentous fungus *Umbelopsis isabellina* was assessed for its ability to degrade separately three estrogen-mimicking compounds (4-*tert*-octylphenol and 4-cumylphenol, nonylphenol) in batch experiments. The non-ligninolytic fungal species was able to degrade 90% of the initial concentration of the three contaminants (25 mg/L) after 12 h of cultivation and achieved their complete degradation within 24 h. Furthermore, the study revealed that biotransformation was the only metabolic process through which the three contaminants were degraded and that the produced metabolites turned out to be less toxic than the parent molecules. Some other examples of microorganism-degrading EDs isolated from the soil are shown in Table 16.1.

The soil's complex character makes applying and assessing the microbial-based biodegradation approach difficult. Despite that, many reported studies have investigated the biodegradation performances of microorganisms in treating different soils that are artificially contaminated with EDs. Hence, Sharma et al. (2021) demonstrated that the application of *Acinetobacter* sp. 33F in pristine agricultural soil was very efficient in removing the commonly used plasticizer dibutyl phthalate. The experiments were conducted in plastic pots containing autoclaved soil supplemented with dibutyl phthalate at different concentrations (100–2000 mg/kg). The pots were then inoculated with *Acinetobacter* sp. 33F at 10^8 CFU/mL and incubated for 10 days. The obtained results revealed that the growth of *Acinetobacter* sp. 33F was negatively affected by dibutyl phthalate concentrations beyond 1000 mg/L. Regarding dibutyl phthalate biodegradation, *Acinetobacter* sp. 33F permitted a degradation rate of approximately 50% for all the concentrations tested after 144 h of incubation, yet a similar inhibitory effect on the biodegradation activity of the strain from 1000 mg/L dibutyl phthalate was observed which was not the case in the experiments conducted in liquid media. The involvement of some inhibitory compounds present in the tested soil was suggested. Also, the authors showed that the bacterial strain used was efficient in eliminating other dibutyl phthalate derivatives (monobutyl phthalate, diethyl phthalate, benzyl butyl phthalate, di-decyl phthalate, and di-octyl phthalate) by using them as the sole source of carbon. In another study, Chen et al. (2017) applied an ultrasonic treatment at 30 W to the biodegradation, in soil, of four estrogens (estrone, estriol, estradiol, and 17α-ethinylestradiol) and bisphenol A by *Pseudomonas putida.* A central composite design was applied to optimize three parameters (amount of inoculum, ultrasonication time, and concentration of rhamnolipid) inherent to the biodegradation process of the EDs under study. Very high biodegradation rates of 96.56%, 94.86%, 94.56%, 94.9%, and 100% for bisphenol A, estradiol, estriol, 17-α-ethinylestradiol, and estrone, respectively, were achieved within 7 days under the following optimized conditions: 3 min, 8 mL, and 100 mg/L for ultrasonication time, amount of inoculum, and rhamnolipid concentration, respectively. Moreover,

Table 16.1 Examples of ED degradation by other microorganisms

ED(s)	Microorganism(s)	Source	Result (removal percent)	References
Di-2-ethylhexyl phthalate (5 mM)	*Bacillus subtilis* No. 66	Soil samples collected from a plastic factory, golf factory, hospital, gas station, sake factory, furnace, and drainage canal	>80 obtained in soil after 5 days	Quan et al. (2005)
Di-2-ethylhexyl phthalate (100 mg/kg soil)	Indigenous soil flora	Saprolitic silty clay soil collected at the campus of the University of São Paulo (Brazil)	99 obtained in soil after 49 days	de Moura et al. (2011)
Di-2-ethylhexyl phthalate bound to small pieces of HL haemopack blood storage bag	A consortium of *Penicillium brocae* BP6, *Aspergillus japonicus* BP9, and *Purpureocillium lilacinum* BP13	Soil samples contaminated by plastics collected from Malappuram, Kerala (India)	~99 obtained in situ after 30 days	Pradeep et al. (2013)
Nonylphenol (NP), bisphenol A (BPA), 17β-estradiol (E2), and 17α-ethinylestradiol (EE2) (0.5 μg/g soil)	Indigenous soil flora	A soil sample collected from a groundwater recharge site in Beijing (China)	>95 (E2) after 15 days >95 (NP) after 20 days >95 (BPA) after 20 days 90 (EE2) after 20 days	Li et al. (2013)
4-Tert-octyl phenol (1 μg/g soil)	Indigenous soil flora	Sandy loam soil collected from Roseworthy farm (South Australia)	>90 obtained in soil after 7 days	Ying and Kookana (2005)
Methylparaben (A) and butylparaben (B) (5 ppm each)	Indigenous soil flora	Agricultural soil located in Huerta de Santa María (Spain)	>99.9 (A and B) obtained in soil after 96 h	Juárez-Jiménez et al. (2019)
Triton X-100 (2-[4-(2,4,4-trimethylpentan-2-yl)phenoxy]ethanol) (5000 mg/L)	*Pseudomonas nitroreducens*	Soil samples collected from the vicinity of the National Central University campus (Taiwan)	>90 obtained in liquid medium after 36 h in the	Chen et al. (2005)

(continued)

Table 16.1 (continued)

ED(s)	Microorganism(s)	Source	Result (removal percent)	References
			presence of 1800 mg/L KNO_3	
Triphenyltin (0.5 mg/L)	*Brevibacillus brevis*	Soil samples contaminated with e-waste collected in Guangdong Province (China)	80 obtained in liquid medium after 5 days	Ye et al. (2014)
Bisphenol A (3 mM)	*Pseudomonas putida* G320	Desert soil samples from southern Tunisia	97 obtained in liquid medium after 4 days	Louati et al. (2019)
Di-*n*-butyl phthalate (2.5–10 mg/L)	*Pseudomonas fluorescens* B-1	Soil collected at Mai Po Nature Reserve in Hong Kong	100 obtained in liquid medium after 96 h	Xu et al. (2005)
Triclocarban (50 ng/g soil)	Indigenous soil flora (*Actinobacteria* and *Proteobacteria*)	Agricultural soil samples collected in Michigan (USA)	>165 days* observed in soil	Thelusmond et al. (2018)
Nonylphenol (2.5 mM)	Indigenous soil flora (*Pseudomonas nitroreducens* strain LBQSKN1, *Pseudomonas* sp. LBQSKN5, *Pseudomonas putida* strain LBQSKN2, *Enterobacter asburiae* strain LBQSKN4, and *Stenotrophomonas* sp. LBQSKN3)	Soil samples collected at different coal-fired power stations (Mpumalanga Province, South Africa)	41–46% obtained in liquid medium after 12 h	Qhanya et al. (2017)
Dimethyl phthalate (400 mg/L)	*Bacillus thuringiensis*	Soil samples collected from cotton field in Sindh (Pakistan)	99 obtained in liquid medium in less than 72 h	Surhio et al. (2014)

*half-life

the authors demonstrated that the higher the polar surface area of the estrogens tested, the lower the biodegradation process. In their recent study, Annamalai and Vasudevan (2020) investigated the degradation in liquid medium of di-(2-ethylhexyl) phthalate using the aerobic bacterial strain *Rhodococcus jostii* PEVJ9 isolated from plastic-contaminated soil collected at Marina Beach, Chennai (India), in combination with biogenic monolayered silver nanoparticles. This approach significantly enhanced the biodegradation potential of the strain, allowing it to completely degrade the plasticizer (1, 10, and 100 μg/L initial concentrations) after 72 h of incubation. It was suggested that the biogenic silver particles acted by improving di-(2-ethylhexyl) phthalate bioavailability to *Rhodococcus jostii* PEVJ9. In another study, Kamaraj et al. (2022) experimented with biodegradation of di-(2-ethylhexyl) phthalate (0.53 mg/Kg), already present in a paddy field soil in Peruvarappur village (India), by the strain *Rhodococcus* sp. PFS1 (at 1 × 107 cells/mL), isolated from the same soil. It was found that the isolated strain successfully degraded (87.66%) di-(2-ethylhexyl) phthalate in sterilized soil. Further, the plasticizer was better degraded by the strain (94.66%) in non-sterilized soil, which is a clear indication of the involvement of the indigenous soil flora in the biodegradation process. Besides, the strain PFS1 was also capable of degrading other phthalate esters, including dipropyl phthalate, diethyl phthalate, dibutyl phthalate, dicyclohexyl phthalate, di-n-octyl phthalate mono-(2-ethylhexyl) phthalate, phthalic acid, di-n-heptylphthalate, and butylbenzyl phthalate with removal efficiencies exceeding 90%. Moreover, it was demonstrated that this ED was completely mineralized and utilized by *Rhodococcus* sp. PFS1 as growth substrate.

The use of microbial enzymes, either wild or recombinant, for ED removal from different environmental media has gained significant interest in the recent past. However, many of them have been performed on synthetic ED solutions. The use of microbial enzymes such as laccases and esterases for treating EDs has been actively researched for many years (Koyani and Vazquez-Duhalt 2016; Sungkeeree et al. 2016; Li et al. 2022). However, the use of purified microbial enzymes in real environmental situations is limited by some drawbacks, such as their sensitivity to numerous environmental factors, which could interfere with their catalytic activities through reversible or irreversible inhibition. Moreover, the indigenous flora in the soil to be decontaminated can negatively affect the enzymes involved in the degradation of pesticides by secreting extracellular enzymes, such as proteases (Rao et al. 2010).

16.5 Conclusion

EDs are found virtually everywhere, and most originate from human activities, mainly agricultural and industrial ones. New molecules of EDs are continuously released into the environment. The exploration of efficient and eco-friendly solutions to eliminate these hazardous compounds is of immense importance. Among all recognized and potential solutions, microbial remediation offers a good solution. The body of studies on ED biotreatment clearly underlined the potential of microbial bioremediation as an effective and handy method to be applied more widely in the detoxification strategies of ED-contaminated soil environments. In fact, many authors have succeeded in screening and identifying highly efficient ED-degrading microbial strains from different soils. These microorganisms are phylogenetically diverse, and many are able to mineralize EDs and use them as a source of carbon and/or energy for growth. Besides, it was evidenced that mixed cultures were more effective in degrading many ED-contaminated soils than single cultures. However, efforts should be continued to screen new and more effective microbial strains from different natural habitats capable of tolerating and degrading high levels of EDs in soils and landfill sites.

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