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Rhizobiont in Bioremediation of Hazardous Waste

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Preface

Owing to the speedy development and sprouting anthropogenic activities and accomplishments, the native biological diversity or our natural ecosystem is being disrupted. Development of technology, unwarranted application of chemicals in agriculture, and unwanted human activities have caused a huge burden on our ecosystem. This has resulted in probably intimidating nature's dynamics by making particular undesirable compounds. Application of microorganisms to bioremediate hazardous contaminants in an environment is a state-of-the-art approach and also a field of passionate curiosity. Though biological know-how has been employed for years in treating contaminants in soil and water system. The success and cost-efficacy of this technology has led to its application in remediating perilous chemicals at contaminated sites. Achievements attained by exploiting the inherent metabolic potentials of microbes to detoxify the soils, sediments, and aquatic systems have reinvigorated continued research interest in biological remediation.

Within the last couple of years, the flora-based bioremediation tactic has evolved into a significant, feasible option for cleansing of polluted sites. This tactic now has earned the novel tag 'phyto-remediation' and has been documented for some specifically interesting features, such as its eco-friendly nature and importantly its cost-effectiveness. Later on, it was felt that this technology is slow and it can be converted into better approach for decontamination of environment. This strategy can be made more efficacious by employing potential and synergistically capable pollutant bioremediating microbiome, which is also quite popular, cost-effective, and environmentally feasible approach. The application of 'rhizobiont' or rhizo-microbiomes in remediation approach will clearly and certainly ascertain an advantage and will be known as 'natural attenuation'.

In this compilation, we also try to encapsulate contemporary and current knowledge about contaminates biodegradation in rhizospheric zone by plant (rhizo)-microbiome interfaces and communications based on evolving techniques and nanotechnology. This will help us in better understanding the process of synergism between the 'plant-rhizo-microbiome' to further exploit rhizo-bioremediation pursuit in a better way. Additionally, a better perception and knowledge of the collaborations might lead to techniques development to bioengineer rhizospheric microbes for better contaminants biodegradation.

The book ‘Rhizobiont in Bioremediation of Hazardous Waste’ attempts to undertake biological remediation issues of contaminated environment and also showcases the explicit know-hows realistic in bioremediation of foremost interest for research in the field, with special attention on advancement in conventional biological approaches. We have paid focus on the role of efficient microbes or exploiting the synergism of plant and microbes towards effective process of bioremediation. We have also discussed management approaches, such as composting technology for managing pretentious environment in an eco-friendly way. Examples of successful bioremediation applications are illustrated in pesticides, heavy metals, wastewater, hydrocarbons, mangrove forest pollution, antibiotics in aquatic system, and many more. For an effective bioremediation process, microbes must attack enzymatically on the contaminants and transform them to innocuous outcomes. Moreover, the bioremediation approach can only be effectual when environmental conditions favour microbial survival, proliferation, and action. In field conditions, managing the ecological factors favouring the microbial growth will certainly lead to degradation of contaminants at a quicker rate, since similar to other approaches, bioremediation technology do have its own limitations.

To better understand the bioremediation process, it is also important to comprehend the particular chemical composition of original contaminant at the site and the autochthonous microbial populations. This edition also provides updated information about microbial bioremediation approaches and an understanding of the challenges in biodegradation technology. It is a beneficial resource for students, researchers, academicians, environmental professionals, and policymakers. We unreservedly thank all the contributors who have proficiency in this field of research for their innovative, interesting chapters and their help in making this book a successful attempt.

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Contents

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Plant–Microbe Interactions for Bioremediation of Pesticides

1

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Denise Brentan Silva, Maria Rita Marques, and
Amanda Dal'Ongaro Rodrigues

Abstract

This chapter is dedicated to examining recent works about pesticides bioremediation by plant–microbe interaction, making them nontoxic, along with metabolite analyses resulting from enzymatic reactions. The worldwide constant progress of farming is directly associated with pesticide consumption. However, the increasing amount in its use is alarming considering its adverse outcomes in humans and other organisms. The over pesticide application causes the formation of non-biodegradable deposit in groundwater and soil. Environmental cleaning requests a cheaper and environmentally friendly bioremediation. Partnerships between microorganisms and plants (called bioremediation of phyto–microbes) are rather important in pesticides remediation by accumulation, degradation, adsorption, and volatilization. This process is able to transform pesticides into nontoxic or inactive compounds. In order to better approach these strategies, it is also important to deal with methodologies applied for analyses and identification of metabolites resulting from bioremediation, such as techniques of chromatography, mass spectrometry, and hyphenated techniques.

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Keywords

Bioremediation · Microbes · Pesticides · Plant

1.1 Introduction

Environmental pollution is increasing with industrial growth and it is affecting soil, air, continental groundwater, and oceans (Azubuike et al. 2016). Annually, polluted air and contaminated water is killing more people than many diseases, such as AIDS, tuberculosis, and malaria, as well as natural disasters, hunger, smoking, and war combined (Langrigan et al. 2018). The application of pesticides has raised the impact to human health. A fraction of applied pesticides generate residue, which can be found in the atmosphere, soil, water, and food. They are even detected in the most southern regions, such as Antarctica (Maggi et al. 2019).

In fact, pesticides are considered indispensable for large agricultural producers to grow more food on less land, controlling diseases in crops, pests, and weeds (Gill and Garg 2014). However, these chemicals act not only on the target organisms but also on pollinizer insects, causing economic loss to other types of food production (DiBartolomeis et al. 2019).

An alternative to reduce harmful impacts to the environment is bioremediation. This technique has been presenting a sustainable alternative for the degradation and detoxification of contaminated sites. This method uses processes or biological activities employing living organisms (microorganism and plants) capable to modify or decompose pollutants, turning them into inert products. The process can be ex situ when the techniques involve removal of contaminants from sites and, transferring to a treatment area. In another way, in situ methods imply that contaminants are treated at the same area where they are present. The choice of any of the techniques is related to the cost, region, nature, and concentration of pollutants (Azubuike et al. 2016; de Lima et al. 2018).

Several different studies of bioremediation of organic compounds are described as, for example, tolerance to toxicity (Cocaign et al. 2013), biotransformation (de Lima et al. 2017), biosorption (Adnan et al. 2017), biodegradation (Perissini-Lopes et al. 2016), or mineralization (Khan and Fulekar 2017). All of them aim to decrease the toxicity of xenobiotic or their complete extinction.

1.2 Pesticides Characteristics and Residue Risks

The definition of pesticide may be “any substance or mixture of chemical substances or biological ingredients intended to repel, destroy or control any pest or regulate plant growth” (FAO 2020). Pesticides comprise many chemicals used for control insects, weeds, pathogenic fungi, rats, etc.; and other substances designed to combat microorganisms, algae, etc. (US Environmental Protection Agency 2010).

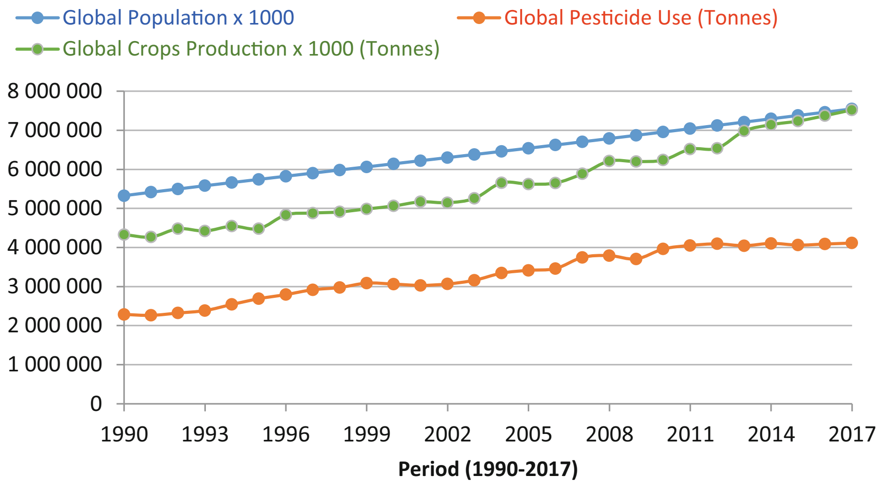

Fig. 1.1 Global population. Source: UN (2019). Global crops production, considering cereals, citrus fruit, coarse grain, primary fruit, legumes, tree nuts, primary vegetables, roots, and tubers; and global pesticide use and global crops production. Source: Food and Agriculture Organization of the United Nations—FAOSTAT (2020). Reproduced with permission

According to data of population growth in the world (Fig. 1.1), obtained from United Nations (UN), between the years 1990 and 2017 there was an exponential increase in the world population, reaching an approximate number of 7.547 billion people (UN 2019). The Food and Agriculture Organization of the United Nations (FAO) on farming statistics for the same period showed an expanding demand for world crop production, which reached an approximate value of 7.524 billion tons in the food production. This value considered only cereals, citrus fruit, coarse grain, primary fruit, legumes, tree nuts, primary vegetables, roots, and tubers (FAOSTAT 2020). If these trends continue, estimates of UN indicate that for the year 2050 the world food production has to duplicate (UN 2009).

In the same period (Fig. 1.1), it was observed that between the years 1990 and 2010 there was also a significant increase of pesticide application and, between 2010 and 2017, there was an apparent stagnation. However, in the year 2017 the value of 4,113,591.25 ton was the highest recorded until today (FAO). This can also be seen from FAO data in relation to the use of pesticides by area in the world (Fig. 1.2), maintaining an average of approximately 2.6 kg/ha (FAOSTAT 2020).

The countries of Asia and the Americas are among the largest producers and also consumers of herbicide by cultivation area (Fig. 1.2). Highlighting 2017, China and Japan used 13.07 and 11.76 kg/ha, respectively, and Brazil and USA used 5.95 and 2.54 kg/ha, respectively (FAOSTAT 2020). Although Brazil and the USA have a lower average use per area, they are considered major world consumers of herbicides. Only Brazil imported more than $ 2.46 billion in 2017 and USA $ 1.25 billion (FAOSTAT 2020).

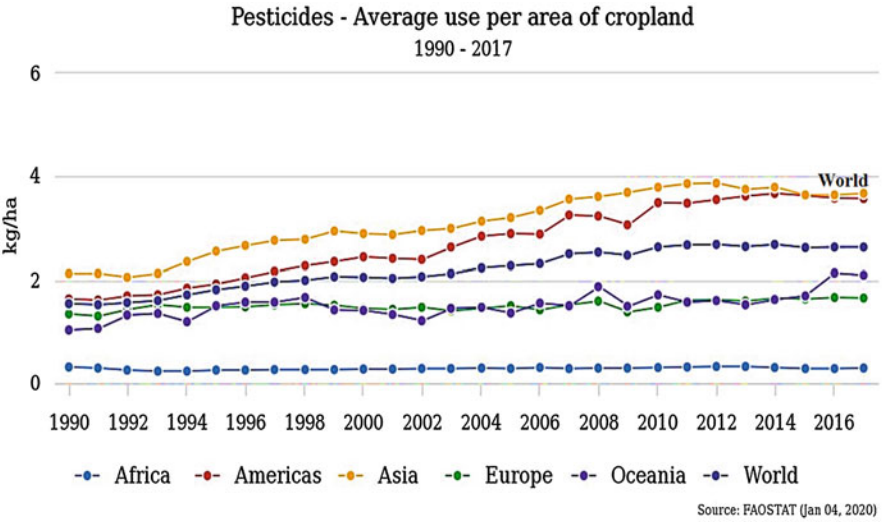

Fig. 1.2 Average amount of pesticides used per area (kg/ha) on continents and worldwide from 1990 to 2017. Source: Food and Agriculture Organization of the United Nations (http://www.fao.org/faostat/en/#data). Reproduced with permission

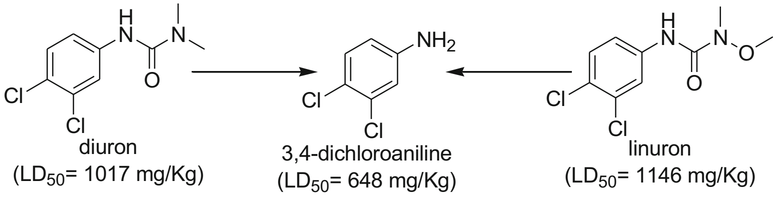

Fig. 1.3 Molecular structure and LD_{50} in rats of the diuron and linuron herbicides and the residue 3,4-dichloroaniline (3,4-D)

Nonetheless, pesticide residues are the main pollutants in agricultural areas, but the contamination can be spread by rain, rivers, and hydric basins (Wilkinson et al. 2017). A few decades ago, a significant increase in the use of more toxic pesticides to the environment and humans was reported (DiBartolomeis et al. 2019; Bilal et al. 2019; Morillo and Villaverde 2017). In addition, the indiscriminate and frequent usage of these compounds can increase the disorders caused by their toxicities, this happens because a large part of them end up accumulating in the soil and reaching groundwater (Gill and Garg 2014). Many of these compounds persist in the environment (Lushchak et al. 2018) and, they can generate more toxic products. For example, the diuron (Fig. 1.3, LD_{50} oral rat 1017 mg/kg) (Lewis 2004) and linuron (Fig. 1.3, LD_{50} rat oral 1146 mg/kg) (Lewis 1996), when deposited in soil or water become 3,4-dichloroaniline (3,4-D) (Fig. 1.3, LD_{50} rat oral 648 mg/kg) (Lewis 1996). 3,4-D is an extremely toxic and persistent substance (Castillo et al. 2014; de Lima et al. 2018).

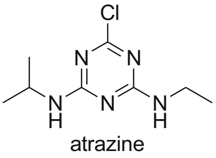

Fig. 1.4 Molecular structure of atrazine

Pesticides affect various organisms, causing harmful effects on the nervous, endocrine, respiratory, reproductive, circulatory, energetic, and hormonal regulation systems (Bilal et al. 2019). As an example of some of these effects, linuron can damage the production and function of male androgen hormones, causing changes in genes that encode testosterone synthesis, consequently, leading to dysfunctions in male reproduction (Bai et al. 2017). The atrazine herbicide (Fig. 1.4) causes endocrine disrupting effects on female and male in vertebrate species. These effects cause interferences in animal reproduction (Gely-Pernot et al. 2017).

In addition, studies with fish larvae have shown that atrazine was responsible for neurotoxic outcomes as the inhibition of the activity of the enzyme acetylcholinesterase (AChE) and disruption of the neuroendocrine system (Liu et al. 2016).

The bioremediation by microorganisms or plants, mainly via enzymes, can treat and recover polluted areas to their original condition (de Lima et al. 2018). More economically attractive, efficient, and scalable bioremediation processes have been used for years to minimize environmental impacts to remove contaminants than physical and chemical techniques (Bamforth and Singleton 2005; Megharaj et al. 2011; Azubuike et al. 2016).

Microorganisms and plants; alone or in association, present important benefits for the reduction of harmful effects of these pesticides, helping in the recovery of degraded or contaminated environments and contributing to the increasing demand for cultivation of food and renewable energy sources (Abhilash et al. 2012).

1.3 Phyto and Microbe Bioremediation

1.3.1 General Characteristics of Uptake and Translocation of Contaminants by Plants

Soil is a primary drain for chemical residues. In this sense, it can represent some risks; it can cause some type of intoxication, or it can be beneficial for live forms (Teng et al. 2014). Origin of the residues is medicines, hygiene products, agronomic products (pesticides and fertilizers in general), and industrial products (nanomaterials, polycyclic aromatic hydrocarbons—PAHs) among others (Qing et al. 2015; Pullagurala et al. 2018). The careless or accidental release of these wastes can endanger soil and biota. It is worth to mention that plants form the base of the food chain (Pullagurala et al. 2018). Consequently, environmental disorders affect the development of plants and, obviously, their consumers (Zhuang et al. 2009).

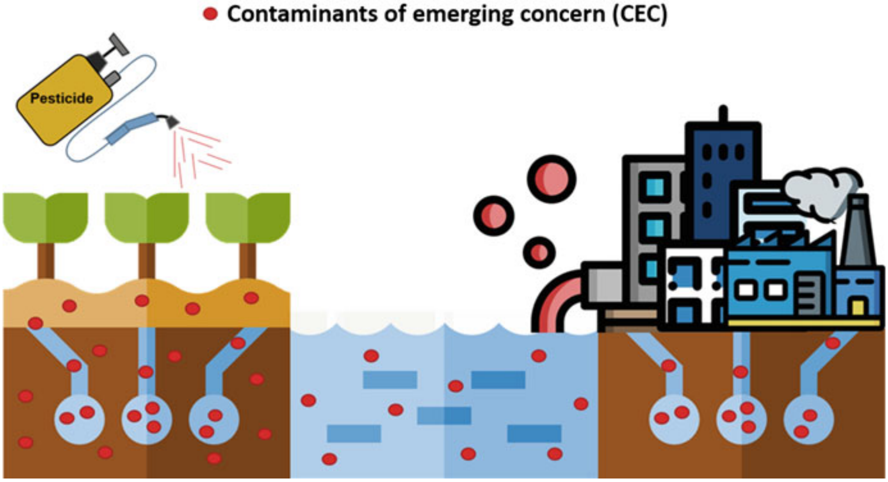

Fig. 1.5 Representation of environmental contamination by CEC

Plants are prone to absorb humic substances present in the soil and are applied for the bioremediation of heavy metals. Plants are able to absorb great amounts of metals in the soil and aquatic environments (Dixit et al. 2015). Phytoremediation has been important to remove heavy metals, such as Pb and Zn, from the soil for more than three centuries in some cultures worldwide (Cunningham and Berti 1993). However, these processes attracted attention nearly three decades ago (Sharma and Pandey 2014). Encompassing industrial progress, new types of chemical compounds were discovered and, most of them causing environmental damages (Pullagurala et al. 2018; Salimi et al. 2017). These residues are the main source of Contaminants of Emerging Concern (CEC), which includes several products, such as pharmaceuticals products, personal hygiene products, plasticizers and flame retardants, industrial dyes, chemical residues and mainly pesticides (Nilsen et al. 2019; de Lima et al. 2018; Salimi et al. 2017) (Fig. 1.5).

CECs fate in edaphic area is unpredictable, as they are subject to several environmental and climatic factors, such as runoff, air currents, and soil erosion (O'Conner et al. 2019; Marquès et al. 2016). Many plants are able to absorb CECs from the soil, changing their growth, development, metabolic pathways, among others (Morillo and Villaverde 2017).

In general, the CECs physical-chemistry properties play a central role since they are absorbed and translocated from the soil to the plant. The stability of some CECs allows them to remain in their original form within the plant. Absorption, in turn, will depend on the degree of hydrophilicity or hydrophobicity of CEC molecules, which Shone and Wood (1974) named "the ratio of chemical concentration in the transpiration stream to the concentration found in an external solution," or "Transpiration Stream Concentration Factor" (TSCF). For example, Garvin et al. (2015) showed that caffeine TSCF values were relatively higher than for endosulfans and trichlorocarbons in soybeans, zucchini, and pumpkin plants. These compounds are more neutral or hydrophobic compounds than caffeine (a more hydrophilic compound), proving that hydrophilic compounds are translocated faster than hydrophobic ones.

Abiotic factors can greatly influence the absorption of CECs by plants. The concentration of humic acid; one of the main components of the soil, is important in the retention of CECs, mainly PAHs. Other factors such as clay crystal content, pH, soil mobility and age, hydraulic conductivity, water absorption capacity and wettability of soil are also parameters that have a major impact on the CECs absorption capacity (Ávila et al. 2014).

Additionally, chelating agents, whether added to soils artificially or secreted by the roots into the rhizosphere, can affect the absorption of contaminants by plants. The literature reports that air contaminants can be exchanged with the soil, forming residues or, they can be deposited on the leaves (Masih et al. 2012). Exchanges between air and leaves are often the main route of entry for some CECs, such as PAHs, phthalates, and polybrominated diphenyl ethers (Pullagurala et al. 2018).

The geospatial distribution of CECs also appears to be trending. The higher proportion of CECs are encountered at tropics and subtropic than temperate zones, due to the higher temperatures and the low concentration of organic matter in the soil (St-Amand et al. 2009). In addition, as expected, CECs are most found in urban than rural areas (Ligaray et al. 2016). Global climate change has a remarkable impact on the elimination of contaminants by photolysis, photodegradation, or biotransformation of PAHs (Marquès et al. 2016).

1.3.2 Phytoremediation

This methodology is associated with plant ability to deposit metals in vacuoles. After that, metals can be transported from the root to other parts through xylem vessels or in the use of complexing proteins or peptides known as phytochelatin and metallothionein. Both of them are rich cysteine residues, whose sulfhydryl group (-SH) is able to form stables complexes with heavy metal ions (Ali et al. 2013). Enzymes from plants play key roles in the metabolism of CECs. For instance, *N*-malonyltransferases, carboxylesterases, cytochromes P450, and glutathione transferases. Lipophilic contaminants can be absorbed and translocated throughout the plant tissue and, subsequently suffer enzyme transformations. The whole process comprises three phases. Phase I: reactive groups participate in hydrolysis and redox reactions of contaminants. Phase II: conjugations of glutathione, sugars, or amino acids to metabolites. Phase III: certain metabolites are either kept into vacuoles or are incorporated into the cell wall. In the absence of a secretory system, phases I, II, and II are of crucial importance for plants (Sandermann Junior 1992; Ohkawa et al. 1999; Dietz and Schnoor 2001).

In terrestrial ecosystems, trunks and branches provide a large part of the plant's visible biomass, which can act in storage or as a source for agrochemicals. Aquatic plants have higher biosource capacity or as in situ biofilter for water pollutants due to their numerosity and low mobility. Additionally, they present a large surface area covered by a lipid-rich layer, providing them the capacity to absorb lipophilic pesticides. (Karthikeyan et al. 2014).

With regard to the bioremediation capacity of large trees, pesticides have been detected in pine and mango leaves in the classes of hexachlorocyclohexanes (HCHs) and hexachlorobenzenes (HCBs) (Calamari et al. 1995). Trees are able to remove pesticides from the soil and retain in their trunks, or storing them in bark, or even biotransform them as observed by Simonich and Hites (1995). In this case, 200 samples of bark from 32 countries were collected and 22 pesticides were identified, including degradation products and active ingredients, such as endosulfans, dichlorodiphenyltrichloroethane (DDT), HCHs, HCBs, dieldrin, aldrin, chlordane, and endrin.

Large trees have high retention capacity of soil xenobiotics such as agrochemicals in extensive areas. One of the most commonly used transformation processes is the use of xenobiotics for the synthesis of lignin (McCutcheon and Schnoor 2003). For bioremediation of contaminated groundwater, an alternative is the cultivation of trees with deep roots at the edge of the aimed areas, which will function as “solar pumps”, in order to absorb contaminated water and eliminate contaminants through transpiration or bioaccumulation (Ferro et al. 2003).

1.3.3 Microbial Remediation

In 1991, Lynn Margulis and René Fester devised the term “holobiont” referring to an assemblage of a host and the many other species living in or around it. The term was later expanded and today, it defines the associations between communities of microorganisms—or microbiota—that interact with a given host. This interaction can vary from mutualistic to parasitic. Thus, the term holobiont is currently used for all metazoans, indicating the constitutive interactions between hosts and their associated microbiota, focusing on humans, animals, and plants (Simon et al. 2019). Therefore, when discussing phytoremediation, all communities associated with the plant species under study should be considered, including soil microorganisms, endophytic microorganisms, epiphytes, which are present not only in the roots, but in all plant tissues. It is necessary to include virus, fungi, actinomycetes, bacteria, and archaea.

When the microorganisms are fungi, the bioremediation performed by them can be defined as mycoremediation, that is, the ability of soil fungi, mycorrhizae, and endophytic fungi in bioremediation of contaminated areas. The fungi metabolic pathways for biotransformation of toxic and recalcitrant compounds are shown in Fig. 1.6. Including the intra and extracellular enzymatic processes made by peroxidases, laccases, transferases, and cytochrome P450 for detoxification and biodegradation or mineralization and a type of biodegradation, in which organic compounds are converted to inorganic constituents (Deshmukh et al. 2016; Olicón-Hernández et al. 2017; de Lima et al. 2018). Fungi can also accumulate xenobiotics and intermediate metabolites by organelles such

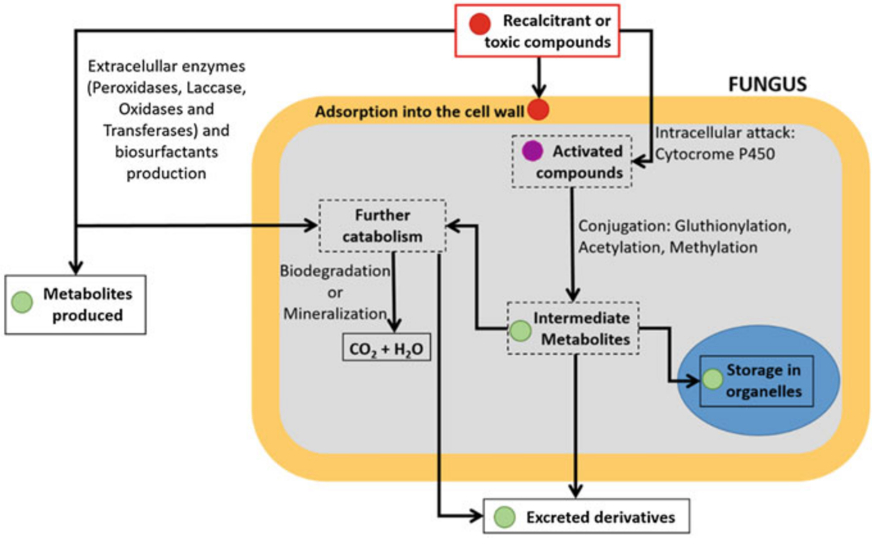

Fig. 1.6 Fungi bioremediation mechanisms of toxic and recalcitrant compounds

as intracellular lipid droplets (Verdin et al. 2005; Chang et al. 2015; Olicón-Hernández et al. 2017). Biosurfactants such as complex primary metabolites can also be excreted by fungi. These molecules have amphiphilic characteristics leading to the increase of molecular interactions (Cicatiello et al. 2016; Günther et al. 2017).

Some process exerted by fungi in the bioremediation of xenobiotics are shared by bacteria (Ijoma and Teker 2017). However, some process carried out by bacteria, such as bioaccumulation and biosorption are more limited to bioremediation of heavy metals (Abbas et al. 2018).

Bacteria associated with plants include phyllospheric, rhizospheric, and endophytic bacteria. The interactions between these microorganisms and their host plants augment plant survival, showing significant performance in the treatment of contaminated sites (Gkorezis et al. 2016).

1.4 Rhizosphere Systems and Plant–Microbe Interactions

Plants associated with bacteria (Zhang et al. 2014) and fungi (Asemoloye et al. 2017) perform an important function in the organic pesticides bioremediation. In these cases, the plants also function as buffer zones, capable of reducing the flow of pesticides, through bioaccumulation and/or metabolization (Morillo and Villaverde 2017).

Plant–microbe partnerships are related as a two-way road, mainly through associations between the rhizosphere and the plant root, aiming at survival in contaminate and nutrient deficient environments (Begum et al. 2019, Abhilash et al. 2012). The rhizosphere comprising the area near to the plant roots supports microorganisms capable of degrading pesticides (Morillo and Villaverde 2017). The number of bacteria in the rhizosphere generally exceeds 10–100 times the volume of the soil itself (Erickson et al. 1995). Most of the soil microbiota are organotrophic and the main source of carbon for edaphic organisms is derived from plant roots and organic waste released during plant growth and development. The soil is enriched by plant nutrients such as simple sugars, polysaccharides, amino acids, low molecular weight exudates, mucilage that are used to microbial communities (Abhilash et al. 2012). A more specific approach to exudates from plant roots is a complex mixture of low molecular weight organic compounds, amino acids, carbohydrates, and certain enzymes during biodegradation and biotransformation of xenobiotics (Alvarez et al. 2012; Asemoloye et al. 2017; Asemoloye et al. 2019).

Angiosperms are commonly associated with fungi. Most of the time, these fungi need the plant alive to maintain their own growth and development. Some fungi form specific associations with the surface of plant roots; called ectomycorrhizae, while the endomycorrhizae grow internally in the roots (Davis et al. 2002).

There is yet another type of interaction between microorganisms and plants called endophytism. Endophytic are fungi or bacteria that live their whole life cycle inside plants, intra or intercellularly without triggering any apparent damage or disease (Wilson 1995). They have been isolated from all the plants analyzed so far. They make complex interactions with their hosts, involving various biosignalization processes that generally end up with mutualistic interactions (Carroll 1988; Parker 1995). Endophytes benefit from the host by receiving protection and nutrition. Besides the production of antibiotics, they act in the protection from diseases in a dispute for colonization and nutrients against phytopathogens (Lee et al. 2004; Das and Varma 2009).

Plant roots have a major positive effect on the remediation of soil contaminants. Walton and Anderson (1990) analyzed a contaminated area by trichloroethylene (TCE) and they observed that the rhizosphere had a much greater capacity to degrade the contaminant than regions without rhizosphere. Subsequently, Anderson and Walton (1995) analyzed the properties of the rhizosphere microbial communities of five plant species associated with TCE degradation. They observed that about 70% was processed by mineralization, incorporation, and volatilization through the plant.

Eventually, in the future, these processes can be used for sustainable production of biomass used in the production of energy such as oilseeds for biodiesel and saccharide for alcohol.

1.5 Plant–Microbial Remediation

If the bioremediation of pesticides was performed solely by the plant, it would be affected by several factors, such as bioavailability in the soil and preclude the efficiency of the process (Morillo and Villaverde 2017). However, microorganisms increase the desorption of pesticides and assist in absorption and biodegradation

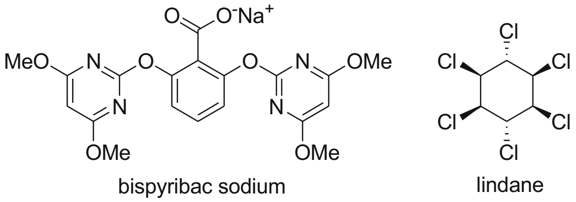

Fig. 1.7 Molecular structures of pesticides that have undergone plant–microbe bioremediation processes

processes while associate with plants by excreting organic acids through their roots (Morillo and Villaverde 2017).

Microorganisms themselves are great for bioremediation of pesticides, this is due to the diversity of enzymes they have, in addition to their expression capacity (de Lima et al. 2018; Huang et al. 2018; Spina et al. 2018). However, association of microorganisms with plants can increase the mechanisms by which biodegradation, absorption, bioaccumulation, and biotransformation of xenobiotics (Pereira et al. 2006; Alvarez et al. 2012; Asemoloye et al. 2017). In situ bioremediation with native microorganisms can be influenced by the unavailability of adequate levels of nutrients and/or environment in the polluted site (Smith et al. 2015).

Alternatively, the complementation with plants can significantly improve bioremediation efficiency, as plants assist in the formation of microbial habitats, such as increasing soil porosity and the transfer of mass of substrates and electron. In return, the plants receive nutrients of microorganisms. However, microorganisms associated with plant also improve plant growth through different processes and, reducing soil toxicity by removing contaminants (Gkorezis et al. 2016).

The phyto–microbe bioremediation strategy of contaminated environments is increasing, especially in the case of toxic pesticides (Asemoloye et al. 2017). As examples, the plant *Triticum aestivum* together with bacterial consortium. This association was able to carry out the degradation of the herbicide sodium bispyribac (Fig. 1.7). It was evidenced that only one bacterial consortium was able to remove the herbicide from the soil and provided the plant growth, increasing of its biomass. In contrast, the plant improved the action of the bacterial consortium to detoxify the soil and in this mutualism (Ahmad et al. 2019).

Another example is the bioremediation of environments containing the herbicide lindane (Fig. 1.7) or hexachlorocyclohexanes, this is an organochlorine pesticide (OP), where all the isomers are highly toxic to mammals (Álvarez et al. 2012). A synergistic association of grown *Megathyrsus maximus* (Jacq.) with rhizospheric fungi was able to remove lindane in the soil in 3 months. The study also highlighted the expression of enzymes, such as phosphoesterases and 1,2-dioxigenase catechol, in strains of rhizospheric fungi species (Asemoloye et al. 2017). The synergistic association was successful between plants and microorganisms and was also observed when plant root exudates are applied in association with microorganisms in bioremediation (Alvarez et al. 2012).

Interaction of plant and microorganisms depends on the climatic conditions in which they are adapted. Changes in the pattern of precipitation and temperature can cause severe impacts, beneficial or not, on the interactions between plants and their symbionts (Rasmussen et al. 2019). This pattern becomes progressively special with current climate changes (Begum et al. 2019), creating ecological and evolutive uncertainties interactions (Rasmussen et al. 2019).

1.6 Metabolite Identification and Analyses of Bioremediation Reactions

The analyses of products and toxic compounds from bioremediation studies can be performed by analytical techniques coupled to detectors capable of responding to the presence of compounds by analytical analyses. Metabolites identification can also be performed when techniques that produce structural characterization information are applied. The main methodologies applied for analyses and identification of metabolites from bioremediation approaches are gas chromatography coupled to mass spectrometry (GC-MS) and high performance liquid chromatography coupled to mass spectrometry (HPLC-MS). Therefore, here it is focused in discussion about these methodologies; GC-MS and HPLC-MS, highlighting issues and application of mass spectrometry (MS).

GC-MS is a widely used trustable methodology to analyze non-polar, volatile, and thermostable compounds in scientific, technological, and industrial applications. It has been used for environmental monitoring, flavor and fragrance analyses (food and beverage), forensic analyses, detection and quantification of pesticides, pharmaceutical and petrochemical analyses, and others (Chauhan et al. 2014). Gas chromatography (GC) is an analytical methodology for separating compounds that use an inert gas as a mobile phase (usually helium) and commonly long capillary chromatographic columns. They are classified as long, medium, and short. Long columns (60–100 m) show higher resolution, but slow speed for the analyses. The most used columns are capillary, they are often fused silica coated with the liquid/polymer stationary phase internal surface (Zoccali et al. 2019; Rahman et al. 2015). This characteristic (different internal diameter) directly impacts in resolution, speed analysis, and capacity. Columns with 0.1 mm internal diameters have showed better results that are related to these properties (resolution and speed) (Rahman et al. 2015).

There are different stationary phases for GC columns and their choice is essential to develop efficient methods for separation of metabolites. In this sense, it should be considered the physical and chemistry properties of analytes (compounds). Different chromatographic columns can be purchased by several manufactures. Non-polar to polar columns can be founded and their applications depend on the chemical properties of analytes. Basically, the non-polar column (e.g., 100% dimethylpolysiloxane) is used for non-polar compound analyses, while for polar compounds it is recommended polar columns (e.g., 90% (cyanopropylphenyl)-10%-methylpolysiloxane) (Rahman et al. 2015). The most applied chromatographic columns for pesticide analyses are 5%-phenyl-95%-dimethylpolysiloxane, which separates the pesticides due to their volatility. Currently, pesticides are being also

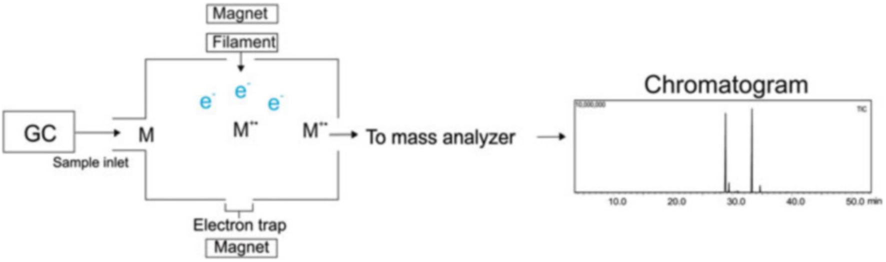

Fig. 1.8 Representation of electron ionization (EI) source that is coupled to gas chromatography (GC) producing chromatogram

analyzed by using two-dimensional gas chromatography, improving the analytical separation and results. In this case, it can be used a column 5%-phenyl-95%-dimethylpolysiloxane in the first dimension and a more polar column in the second dimension (e.g., 50%-phenyl-50%-dimethylpolysiloxane) to add another factor in the separation like as polarity (Pico et al. 2020).

GC has been applied in pesticide residues from several matrixes, as well as to analyze products and metabolites obtained by bioremediation studies, mainly GC-MS because its applicability for qualitative and quantitative analyses, including structural characterization of their products (Sidhu et al. 2019) such as for pyrethroids (Castellarnau et al. 2016) and polychlorinated biphenyls (Guo et al. 2019).

GC-MS uses electron ionization (EI) source, since the analytes are ionized from gas phase state in this MS technique and thus its coupling to GC is easy and possible (Fig. 1.8). In EI, the analyte is volatilized, and the electron is a cross molecule. This disrupts the analyte's energy and one or more electrons are detached, producing radical ions and subsequently, fragment ions are formed. Therefore, EI is named a hard method (Meyer 2016).

Although GC-MS is a robust method, the LC-MS has been widely used for pesticide analyses. It has demonstrating to be valuable for pesticides in qualitative and quantitative studies (Pico et al. 2020; Van Der Hoff and Van Zoonen 1999). Comparison between GC-MS and LC-MS for analyses of several pesticides demonstrated that LC-MS was better and more sensitive, and GC-MS was the best only for pyrethrins and organochlorines (Alder et al. 2006). From 2003 until now, the number of articles that applied LC-MS for pesticides is higher than GC-MS (Pico et al. 2020). Thus, LC-MS is applicable to analyze polar pesticides, for example, quaternary ammonium salts, urea derivatives, and others. The non-polar pesticides are recommended to analyze by GC-MS. In addition, polar analytes can be performed derivatization reactions and analyzed by GC-MS, but the structural characterization can be difficult, as the mass of compounds will be altered and will need to be considered to propose the metabolites (Samsidar et al. 2018; Sidhu et al. 2019).

Bioremediation reactions have been monitored and their metabolites identified by GC-MS, such as for endosulfan and petroleum biotransformation by

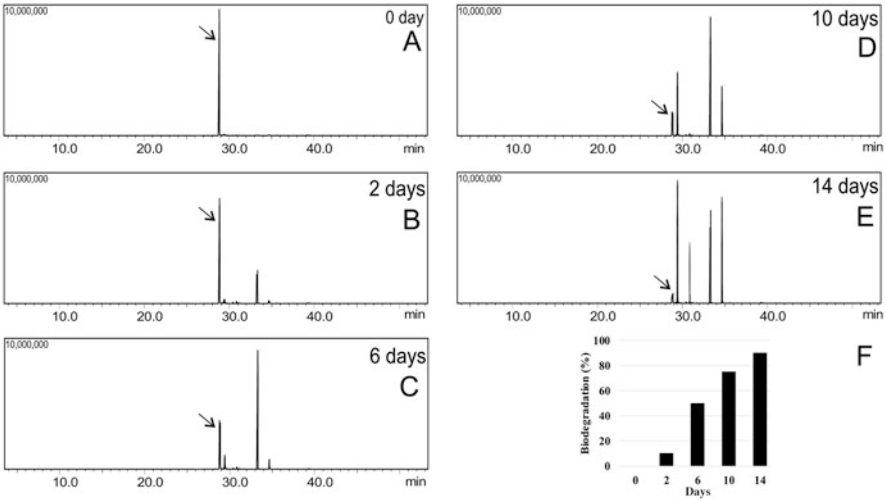

Fig. 1.9 Total ion chromatograms obtained by GC-MS from biodegradation of a pesticide after 0 (**a**), 2 (**b**), 6 (**c**), 10 (**d**), and 14 days (**e**). Graphic of biodegradation percentage (%) by microorganism (**f**)

microorganisms (Wang et al. 2019; Kumar et al. 2008). Their biodegradation was determined by GC-MS, but the structural identifications of products were not performed. Thus, GC-MS analyses are also applied for the determination of degradation percentage, performed from the different time reactions (Fig. 1.9).

EI-MS produces mass spectra highly similar to the possible databases used to identify the compounds, making it possible to compare with more than 240,000 spectra from databases. Although there are databases with EI-MS spectra, the identification by these spectral comparisons is not widely explored in bioremediation studies (Steckel and Schlosser 2019; Cook et al. 1999), since these biodegradation products were not frequently included in the commercial libraries. Therefore, the analyst, using the information about the molecular ion and its fragment ions, realizes the structural identification and this is a bottleneck, because it depends on the experience of the MS analyst.

Although few studies report the fragmentation pathways of biodegradation products. The fragmentation mechanism can be suggested from the fragmentation of molecular ion, the addition or losses of mass from initial compound (pesticide) and the comparison with classical losses described for EI reactions (Steckel and Schlosser 2019). These reactions are studied for a long time and it can be founded in good textbooks and materials about the classical fragmentation reactions on EI-MS (McLafferty and Turecek 1993).

Compared to GC-MS, HPLC-MS has been more widely useful to pesticide analyses. In addition, it can be applied as multi-residues method (Alder et al. 2006).

There are several types of commercial stationary phases for HPLC, such as C8, C18, hydrophilic interaction chromatography (HILIC), pentafluorophenyl (PFP),

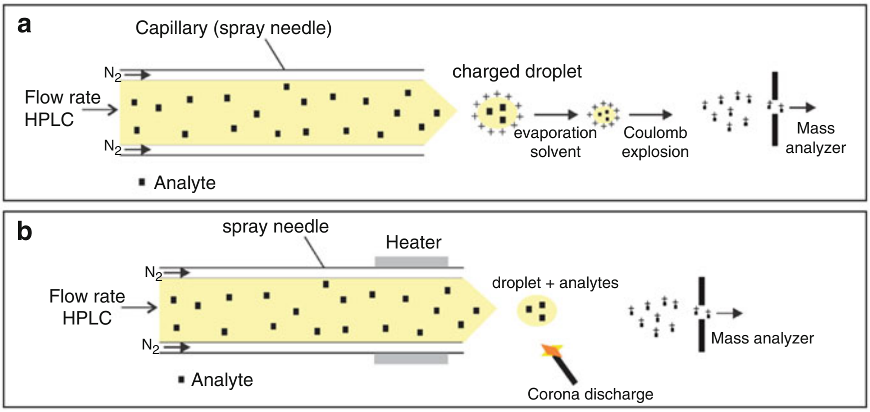

Fig. 1.10 Scheme of ESI and APCI sources

pentafluorophenyl propyl (PFPP), and others, as well as different particle types, including porous, monolithic, and fused core. Several materials can be found in the literature that explain about the differences of these chromatographic columns (Silva et al. 2019; Chester 2012), but C18 columns are the most used for pesticide analyses, showing efficient separation of them (LeDoux 2011; Primel et al. 2012; Alder et al. 2006).

Electrospray ionization (ESI) or atmospheric pressure chemical ionization (APCI) is normally applied in HPLC analyses. These techniques have shown better sensitivity and applicability. In addition, they are soft techniques, making easer the molecular weight determination and they are recommended for thermostable analytes. A mass spectrometer can be divided into three parts: ionization source (such as ESI, APCI), analyzers, and detector (Kebarle and Verkerk 2010). In ionization source, the molecules are transformed into ions, subsequently, the ions are separated based on *m/z* values (and fragmented when is required) in the analyzers, and finally they are tracked in the detector (Kebarle and Verkerk 2010; Ernst et al. 2014; El-Aneed et al. 2009).

Using ESI source, an analyte solution, when into the capillary, receives an electric potential (2–5 kV) and charged droplets are produced. The evaporation process with nitrogen reduces these charged droplets, increasing the repulsive forces until rupture of droplets (named Coulomb explosion) transferring the charges to analytes and liberating them into the gas phase (Fig. 1.10) (Fenn 2000; El-Aneed et al. 2009). The main reactions in the ESI source are acid–base and coordination reactions. Thus, the main ions observed in ESI are: $[M + H]^+$, $[M + K]^+$, $[M + Na]^+$ and $[M\text{-}H]^-$, $[M\text{-}Cl]^-$, as well as their dimeric ions (e.g., $[2\,M + H]^+$). Acid compounds are better ionized in negative ion mode, while basic compounds in positive mode (Crotti et al. 2006). Therefore, both modes can be acquired in bioremediation reactions to obtain wide chemical information (Ferrer and Thurman 2003).

APCI is also a soft technique, similarly to ESI, and to produce fragments is necessary a part in the analyzer that allow the fragmentation of parent ions, such as collision-induced dissociation (CID). The analytes are solubilized and introduced into a heated capillary to produce a spray, but differently of ESI, the electric potential is applied by corona discharge and the ionization is transferred to analytes (Silva et al. 2019; El-Aneed et al. 2009). ESI is more widely used than APCI, including for pesticide analyses. ESI is recommended to ionize polar compounds, while APCI is applied for less polar compounds and low molecular weight (<1500 Da) (Alder et al. 2006; Ernst et al. 2014). The more widespread technique applied for pesticide analyses has been ESI, but many studies have reported APCI in analyses of trace pesticides (Alder et al. 2006; Thurman et al. 2001; Hernandez et al. 2005).

An important point in MS analyses is the low or high resolution analyzer. Resolution is defined as the ability of the analyzer to separate two ions with mass differences ΔM and the resolution is calculated by the eq. $R = M/\Delta M$. The analyzers can exhibit low-, high-, and ultra-resolution, which can separate ions with mass differences of units (e.g., Q, QIT), 0.0001 (e.g., TOF), and 0.00001 (e.g., FT-ICR, Orbitrap), respectively (Bier 1997; Cooks et al. 1992; El-Aneed et al. 2009).

High resolution (HR) analyzers can provide accurate mass of ions, that is important to define and confirm the molecular formula of an unknown analyte, beyond it provides better discrimination of background (El-Aneed et al. 2009). HR is extremely relevant in bioremediation studies, mainly to characterize the biodegradation products. In this sense, it is normally applied high resolution in the MS analyses and TOF is the most used in pesticide and bioremediation analyses (Alder et al. 2006). However, the sensitivity of HR mass spectrometers can be a problem to quantify traces residue levels and others analyzers can be better applied in determinations of quantification, such as QqQ (Alder et al. 2006; Hernández et al. 2004; Soler et al. 2006).

A post-genomics tool (metabolomic) has also been applied in bioremediation research. This is an emerging technique applied, for example, in nutrition, microbiology, pharmaceutical, chemistry, and biotechnology (Puchades-Carrasco and Pineda-Lucena 2015). Metabolomics is based on metabolome determination, which includes only metabolites of low molecular weight, their acquisition (by LC-MS, GC-MS, or other), and processing of a high amount data (Ernst et al. 2014). Some metabolomics strategies can be applied in bioremediation research which can be useful to determine biodegradation pathways by isotope distribution analysis, molecular networking, and multivariate statistical analyses (Villas-Bôas and Bruheim 2007). However, metabolomics strategies are rare to get chemical information in bioremediation nowadays. In addition, metabolomics can be associated to proteomics data, which determine a quantitative protein correlation of gene expression and thus, they can give important information for bioremediation research (Singh 2006).

There are several examples of the application of these techniques for the identification of metabolites generated in the bioremediation of environments contaminated by herbicide. Among the identification of metabolites generated in the biodegradation of the herbicide bispyribac by the bacterial consortium BDAM and the plant *Triticum aestivum*, carried out by LC-MS analyses, it was possible to detect the products showed in Fig. 1.11 (Ahmad et al. 2019). The final product was identified as 3-(carboxyamino)-2-methylpropanoic acid (iv), a derivative of beta-alanine.

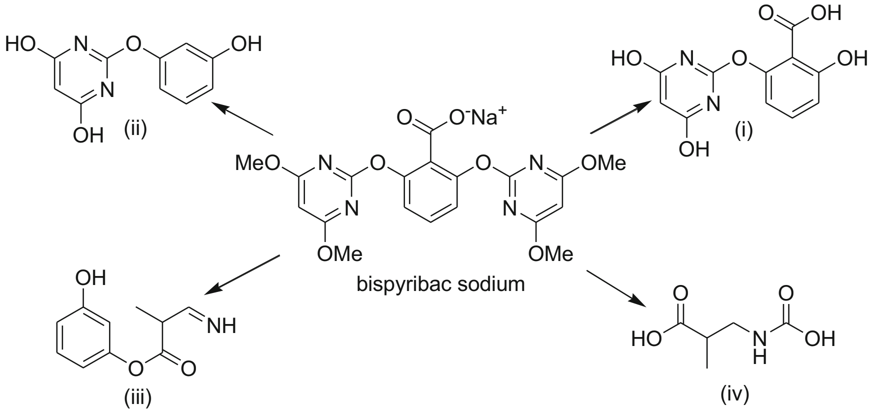

Fig. 1.11 Proposed metabolites generated by biodegradation of bispyribac sodium in contaminated wheat vegetated soil, detected by LC-MS technique (Ahmad et al. 2019)

A path of the biodegradation of the organochlorine chemical lindane by rhizospheric *M. maximus*, was depicted using GC-MS technique (Asemoloye et al. 2017). In a process of biodegradation or biotransformation for bioremediation of environments contaminated by pesticides, the identification of the generated species becomes crucial to detect possible less toxicity or even inert compounds in relation to the initial toxicity, which is intended for the processes of bioremediation and compounds that in turn have higher toxicity (de Lima et al. 2018).

1.7 Conclusion

The bioremediation of environments contaminated by pesticides is and will be increasingly important in the recovery and reduction of damage caused by them, mainly due to the growing demand and need for food in the world. From the most diverse types of processes used to remedy pesticides, the coupled application of plants and microorganisms stands out for their synergisms, increasing the expression of biodegradable enzymes, which provide more favorable environments for bioremediation. Although works in this direction are still scarce, the discovery of bacteria and fungi endophytic or found in the rhizosphere could be a pivotal tool in association with plants for bioremediation. The study of the influence of plant exudates, mainly from their roots, on strains of fungi and bacteria that are known for their potential for bioremediation of environment contaminated by pesticides, seems to be the best way to potentiate their action and evaluate the behavior of these microorganisms in the application environment, mainly in the soil. LC-MS and GC-MS techniques are helpful in detecting metabolites formed during the biodegradation or biotransformation process of the pesticides. In addition, these techniques assisting in the elucidation of the biodegradation route. The identification of intermediates and products allows the classification of the bioremediation process and the success of its application.

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Combined and Sustainable Techniques in Remediation of POPs-Contaminated Soil Sites

2

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Abstract

Modern environmental technologies face massive challenges in dealing with persistent organic pollutants (POPs). The storage and disposal of POPs is now strictly controlled in most countries. However, sustainable techniques for POPs disposal are still lacking. Here we are going to raise a discussion on new approaches in hazardous waste management. Moreover, it is appropriate to discuss what is meant by the modern "POPs" concept. It is obvious that POPs comprehension has widened significantly from the times this group of substances was first determined by the Stockholm convention. Now the modern understanding of contaminant persistency requires new determinations and, therefore, new treatment approaches.

Keywords

POPs · CHC · PCB · DDT · Oil pollution · Sustainable remediation

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2.1 Introduction

In this article, we present our insight into the problem of persistent remediation of hazardous and stable organic pollutants traditionally pertaining to the group of persistent organic pollutants (POPs) prescribed in the Stockholm Convention (Stockholm Convention on Persistent Organic Pollutants (POPs) Texts and Annexes 2017). It should be pointed out here that at the time of creating documents under the Stockholm Convention, POPs meant a much narrower group of pollutants than it is conventional to consider today. "The Dirty Dozen" specified in the first version of the convention can be conditionally divided into two groups of substances: pesticides and polychlorinated hydrocarbons. After the fourth meeting of the parties to the convention, the list of pollutants was extended with nine more substances. It is currently obvious that further extension of the POP list under the Stockholm Convention is a matter of time. So what properties are most critical so far to determine a certain substance as hazardous for the environment as regarded by the international community, local regulators, and the environmental industry?

Here we want to list the criteria in turns, starting from those that are to cause the greatest concern, in our opinion:

1. Toxicity for humans or for the critical components of the ecosystem, which jeopardizes the collective health or economic interests of the society
2. Ability to bioaccumulate in critical food pyramids
3. Resistance to destruction under the influence of natural environmental conditions

It should be noted that these criteria are applicable for synthetic chemical compounds, and each of these items for a specific chemical can play an essential role and lead to far-reaching consequences in the public perception of the industry and/or regulatory control.

Thus, it can be demonstratively exemplified with the information campaign launched around microplastic pollution where the toxicity of microplastic particles itself does not seem so threatening yet, but it is the recently discovered bioaccumulation ability of microplastic that is of general concern. It has turned out unexpectedly that the propagation scales of microplastic particles are so vast that, having even a slight accumulation effect in the food chain, they will eventually get into the human diet. The emergence of such unexpected "marinade" naturally caused fierce debates, and only a few years after the problem of microplastic was publicly declared, scientific reviews already classify it as a "new persistent environmental pollutant" (Yu et al. 2018).

It must be noted that the above-mentioned characteristic, although it has been given to the contaminant only by the research community so far, is well-placed to get spread into the field of regulatory documents of the upcoming conferences of the Stockholm or some other global convention. The wording "persistent environmental pollutant" is obviously very close to the traditional term—POPs, and we are only one semantic step away from the extension of the POP list in this specific case. New environmental threats are identified regularly and continuously, thus we are sure that the POP family is bound to be rising over time.

Understanding the global nature of the POP problematics urges the industry and the scientific community to elaborate an equally global methodological approach to solve the problems of disposal of POPs. This approach apparently should be concerted and, what is more, get enshrined in such international initiatives as SDG and the general policy for sustainable development led by the UN (Warner and Hadley 2012).

In this context, we will feature a partial vision of applying the SDG principles to POPs disposal in soils only, since, turning to the basic concept for POPs, most of which were used as pesticides, exactly soil sites were originally most susceptible to pollution. POPs further ingress into the water medium is only a consequence of natural leaching or improper irrigation. We assume that it is understanding the right methodology of POP disposal on soil sites underlies the control of the POP situation in the whole ecosystem. Moreover, water treatment, if pollutants are persistent, also finally resolves into their primary accumulation in solid phase, for instance, in sludge, with subsequent disposal of compact sludge with concentrated pollutant.

Therefore, we can postulate that the solutions applicable to the remediation of POP-contaminated soils are also basic for water treatment and POP disposal in wastewater treatment plants. It follows that the model of sustainable remediation of POPs in soil substrate is the most relevant one.

Additionally, in the text below, we encompass only the in situ remediation methods where each definite site is too extended to perform treatment in ex situ mode, and it can be treated only without moving the full volume of contaminated substrate. For reactor systems of treatment, the presented ideas and approaches can be only partially relevant.

Now we need to outline a range of technologies which we can characterize as stable in remediation of POP-contaminated sites. In general, site remediation and selection of a definite technology within the sustainability concept should be decided upon based on a comprehensive evaluation of their possible impact on the environment. In our opinion, the Net Environmental Benefit Analyses (NEBA) algorithm is best suited for it. NEBA may be thought of as elaboration of ecological risk assessment. That is, it is a risk–benefit analysis applied to environmental management actions. However, since risk assessment does not normally consider benefits, and risk assessors are not familiar with the requirements of an assessment that estimates benefits, the NEBA framework is useful to accentuate the specific features of such analyses (Efroymson et al. 2004). Thus, NEBA may help to avoid the possibility that the selected remedial or ecological restoration alternative will fail to provide any net environmental benefit (e.g. the remediation alternative causes environmental injuries greater than the damage associated with the contamination) over natural attenuation of contaminants and ecological recovery. However, we are not going to set an example of conducting the NEBA procedure in this article, since we are guided by the reference that the remediation decision has already been made, thus we discuss only the definite technology and the ways to implement it.

2.2 Sustainable Soil Remediation: Main Principles

A sustainable remediation technology may be characterized as “a remedy or combination of remedies whose net benefit on human health and the environment is maximized through the careful use of limited resources” (Mudhoo and Mohee 2012). Sustainable remediation is determined more specifically by SD. Warner, PW. Hadley: “Striving to balance the environmental, economic, and social benefits and costs associated with remediation while maintaining a resource conservative approach” (Warner and Hadley 2012). Here, three mandatory components of a sustainable process are most accurately indicated, however, we will take the liberty of asserting the following ranking of sustainability criteria for remediation in the modern environmental industry:

1. Economic
2. Social
3. Environmental

Such ranking is empirical in our case, showing the primitive importance of the economic component of the remediation process. In our industrial experience, many technologies which were environmentally optimal for a specific case were rejected due to their high cost or social concerns.

The social sustainability factor is not less important, and the social appraisal of “purity” of a technology often affects the future of its implementation. The society should be understood widely, including the scientific community. Thus, we will set an example of soil remediation by using nanoparticles and GMO (Sarkar et al. 2019; Wang and Chen 2007). We assume that it is the bias and fears of the society today that build up one of the main barriers to a wide implementation of such technologies in the industry. At the same time, it is impossible to deny that both technologies undoubtedly have a number of risks, however, we believe that they are currently evaluated too “emotionally” for calculation of actual benefits and risks of their usage for specific cases. Thus, the controversial perception of a particular technology by the scientific community obviously shapes the assessment of its sustainability over its direct environmental benefit.

It follows from the foregoing that not every advanced and progressive remediation technology in itself can be considered to be sustainable. And, turning to the POP problematics, it should be noted that the conventional techniques often fail to provide technical possibilities for disposal of persistent contaminants, which has produced POPs concerns in the international community.

So, what can be the solution for sites which are too complicated for traditional remediation methods, and are not enough high-tech or overregulated for cutting-edge methods to be applied? We believe that the only right approach is currently the combination of two or more conventional remediation techniques aimed at obtaining a synergistic result. At the same time, we are talking precisely about operating the industry’s basic technologies, which, if summed up, produces high results in restoring natural sites and, at the same time, enables preserving efficiency in economic terms.

Thus, for instance, successful model experiments on the combination of chemical oxidation and bioremediation to clean the substrate from polycyclic aromatic hydrocarbons (PAHs) (Wang et al. 2004) or pesticide derivatives are described (Arnold et al. 1996). In both cases, the Fenton reagent, which is basic for in situ oxidation, operates as a chemical oxidizing agent.

It should be noted here that oxidation is a universal principle of decomposition of a pollutant, regardless of the method chosen: burning a pollutant means quick oxidation, whereas its decomposition by chemical or biological methods is a slow oxidation process, with a rare exception of highly specific enzymatic reactions targeted at a specific substance or class of compounds.

However, since soil contamination is heterogenous in the vast majority of cases thus disabling us from using highly specific methods, we tend to generalize the modern techniques of soil decontamination as oxidation reactions. At the same time, it is obvious that chemical oxidation, being used correctly, is a good basement to start a biological oxidation process. Meanwhile, there is a range of substantial factors restricting the usability of bioremediation, which limit the chemical techniques, basically due to the nature of possible reaction products (Chang and Kikuchi 2012).

1. Toxicity
2. Unacceptable acid-alkaline medium
3. Low bioavailability of reaction products

The substrate itself must also conform to a range of requirements mandatory for growth of microbial flora (Haller 2017). For example, a suitable soil texture is needed both to sufficiently provide aeration capabilities and to retain moisture well. Such texture is characteristic of natural or reclamated soil substrates, but some chemical processes can cause excessive aggregation of substrate particles or otherwise disrupt their structure, which then will adversely affect the bioavailability of the pollutant (Ifon et al. 2019).

Among other things, such methods as high temperature acid sludge extraction, for example, for elimination of heavy metals (Stylianou et al. 2007), are capable of effective sterilization and aggregation of substrate, so it will become technically of little utility for bioremediation, although it will not manifest apparent toxic properties. Therefore, given the subsequent use of biological methods of remediation, appropriate chemical oxidation methods should be selected correctly by taking into account the final result preferred. What is more, we should also consider the intermediary nature of any technology used.

We explain this statement as follows: basically all technologies of in situ soil remediation currently available employ the waste-to-waste (European Environment Agency 2014) approach, which means that:

1. They transform more hazardous waste into less hazardous waste.

2. They reduce the amount of the target pollutant to levels below the LOC (by so doing, they often increase the collateral pollution (Saier and Trevors 2010; Surriya et al. 2015)).
3. They concentrate the pollutant in small volumes to isolate it subsequently from the substrate and to dispose it by using other methods (Mosa et al. 2016).

In a range of cases, several approaches of the above-mentioned ones are implemented simultaneously, which shows that substantially each remediation measure constitutes only one of the stages of a long pollutant disposal process, which particularly concerns POPs.

We exemplify it with the following case: having been amended in 2019, the Environmental Management Act (Environmental Management Act Pub. L. No. B.C. Reg. 375/96 2019) of British Columbia (Canada) currently limits the DDT (dichloro-diphenyl-trichloroethane) concentration for industrial sites at the level of 1000 ppm, although it did not always use to be so: as long ago as in 2013, according to the Stage 8 Amendments to the Contaminated Sites Regulation (Stage 8 Amendments to the Contaminated Sites Regulation Environmental Management Act 2013), this indicator was specified at the level of 3500 ppm. It follows that, if we had been taking measures for remediation of the DDT-contaminated industrial site in British Columbia in 2013, treatment lower than 3500 would have been a satisfactory result. POP disposal procedures are typically very costly: the price for POPs storage on a disposal site alone reaches 500$ per ton of substrate (Collins 2009), and it is logical to assume that our purpose would have been an ultimately fast and cost-effective achievement of a level substantially different from the level of concern (LOC) within the analytical evaluation method selected, namely 3000 ppm approximately. Such pollution level would have been reliably evaluated as lower than the LOC by using any standard analytical method, and its achievement through chemical oxidation would have required less reagents, resources, and working hours than for complete DDT decomposition in substrate, provided that complete decomposition is possible for this specific case in general. Thus, a compromise was reached between all stakeholders of the remediation process: the customer, the contractor, and the regulator. Based on the above criteria, the stated solution can be deemed to be sustainable. However, as new standards were adopted, repeated remediation of this site becomes a matter of time.

The environmental legislation all over the world is becoming stricter, which is particularly obvious in the growing economies, such as China where several major reforms in the field of soil protection and degraded soil restoration have been implemented over the latest decades, which have considerably reframed the attitude of the regulators to a wide range of pollutants (Li et al. 2015; Zhilin et al. 2014). Meanwhile, quite a small range of soil remediation solutions may be deemed reliably sustainable in future, therefore, in conducting site treatment works, the possibility of repeated remediation necessary some time later should always be taken into account.

It means that the industry evolution by itself urges executives to opt for remediation methods which can be successfully harmonized between themselves and potentially with other techniques.

At the same time, if several different remediation techniques are sequentially used at a site, bioremediation should be mostly preferred in selecting the final method. This is predetermined by several reasons:

1. The biological processes enable creating self-healing systems in which destructive microorganisms continue to destroy the pollutant for a long time after the works are finished (Haller 2017).
2. The biological methods improve the substrate quality and normalize its main indicators, e.g. the acid-base balance and texture (Haller 2017), which will enable subsequent selection of any convenient approach to further site treatment.
3. Bioremediation is almost always associated with prolonged decrease in toxicity of wastes, their immobilization and/or accumulation in a compact volume (as in phytoremediation or where mushroom mycelium is used) (Mosa et al. 2016).

Now it should be noted that bioremediation itself does not necessarily restrict us to use only one type of microorganisms or plants since the purpose is to restore (or even create from the scratch) an entire ecosystem. What is more, we can be confident in asserting that such system will be created eventually and naturally regardless of our endeavors: even the sites of man-made disasters are gradually overgrown by the most diversified biological species without human intervention.

What process operators should do is only to be willing to control the formation of such ecosystem, or to decide upon its spontaneous development influenced by nature.

One more important implication arises from the above: the primary treatment method which is basically chemical remediation (as we envisage it here) should not necessarily have a high degree of conversion by itself. It has been empirically displayed that the cost performance rate for chemical or physical remediation methods has non-linear dependence, and the greater amount of pollutant needs to be treated, the faster the price will be growing: essentially, the price growth depending on the case volume for physical and chemical methods is close to the exponential one (see Fig. 2.1) (De Waele 2017). Additionally, the use of such reagents as, for instance, iron oxide and permanganate in large volumes necessary to achieve effective pollutant destruction will lead to mineralization of soils and to degradation of their microbiota (Liao et al. 2019). At the same time, as shown below, even with low actual results of conversion, chemical oxidation done before bioremediation provides the whole process with a powerful systemic boost effect which finally significantly exceeds the sum of conversions of the both methods used separately. This very principle of “the integer which is higher than the sum of its parts” makes it possible to mention the holistic approach to site restoration through the use of combined techniques.

Turning to Fig. 2.1, it should be noted that the holistic approach is empirically shown to be most effective in terms of the cost/performance ratio for large volumes of contaminated substrate. Below we will describe examples of particular technological solutions which are the ones making combined chemical and biological

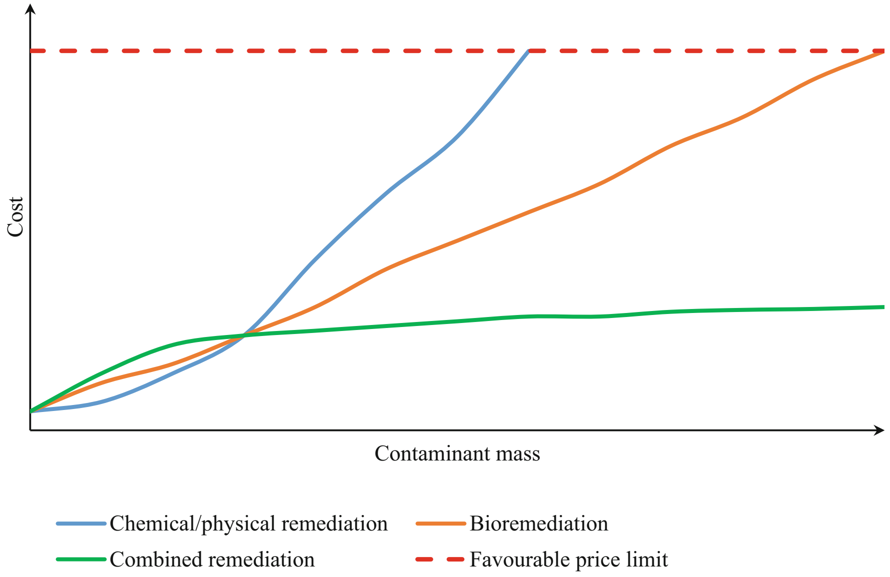

Fig. 2.1 Cost performance rate for chemical/physical, biological, and combined methods for soil remediation depending on case volume (contaminant mass). Easy to see, that in big projects combined techniques are preferable

methods progressive and increasingly demanded in the market of environmental technologies.

2.3 Chemical Remediation

So, let us consider the fundamentally possible ways of conducting chemical oxidation of contaminants in the soil in situ.

We should stipulate right now that here we primarily describe the very solutions which are successfully harmonized with bioremediation, being used before, after, and simultaneously with it. It should also be noted here that In Situ Chemical Oxidation (ISCO) in industry usually means the methods intended to destroy the pollutant in the bulk of substrate by deep injection of strong chemical oxidizers. Meanwhile, the specific features of in situ detoxification of the POPs-contaminated open grounds or wastewater sludges with similar oxidative reagents require absolutely different infrastructure solutions. Nevertheless, here we will also encompass some techniques of underground contaminant disposal, since their harmonization with biological methods is quite critical and demonstrative in a number of cases (Sutton et al. 2011). In this research, we also pay attention to the methods based on zero valent iron (ZVI) nanoparticles (Mu et al. 2017). These solutions are positioned separately, since they deoxidize the pollutant, in contrast to the overwhelming majority of the chemical remediation techniques, but in our opinion, they may be considered in the general canvas of redox reactions. Despite the aforementioned ZVI toxicity concerns, there are also successful solutions for combined remediation, ZVI + bioremediation manifesting a decrease in the total ecotoxicity of a contaminated site (Galdames et al. 2017).

At first, we will outline the fundamentally possible technical approaches to chemical contaminant destruction in substrate which are widespread in industry:

1. By using acids (Stylianou et al. 2007)
2. Based on decomposition reactions of liquid peroxide
3. Based on dry peroxide producing compounds (De la Calle et al. 2012)
4. Based on permanganate (Huling and Pivetz 2006)
5. Based on gaseous oxidizing agents (ozone) (Huling and Pivetz 2006)
6. ZVI

All these approaches can be implemented depending on the nature of pollution and on the site infrastructure by using various catalysts and equipment improving the efficiency of the remediation process.

Moreover, potentially the most and least bio-friendly technologies should be determined at once. Thus, acids and permanganate obviously destroy the substrates' chemical composition to the greatest extent, whereas hydrogen peroxide and ozone alone do not have any prolonged harmful effects. Dry peroxide-ion producers here are positioned in between, since, on the one hand, they decompose not only into water and oxygen as peroxide and ozone, but, on the other hand, the typical products of their reaction are sodium, calcium, magnesium and other salts which in small quantities may be acceptable in soils even for agricultural purposes.

Catalytic additives and auxiliary reagents can make a certain contribution to the suitability of the substrate for bioremediation. As mentioned above, one of the most common methods of chemical remediation is the Fenton reaction based on the interaction of hydrogen peroxide with iron ions (Fenton 1894). Obviously, the use of this reaction leads to supersaturation of substrate with iron salts (an excess amount is added consciously, due to the instability of Fe II ions), which can be critical in future, for example, for higher plants (Bartakova et al. 2001). It is curious that the need for iron for the Fenton reaction can be partially covered by iron-containing minerals that are basically contained in the soil of a particular site, which eliminates the need for saturation of the substrate with exogenous iron (Santos et al. 2018). However, such approach is not applicable for soils with originally low iron content. It predetermines the necessity to add it, for clear reasons, and subsequent removal of such exogenous iron becomes rather a complex task: it is possible to change the nature of a specific chemical iron compound, but the only possibility to remove it is to wash it away with great volumes of liquid. Iron compounds are not the only additive used to increase the efficiency of Fenton reaction in particular and of peroxide decomposition reactions as a whole. The popularity of such reactions in organic contaminant decomposition in substrate in situ remains consistently high (Baldissarelli et al. 2019), and it is the new approaches for catalysis and modification of oxidative reactions that make it possible to increasingly extend the scope of application of the solutions based on liquid peroxide. Thus, for instance, the Fenton reaction is shown as effective also for decomposition of POPs, such as DDT, as demonstrated in the research work by Cao et al. (2013). It should be noted that, to reach the best result in DDT decomposition, the authors resorted to adding EDTA, ZVI, and artificial aeration to the standard formula. EDTA and ZVI can significantly influence the substrate's condition after the first stage of remediation and on its suitability for biological treatment. Meanwhile, EDTA, due to its propensity to chelate ions, can disrupt the electrolyte balance of the substrate, and ZVI nanoparticles, as mentioned earlier, raise concerns about their potential toxicity.

However, such risks are inherent in the use of any nano-size agent (Gupta and Xie 2018), and, what is more, numerous research works show the toxicity of nanoparticles exactly for the soil microbiota. At first glance, it clearly discords with the aforementioned results of Galdames et al. (2017), but we believe that the contradiction is only imaginary: the fact is that the situation of POPs disposal always compels us to evaluate not only (and not so much) risks of a definite technological remediation solution, but primarily the benefits. Here we should note that namely the risk/benefit assessment for ZVI in soil remediation was performed in the report by Bardos et al. (2011), although we have a wider vision of the problem: apparently, knowing the specific toxicity risks of reagents in use, we should regard them not separately from the reality of a particular contaminated site, but only by taking into account the nature and level of POP contamination we are dealing with.

Obviously, the toxic effects of POPs in substrate can be so considerable that it may be expedient to use reagents whose residual toxicity will be much lower than the contaminants, where it is prone to decrease in the course of subsequent bioremediation.

In contrast, some catalysts and additives applicable for chemical remediation may turn out to be useful for subsequent biological processes. The proportion of anaerobic processes is inevitably significant in the total biological activity of microbiota at an open non-equipped site, and obviously the deeper the contamination is the greater is the proportion. Thus, in case of future anaerobic remediation, according to a number of studies (Hatzikioseyian 2010), the microbiota will use nitrogen and metal oxides as oxidizers, for instance, iron and manganese oxides (MnO_2). The latter should be emphasized, since, firstly, the Mn IV oxide is a powerful catalyst of peroxide decomposition, and, according to some research works (Dessie et al. 2020; Hooda et al. 2013; Morsi et al. 2020), manganese oxide in various forms, including the form of nanoparticles, can activate also the function of the oxidative enzymes of aerobic organisms. Thus, we can assume that the catalyst initially used to increase the efficiency of peroxide decomposition, e.g. in the composition of Fenton's modified reagent, can not only fail to damage subsequent biological processes, but it also can intensify them. Thus, in the course of the chemical phase of remediation, it is essential to use components which can be harmonized with the upcoming biological process, and which correspond to the specific nature of the substrate's mineral composition on a particular site. It also follows from the above that some catalysts or reagents can hardly be eliminated from soil upon completion of the contaminant decomposition process, and thus their use should be predetermined only by an unconditionally high ultimate environmental or economic benefit, e.g. comply with the sustainability criteria. This is the very nature of permanganate, a reagent popular in chemical remediation, which removal from the treated sites has become the subject matter of numerous bioremediation studies. Nevertheless, sustainable use of permanganate and persulfate oxidation of contaminants in the soil followed by successful bioremediation eliminating both contamination residues and secondary substrate contamination with excess reagents are currently being exemplified with positive cases (Mora et al. 2020).

Here we should also mention three other aspects of harmonization of chemical and biological remediation methods which primarily concern exactly the chemical oxidation techniques based on liquid peroxide or dry peroxide producing compounds. Chemical oxidation can be used for the following purposes:

1. Increasing the contaminant's availability for bioremediation
2. Intensification of biological processes influenced by oxidative stress
3. To control the pattern of bioremediation (primarily aerobic/anaerobic)

2.4 Increasing Contaminant Availability for Bioremediation

Turning to Fig. 2.1, we should explain the exact way the combined methods beat the mono-technique approaches. As the illustration displays, the biological methods of treatment are generally cheaper than the chemical ones, although they grow in value over time—basically due to the necessity for repeated adding of bacterial preparations and long-term maintenance of vast waste grounds equipped with special infrastructure. Meanwhile, each new portion of substrate requires increasingly vast areas for waste ground storage for treatment, as well as increasingly extensive infrastructure the scaling of which does not always raise the price linearly. A simple conclusion follows: bioremediation can be made critically cheaper if it is accelerated, with an ultimately short cycle of using a waste ground area unit for treatment of a substrate mass unit. What is the possible way to speed up the natural biological process going in not the most favorable conditions? Several fundamental approaches may be used here:

1. Increasing the amount of destructor organisms, "hungry mouths" eating the contaminant
2. Enhancing the quality of strains, selection, "training" of biodestructors for a more effective remediation process
3. Reducing toxicity and making the contaminant more available for such destructors

The first two approaches require additional trophic factors, such as fertilizers (or prebiotics), to be added to the substrate, as well as using reactor technologies or introduced strains. In such case, a reactor is necessary either for proliferation and selection of native microflora inoculated from soil or for proliferation of an effective introducing destructor from a stock culture (Kantachote 2001). Such measures can be fully justified, but it should be noted that the top efficiency limit for bioremediation should still be predetermined by the toxicity/availability of the target contaminant. And oxidation is one of the effective methods to make contaminants more available for destructor microorganisms (Seryy et al. 2020). At the same time, it causes a certain confusion in terminology: “bioavailability” typically means the contaminant’s availability both for organisms involved in remediation and for the ecosystem in general, i.e. the contaminant’s capability to ingress into food chains and to reach the top trophic levels in them. Although these concepts are obviously interrelated, the contaminant’s availability for decomposition is considered to be a positive criterion, and its availability for ecosystems in general and for humans, as described above, is always a subject of concern. That is why the potential of a specific remediation method for immobilizing a pollutant at a processing site is becoming very important with parallel increase in its “edibility” for microbiota and a decrease in the toxicity of end metabolites. For POPs, e.g. for DDT, it is indicated that long staying in soil under the influence of oxidation processes reduces the contaminant’s mobility in the ecosystem (bioavailability in its broad sense), but it makes it more “attractive” for the microbiota on the site (Mansouri et al. 2017; Morrison et al. 2000).

2.5 Intensification of Biological Processes Under the Influence of Oxidative Stress

The intensification of biological processes by means of oxidative stress is a complex process which is typically applicable for substrate microbiota and which predetermines both the selection of the most effective and adapted destructor organisms and activates strains already selected. Oxidative intensification is a universal process for various substrates, and it can be used both in soils and in water treatment, or in sludge activation on wastewater treatment facilities (Кузнецов et al. 2013; Листов et al. n.d.). It is curious that for multicellular organisms, such as fungal mycelium, it is indicated that oxidative stress boosts the activeness of enzymatic systems involved in the disposal of the target contaminant, as it was demonstrated on two strains of fungi by Russo et al. (2019) for DDT biodegradation in soil.

Thus, through the example of experimental remediation of a contaminated site (Fig. 2.2), we have shown that partial chemical oxidation of contaminants catalyzed by MnO_2, carried out before bioremediation, considerably intensifies biological processes. Moreover, it concerns both POPs and more trivial cases, e.g. oil pollutions (Babayev et al. 2019; Seryy et al. 2020). It is noteworthy that when DDT is destroyed in soil substrate, only 18% of contaminant was chemically destroyed, and biological remediation after oxidative treatment showed 98% of the total DDT destruction. Furthermore, the full site remediation cycle was 90 days, which is a high speed for the industry: the normal DDT biodegradation speed in soil can be equal to 6–30% for 42 days (Foght et al. 2010). At the same time, faster

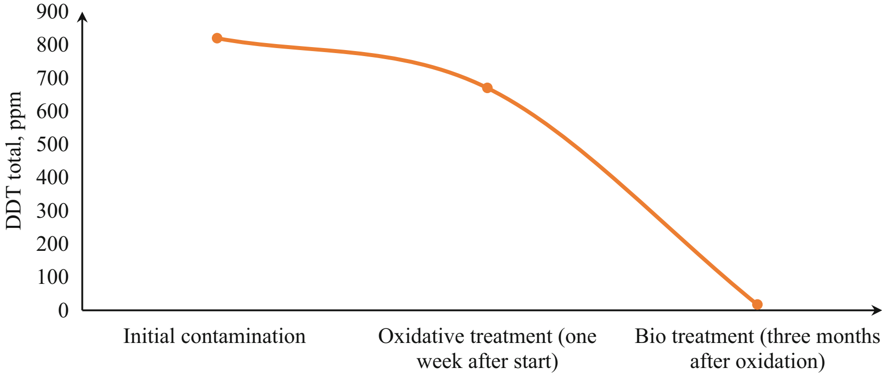

Fig. 2.2 DDT-polluted site decontamination through 90-day combined chemical-biological process, where the chemical oxidation created beneficial environment and effective booster for further bioremediation

methods of DDT bioremediation have been described (Purnomo et al. 2011); however, they require a developed infrastructure or are realized by more highly developed, multicellular organisms, which often leads to bioaccumulation.

In this context, different understanding of DDT destruction should be mentioned as a particular example of POPs in substrates. Due to a vast variety of remediation techniques, especially the biological methods, three possible outcomes of DDT-contaminated site remediation reported in the literature can be distinguished (Huang and Wang 2013; Purnomo et al. 2011):

1. Mineralization: complete decomposition of the contaminant's organic matter to CO_2
2. Degradation: decomposition of the contaminant to intermediate metabolites
3. Accumulation: concentration of a native or slightly modified contaminant in bacterial cells, plant tissues, or fruit bodies of fungi

As we can see, these are three possible outcomes almost completely repeating the waste-to-waste concept set out above herein, with the only difference that, in conditions of a real technical solution, these outcomes are not divided fundamentally, but they occur simultaneously virtually in any solution in different percentage shares.

Turning to the issue of oxidative intensification of biological remediation of POPs, we obviously allege that such intensification leads to a shift in the resulting remediation balance towards degradation and mineralization from simple accumulation of contaminant in live cells.

Among other things, as mentioned before, oxidative intensification consists in a slight oxidation that does not require infrastructure solutions on the site, is quick and cheap, but makes the combined process much more powerful, thus making it cheaper as well (Seryy et al. 2020). It is especially relevant for microbiota and plays a less considerable role for phytoremediation in particular.

One more important aspect of oxidative acceleration of bioremediation should also be noted: the efficiency of biological processes is often very strongly dependent on its seasonal climatic changes. In a desert, continental or other harsh climate, 90–180 days in a year can be effective, and in the rest of the time, contaminated soil just occupies the remediation site with negligible efficiency of treatment processes due to unsuitable temperature conditions and improper humidity. It means that if the required LOC is not reached within the favorable season, the waste ground rent may rise significantly, which will naturally affect the total price for the process. In such case, if oxidative intensification makes it possible to reduce the process duration and fit into the favorable season, it will obviously become the most sustainable solution.

2.6 Managing the Bioremediation Pattern

As mentioned before, bioremediation in substrate can flow in various patterns. With good natural aeration or with intensive cultivation or forced aeration, aerobic flora will prevail for natural reasons, and, at the same time, biological processes will take course in the soil depth with no access of sufficient oxygen. Apart from apparent narrowing of the range of potential destructor organisms to the level of unicellular microbiota, the metabolism intensity obviously decreases in the microbiota. To understand the degree of decrease in the intensity of metabolic processes, we can compare the amount of ATP (adenosine triphosphate) obtained upon oxidation of one glucose molecule in both cases: the anaerobic process produces two molecules, whereas 38 or 39 molecules are produced by the aerobic process.

However dramatic decrease in the speed of processes is not the only adverse effect of exclusively anaerobic bioremediation. Thus, for instance, a part of anaerobic bacteria are capable to produce methane. It could pose a serious problem for underground ISCO methods, the drilling-wells system starts producing large volumes of gas. Gas is very intensively produced if such additives as natural gums or polysaccharides serving as excellent substrate nutrients for bacteria which are so widespread in drilling are used in pumping reagents into the layer. Instead of decomposition of the target contaminant, a part of microbiota will inevitably proceed to the consumption of a more bioavailable and “healthy” substrate. On the one hand, such fertilization is good because it finally increases the total amount of potential destructors, which should additionally accelerate remediation in the outcome. On the other hand, disadvantages of side effects are apparent.

To surmount such problems in industry, oxidants intended for pumping into layers have become widespread, and, what is noteworthy, they are targeted at partial reorientation of decomposition processes towards the aerobic path rather than at contaminant oxidation (e.g. the hydrogen peroxide aqueous solution).

Therefore, biocenosis is created in the layer, thus creating a highly productive microbiological consortium which not only accelerates contaminant degradation processes, but is also free of adverse side effects. For the ISCO processes usually lasting for several months to a year of active operation of costly infrastructure, such acceleration is very substantial, as well as reduced risks of gas generation.

2.7 Bioremediation Approaches

There are a lot of bioremediation methods, and they are obviously much more long-standing than their mindful utilization. In part, any soil cultivation, moreover the use of such techniques as green manure, is already bioremediation.

However, current understanding of the process in industry is based upon the sustainability principles and, in part, upon the use of the newest biotechnologies. Here it is relevant to classify the approaches to the bioremediation of the POPs which have become widespread in industry, namely (Kantachote 2001):

In situ approach which is confined to:

- manipulations with the adding liquid trophic factors with concurrent humidity control on the site (bioaugmentation and biostimulation)
- bioventing

Ex situ approach including the following:

- reactor technologies
- partially landfarming and biopiling
- biologically enhanced soil washing
- composting

However, this division is conditional, and for instance, landfarming technologies can be applied in situ, whereas bioventing is used in infrastructure solutions for biopiling.

In this work, we also want to express our opinion about the role the “high” biotechnologies play in the field of remediation of POP-contaminated soils. To achieve high performance of the process in biotechnology, it is specific nature of the action that is essential. Thus, many contemporary achievements, e.g. in medicine, are built upon the possibility of specific interaction between the drug molecule with the definite pathogen.

Precise and specific interactions lead to reaching high efficiency of treatment with a small amount of side effects.

But what should be done if it is difficult to determine the particular target for treatment or remediation in our case? Relatively rarely are soils contaminated with one particular high purity pollutant. Pollution, especially long-standing, typically involves different molecular types of the contaminant at different decomposition stages. When it comes to soils contaminated with prohibited POPs from the list specified in the Stockholm Convention, more often such contaminations are long-standing and already partially transformed as a result of biological activity, under the influence of ultraviolet radiation, etc. It follows that when dealing with a mixture of various forms of the contaminant associated with soil organics and partially assimilated microbiota, very rarely we can use quite specific methods, such as the GMO-enzymatic methods described above (Wang and Chen 2007), therefore, we should be guided by the conventional approaches

Such approaches are more confined to monitoring the ecosystem developing on a particular contaminated site of such type, and to its enrichment with new components, enhancement through adding trophic factors or chemicals boosting its effectiveness. Methods based on breeding followed by inoculation of native destructive microbiota in reactors (where it proliferates in the presence of low concentration of the target contaminant in favorable conditions) are also widely used. After a sufficient mass of destructors is accumulated, they are reinoculated back to the site, thus increasing the productivity of bioremediation, as described above (Kantachote 2001). It is essential to note that such approach does not imply specific discharge of any single strain: a holistic microbiological consortium is selected from the soil, and then it is cultivated and/or selected depending on the best ability to destroy the target contaminant. It is also important that empirically such approach often demonstrates a greater effectiveness than introducing destructors from another region or climatic zone (even proven to be efficient). It is quite logical: native or autochthonous destructors that are already adapted to the conditions of a particular site are able to show greater tolerance to POPs than introduced organisms (Russo et al. 2019) which have to adapt to such conditions under the influence of stress caused by an increased content of the contaminant in the substrate.

At the same time, numerous works are currently underway to determine the diversity, to classify, and to transcript the genomes of destructive microbiota, which are of great academic interest and are gradually being implemented in industry with proven effectiveness.

For example, in the research work of Pan et al. (2016), the strain of *Stenotrophomonas* sp. extracted from the soil is selected as a monoculture in the presence of DDT, and at the same time, it is characterized both in terms of detailed genome study and by means of chromatography and mass spectrometry, with a view to determine the destructive capabilities of this strain and to potentially distribute DDT metabolites in the soil after its inoculation.

Increasingly numerous works convincingly prove the necessity for complex bioremediation involving microbiological cenosis or even for more complex systems: for example, it was shown (Tarla et al. 2020) that the diversified microbiota most actively degrades DDT and other persistent pesticides exactly in the rhizosphere of plant roots due to the interaction between bacterial and plant enzymes.

Therefore, we face the necessity to evaluate the ecosystem on the remediation site quite traditionally, based on the very basic features which we regard through their practical meaning: aerobic/anaerobic, resistant to a wide range of pH and salinity/unstable, etc.

Thus, we believe that creating a harmonious and stable multilevel ecosystem which would be ultimately close to the native one for this site, i.e. most adapted to the environmental conditions, is an important fundamental for arranging bioremediation processes.

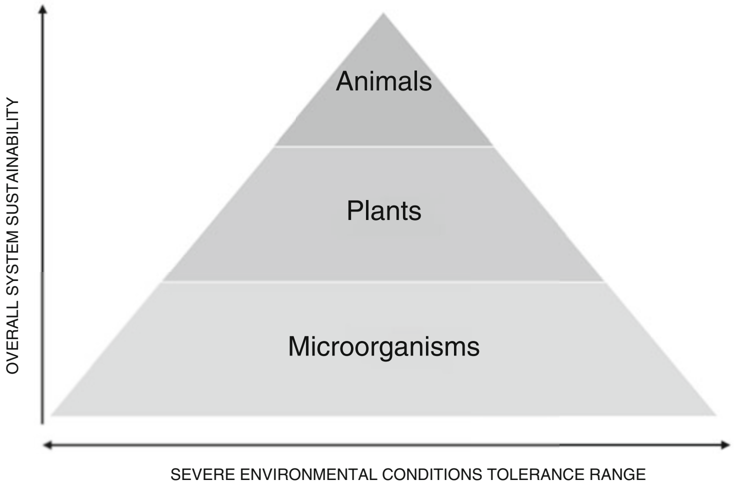

Fig. 2.3 The diagram shows that the ecosystem made from different species demonstrates high resulting sustainability, even if the species applied by themselves are sensitive to the severe environment. The microorganisms that possess the biggest tolerance range for bearing severe conditions make the basis for more sensitive plants (or sometimes fungi) and animals, thus restoring or creating ad hoc the healthy ecosystem. For a good reason they create the most sustainable form—pyramid

At the same time, if we deal with a remediation site, for instance, in a desert with meagre soils and climatic conditions disabling any development of complex highly productive ecosystems while we need an intensive process, we can be guided by one most crucial factor of the environment. For instance, if the substrate's nature is a critical factor for the system which we intend to create, we may try to construct an ecosystem based on the example of other sites with sandy soils, but more humid ones, since we are going to carry out intensive artificial moisturizing. Thus, for instance, the study conducted by (Benyahia and Embaby 2016) displays a classical approach to bioremediation of meagre desert substrate by adding necessary biomass (bioaugmentation) and trophic factors (biostimulation) to create suitable conditions for the life of a prepared microbiological consortium which the authors found the most appropriate one for solving their problem, given that it was suitable for the site's critical conditions.

Each new level of the ecosystem itself is less stable and more fastidious than the previous one, but being correctly realized, it significantly increases the stability of the system as a whole (Fig. 2.3). Thus, it follows that each element introduced into the ecosystem should improve the conditions for the subsequent ones, by narrowing the possible variety of conditions to the optimal pattern in which the most highly organized life forms can potentially exist.

Let us examine the following example: various types of higher plants are used for phytoremediation of contaminated soils. Most commonly, unfastidious species which should accumulate contaminants in their tissues for subsequent disposal are selected as technical site purification cultures. And still, higher plants rather badly tolerate high soil salinity, being vulnerable to toxic effects, such as from heavy metals. At the same time, less organized life forms, such as microscopic fungi are more tolerant to high levels of salinity and contamination with metal ions, but they are much less effective in remediation of such contaminants.

Li et al. (2019) took advantage of such specific features in their work, by utilizing the aboriginal fungus *Trichoderma asperellum* for bioaugmentation of the phytoremediation in the saline substrate contaminated with lead ions. The fungus prepared the soil and considerably improved the growth conditions for *Suaeda salsa* badly affected simultaneously by salinity stress and by lead phytotoxicity in the absence of suitable microflora. Influenced by the mycelium of the fungus that formed mycorrhiza with plant roots, the latter began to grow better, experienced less toxic stress, their green mass grew faster, and most importantly, they started a better accumulation of the target lead contaminant.

Our next example is more complex, with combined soil contamination with cadmium and DDT, studied by (Zhu et al. 2012). In this research the authors opted for the original strategy of simultaneous cadmium phytoaccumulation by the *Sedum alfredii* plant and DDT destruction by the bacterial strain *Pseudomonas* sp., where the latter was specially extracted from a DDT-contaminated site in the same region where the experiment was conducted. Such combination had a cumulative effect: cadmium was accumulated faster, since the use of the inoculated strain beneficially influenced the development of plants by increasing their biomass, whereas DDT destruction was accelerated, since the destructor bacteria found a favorable medium for the growth on plant roots, which was separately denominated by the authors as “DDT rhizodegradation” in their work.

Thus, the bioremediation system which is more complicated to create finally manifests much higher efficiency and self-recovery resource, which means a higher sustainability, provided that the process is adequately cost-effective. At the same time, the logic of the process apparently implies using a less effective biological form with low remediation rates in the base for the activity of a more organized and more effective form.

Among other things, the aforementioned complex approach obviously enables increasing the amount of the organic component in soil, which is very important for subsequent return of purified soil into soil turnover—and we believe that it is the very ultimate objective of remediation. It is currently evident that the organic content in soil is a significant evaluation criterion largely predetermining the success of remediation procedures (Haller 2017).

Figure 2.3 also shows which destructors can be used for remediation: unicellular aerobes and anaerobes, multicellular plants and fungi, as well as some animals, where the most common example is earthworms which are equally used for remediation and for testing of its results (Fründ et al. 2011). The fact of using earthworms as a biological indicator does confirm the statement on correlation between narrowing of the range of acceptable site conditions, the growth of the organization degree of biodestructor organisms, and an increase in system sustainability. Therefore, the purest soil will be suitable for the growth of earthworms, whereas they accomplish the destruction of the contaminant's metabolites with high efficiency after fungal and bacterial/plant flora.

This approach is excellently demonstrated in the study conducted by Cheng-Kim et al. (2016) who succeeded in using bioaugmentation, fungal mycelium, and the *Lumbricus rubellus* earthworm to remediate a site contaminated with heavy metals: this complex system made it possible to enhance the bioavailability of heavy metal compounds for worms which, while building up the biomass, were bounding the heavy metals in their tissues, thus removing them from the substrate, and, in parallel, reducing the bioavailability of the heavy metal residues in the soil for the ecosystem as a whole. Our specific experience in DDT disposal (Fig. 2.2) evidently included only one organization level of bioremediation, which is developing a stable cenosis of aerobic and anaerobic microorganisms, still remaining quite difficult to implement. And such microbiological consortium, if used properly, enables achieving sufficiently high process efficiency.

Nevertheless, the above examples make us confident that it is construction of multilevel systems that is the most promising way.

2.8 Analytics

It should be noted in conclusion that whatever remediation strategy is chosen, it is analytics that finally evaluates its success, whether it be intermediate analytics performed by a contractor as part of internal project audit or a final assessment carried out by a regulator. Based on the industry's experience, we can assert that, irrespective of the degree of excellence of site remediation, improper selection of an analytical methodology can lead to dramatic underestimation of project success both by the contractor and by the regulator.

This seemingly evident statement encounters a lot of obstacles in practice for coordination of analytics between process stakeholders both at the level of methodology selection and within one technique. We explain it through the example of DDT: to analyze the DDT content in soil and water medium, the techniques based upon EPA recommendations are commonly applied. At the same time, there are currently several such methods: US EPA 8081 (GC ECD), US EPA 1699 (HRGC/HRMS), US EPA 525.3 (GC MS), etc. (Method 1699: pesticides in water, soil, sediment, biosolids, and tissue by HRGC/HRMS n.d.; Munch et al. 2012). Apart from the EPA technologies which are considered to be the "golden standard" in industry, there are also the ISO methods and local interpretations of EPA and ISO, which are arbitrarily applied by laboratories of customers and regulators. And such variety of methods is used to determine only one type of POPs!

We must not forget that the most accurate and up-to-date analytical techniques capable of detecting very low contaminant amounts with a high accuracy in a homogeneous carrier (matrix), for example, in pure water or in sand, appear not to be adapted for analyzing "dirt" in which several contaminants are mixed, their metabolites and decomposition products in a matrix rich in organic matter (almost any fertile soil or silt). In such case, the method requires rather a complex adaptation, and, having achieved accuracy in realizing one method, an analytical laboratory will specialize exactly in such method. Apparently, to attain convergence in findings, all process stakeholders should agree upon using only one analytical method in a project, otherwise, as it often happens, the contractor, customer, and regulator will obtain contradictory and incomparable results, which will immediately case a doubt on the quality of works performed. It particularly concerns express evaluation of findings on a site, which is sometimes carried out by means of IR detectors, for instance. Being accurate and sensitive to one type of molecules (pure target contaminant), such devices turn out to be blind to the target contaminant once it is oxidized or otherwise changed. Thus, an insufficiently intensive procedure can show enormous effectiveness on an express test, which will not be confirmed by a laboratory afterwards.

At the same time, there is one unobvious and purely empirical consequence: subcontractors may question third-party analytics, even though it is provided at a very high technical level, but by an "unverified" laboratory. But, what is strange, findings obtained through bioindication have a large, purely emotional weight, and for several reasons:

1. A green lawn with animal species (e.g. earthworms and insects) on the site of a former "lunar landscape" always looks convincing.
2. By and large, any remediation is intended to critically decrease the threat of a contaminated site for the ecosystem in which it is contained, and for the human as for a part of such ecosystem. Therefore, it is the well-being and health of the inhabitants of such ecosystem that is the final criterion for the success of the whole process.

This is the very reason why bioindication is universally recognized as the "final" test for almost any soil and water system purification project. Bioindication methods are typically simple and do not require any complex equipment, but their effectiveness and convincing nature have been attracting both private contractors and global regulators to them for many years.

2.9 Conclusion

The application of the combined chemical-biological methodologies in soil remediation described above becoming more and more widespread all over the world and out of doubts has big future in the industry. Especially this is relevant to POPs contamination that offers big difficulties and strong challenges to the world. Today it becomes obvious that scales of POPs emergencies in the world are so high, that it is no chance to turn a blind eye to the problem: it directly refers to the UN SDGs troubling, such as "zero hunger" or "no poverty" by undermining agriculture and overall life safety. This means that the industry has a lot of work ahead, and this work would not always be provided on well-equipped small sites with modern infrastructure and advanced technologies. We rather will deal with big and unfitted spaces, where the only weapon against the POPs would be well planned combined application of the basic and approachable technologies. The art of such combination and balance between the conventional chemical and biological technologies to gain the truly sustainable results is what we consider the very demanded skill in upcoming period.

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Biosurfactants: A Green and Sustainable Remediation Alternative

3

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Abstract

The wide range of human interventions on the environment has made easier the lifestyle of people worldwide; on the other hand, these interventions have serious environmental drawbacks, since petroleum derivatives, solvents, heavy metals, among others, that are potentially toxic, are used. Thus, there is an increasing concern for the development of green and sustainable alternatives to reduce the contaminant effects, including soil contamination which is well-known as bioremediation. Biosurfactants are amphipathic molecules that are synthesized by living cells, in particular microorganisms. Also, biosurfactants can be organized into five clusters, in which lipopeptides and glycolipids are the most well-known groups of biosurfactants. In this sense, biosurfactants can be applied as a bioremediation agent. Therefore, this chapter aims to put light on the chemical structures of biosurfactants and also some biological properties. Then, it focuses mainly on the application of biosurfactants for soil remediation, that is, bioremediation, which is one of the most promising alternatives for environmental safety and green technology. In conclusion, the group and also the subgroups of biosurfactants should be related to their applications (bioremediation), in which the current literature is scarce, however, some trends can already be spotted, such as iturin shows great potential as a remediation agent for both soil and water remediation (oil); lichenysin can be used for chelating divalent cations; rhamnolipid can be used to Cu and Ni remediation and also drill cuttings and oil-contaminated soil; There are few studies on MELs for remediation, and the

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majority of them is for oil contamination or contaminants derived from the oil industry, such as aromatic hydrocarbons, alkanes, and kerosene.

Keywords

Biosurfactants · Bioremediation · Organic contaminants heavy metals

3.1 Introduction

Technological advances have assisted mankind in the life quality, laboratory research, exploration of natural resources, among others. Thus, activities such as the arrival of pharmaceutical products, agricultural chemicals, crude oil exploration, excavation of fossil fuels, and related product usage have eased the lifestyle of people worldwide (Jimoh and Lin 2019). However, these interventions have some drawbacks, since chemicals, solvents, heavy metals, etc., that are used are potentially toxic to the environment, including human health. In this sense, there is an increasing concern for the development of green and sustainable alternatives to reduce the contaminant effects, including soil contamination which is known as bioremediation.

Ideally, the technology used for the recovery of soil properties should be produced at an industrial scale and also be environmentally friendly. A green and sustainable remediation alternative is related to surface-active molecules that are synthesized by living cells, well-known as biosurfactant since biosurfactant are compounds produced by particular microorganisms with amphiphilic behavior (Parthipan et al. 2017), good ecological compatibility, low toxicity, and biodegradability (Singh et al. 2019). Biosurfactants can complex heavy metals, lower the surface tension of hydrophobic compounds (higher surface area; higher microbial degradation rate), among others.

This chapter aims to put a light on the chemical structures of biosurfactants and also some biological properties. Then, it focuses mainly on the application of biosurfactants for soil remediation, that is, bioremediation, which is one of the most promising alternatives for environmental safety and green technology.

3.2 Biosurfactants; Chemical Structure and Properties

Amphipathic molecules that are synthesized by living cells are known as biosurfactants. Biosurfactants are biosynthesized fundamentally by microorganisms, in which they are mainly separated into five groups, according to their chemical structure: (1) fatty acids, neutral lipids, and phospholipids, (2) glycolipids, (3) lipopeptides and lipoproteins, (4) particulate, and (5) polymeric surfactant. Lipopeptides and glycolipids are the most important (industrially) biosurfactants—briefly described below. In addition, there is a variety of applications of biosurfactants such as bioremediation, skincare products, and substitutes to pesticides, biostimulants, microbial enhanced oil recovery, among others.

3.2.1 Lipopeptides

The chemical structure of lipopeptides consists of fatty acid(s) that are chemically bonded to peptide moiety. The main subgroups are surfactin, iturin, bacillomycin, and mycosubtilin. It is worth noting that the peptide moiety contains (often) D-amino acids, which are the most unusual amino acid form in nature—and thus probably related to their biological properties.

3.2.1.1 Surfactin

Surfactin is composed of seven amino acids—lactone ring connected to one β-OH fatty acid chain. The amino acid sequence changes according to the surfactin producer, culture medium, bioprocess conditions, etc. However, the most usual amino acid sequence is Glu (1st); Leu (2nd); Leu (3rd); Val (4th); Asp (5th); Leu (6th), Val or Leu (7th—mostly) (Fig. 3.1).

3.2.2 Glycolipids

Similar to lipopeptides, glycolipids also have fatty acid(s) in their chemical structure (hydrophobic moiety) but fatty acid(s) is bounded to one or more monosaccharide moieties instead of peptide moiety. It is noteworthy that, when compared to the

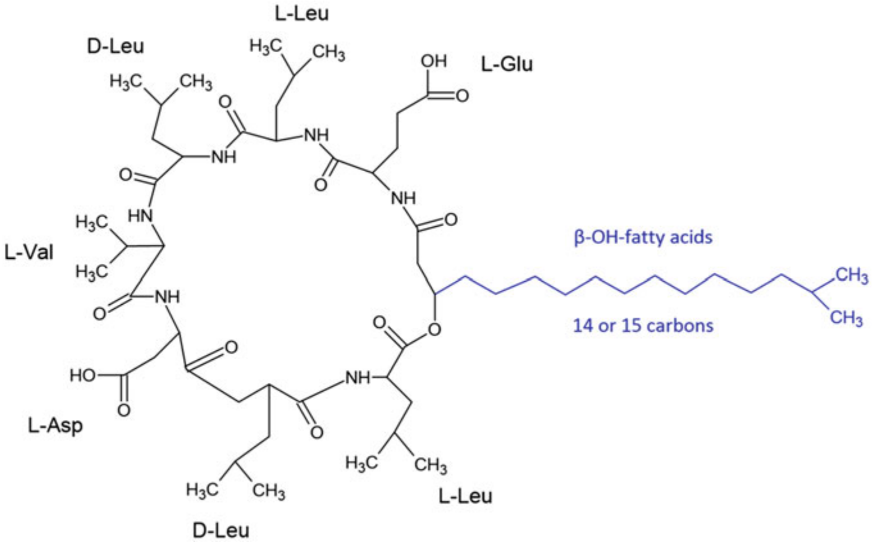

Fig. 3.1 The structural formula of surfactin

yields of lipopeptide production (≈mg/L), glycolipids show much higher yields of production (g/L). This difference occurs, very likely, due to their simpler chemical structure, a smaller number of metabolic pathways involved, among others. The most well-known subgroups of glycolipids are rhamnolipids, sophorolipids, and recently mannosylerythritol lipids (MEL)—briefly described below:

3.2.2.1 Rhamnolipids

Rhamnolipids (Fig. 3.2) are glycolipids obtained from reactions performed using bacterial species, in particular *Pseudomonas aeruginosa*. The chemical structure of rhamnolipids includes 4 congeners (Radzuan et al. 2018):

- *α*-*L*-rhamnopyranosyl-*α*-*L*-rhamnopyranosyl-*β*-hydroxydecanoyl-*β*-hydroxydecanoate (Rha-Rha-C_{10}-C_{10}),
- *α*-*L*-rhamnopyranosyl-*α*-*L*-rhamnopyranosyl-*β*-hydroxydecanoate (Rha-Rha-C_{10}), and
- mono-rhamnolipid congeners Rha-C_{10}-$C_{10}$and Rha-C_{10}.

3.2.2.2 Sophorolipids

Sophorolipids are composed of disaccharide sophorose—as hydrophilic moiety—bonded to long-chain hydroxylated fatty acid—as hydrophobic moiety (Fig. 3.3).

3.2.3 Mannosylerythritol Lipids

Mannosylerythritol lipids (MEL) are amphiphilic glycolipids that present high surface activity and low toxicity, functional properties, and production yields (Fukuoka et al. 2012; Fai et al. 2015; Simiqueli et al. 2017; Beck et al. 2019). MEL consists of a mix of a partially acylated derivative of 4-*O*-*β*-D-mannopyranosyl-D-erythritol as shown in Fig. 3.4. In general, MEL can be classified as MEL-A, -B, -C, and -D depending on the mannose acetylation in the positions

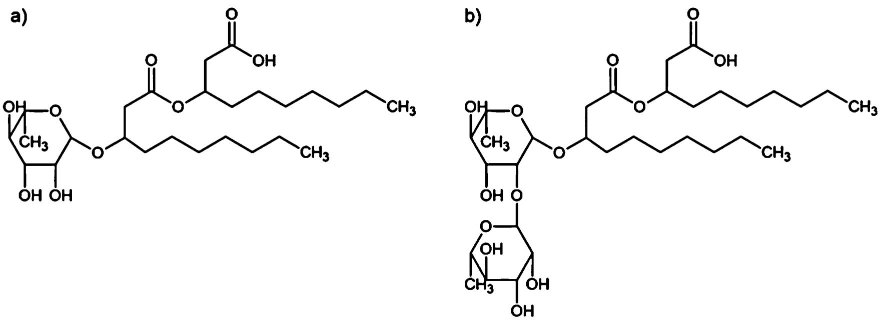

Fig. 3.2 Chemical structure of rhamnolipid: (**a**) mono-rhamnolipid and (**b**) di-rhamnolipid

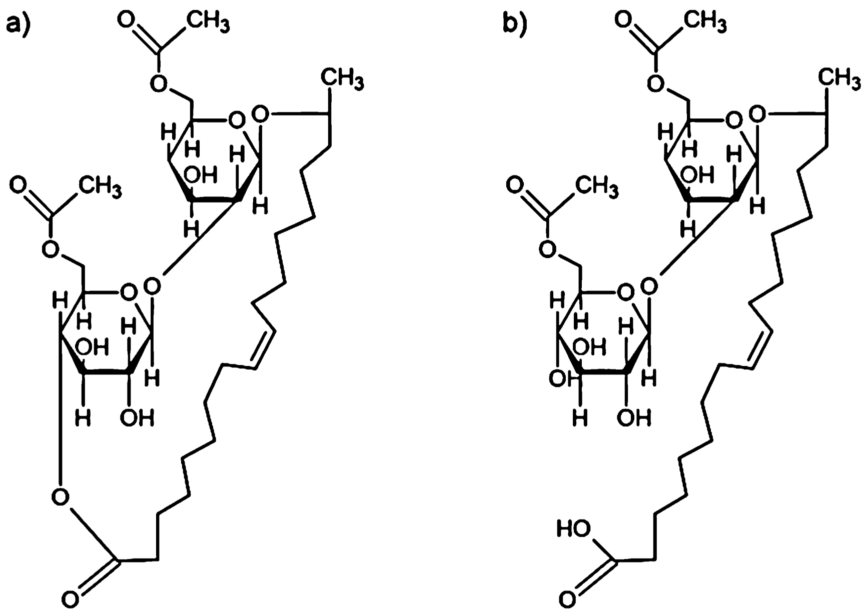

Fig. 3.3 Chemical structure of (**a**) lactonic sophorolipid and (**b**) acidic sophorolipid

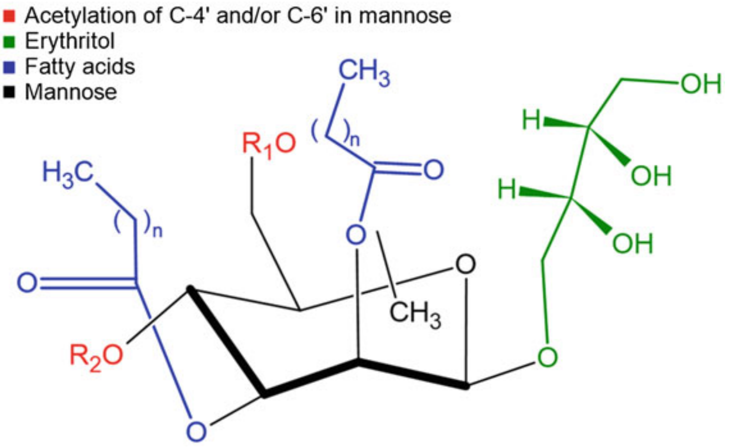

Fig. 3.4 Chemical structure of MEL, with n ranges from 8 to 14 carbons

C-4′ and C-6′. MEL-A has acetyl groups in both R_1 and R_2 (see Fig. 3.4), MEL-B presents an acetyl group at R_1 and hydrogen at R_2, MEL-C has hydrogen at R_1 and an acetyl group at R_2, and MEL-D has hydrogen at both R_1 and R_2 (Simiqueli et al. 2017).

Microorganisms have the ability to produce MELs, such as some of *Ustilago* genus (Boothroyd et al. 1956; Spoeckner et al. 1999; Morita et al. 2008; Morita et al.

2009), *Kurtzmanomyces* sp. (Kakugawa et al. 2002), and yeast strains belonging to the genus *Pseudozyma* (Fukuoka et al. 2012; Yu et al. 2015; Simiqueli et al. 2017; Konishi et al. 2008). *Pseudozyma tsukubaensis* has been outstanding due to its ability to exclusively produce MEL-B, while other species generally produce a concoction of distinct MEL homologs (Arutchelvi et al. 2008; Fukuoka et al. 2008; Simiqueli et al. 2017).

3.3 Biosurfactants for Remediation

Currently and near-future the energy resources are, heavily, related to fossil fuels. In this sense, petroleum hydrocarbons and their derivatives can harm the environment, since they have low water solubility and high interfacial tension, thus petroleum hydrocarbons and their derivatives are not easily removed from the environment. Therefore, sustainable alternatives for remediation of these contaminants have been developed, in which biosurfactant is one of the most promising technologies, mainly due to low toxicity and high biodegradability. However, biosurfactants are not commercially competitive to synthetic surfactants, yet. The two main groups of biosurfactants (lipopeptides and glycolipids) that have been applied for bioremediation are described below.

3.3.1 Lipopeptides

Lipopeptides are the greatest preferred and efficient biosurfactants. Synthesized by the strain belonging to the *Bacillus* genera, especially by *B. subtilis* that is normally found in the soil, these surfactants facilitate the emulsification process of hydrophobic molecules in water-based solutions by micelles formation, which can favor the access of microorganisms to these molecules, increasing biodegradation (Mnif et al. 2012; Rufino et al. 2013).

Surfactin is a lipopeptide with potent interfacial and self-assembly characteristics. The peptide portion of surfactin assumes a “horse saddle” configuration which affords stability to the molecule and provides its application as antiviral, antimicrobial, hemolytic being the widest surfactant used in therapeutic purposes (Peypoux et al. 1999; Hoefler et al. 2012; Liu et al. 2015).

Surfactin has been evaluated for bioremediation because of its exceptional surface activity, by the reduction of surface tension of water (20 °C) from 72 to 27 mN/m, considering concentrations below 20 μM, (Walia and Cameotra 2015). In a tertiary oil recovery process, known as microbial enhanced oil recovery (MEOR), the induced production of this lipopeptide can diminish the interfacial tension and promote the required pressure to liberate the oil that is contained in the pores of the rocks (Banat 1995; Sen 2008). This technique can be useful by in situ or ex situ conditions. The in situ process is grounded on the use of isolated microorganisms capable to grow under critical conditions (extreme salinity, oxygen, pH, and temperature), but do not make possible complete control of bioproducts production and cell growth. The opposite is observed by the ex-situ condition process, where the peptide can be directly applied for oil recovery enhancement besides providing a feasible production of biosurfactants in the external area of an oil well (Al-Wahabi et al. 2014; Lazar et al. 2007).

Kotoky and Pandey (2019), applied surfactin for the bioremediation of benzo (a)pyrene (BaP), a polycyclic aromatic hydrocarbon with high-molecular-weight and high persistence in the environment, that representing a biohazard. *Paenibacillus* sp. S1I8 (KX602663) and *Bacillus flexus* S1I26 (NCBI accession nº KX692271) were used isolate to produce surfactin which presented an excellent emulsification index that solubilized BaP efficiently. Solubilization levels of BaP were found up to 24.41 and 23.25% from *B. flexus* and *Paenibacillus* sp. S1I8, respectively. The potential to solubilize BaP of the extracted produced surfactin showed great performance and possibly could be used in the recovery of oil, also as an important object in the bioavailability of hydrocarbon.

Surfactin obtained from *Bacillus subtilis* was also practically applied for the remediation of heavy metals contaminated soil and also sediments. After 1st and 15th washings of soil samples with 0.1% surfactin along with 1% NaOH, the results were 6% and 25% of the Zn; 25% and 70% of the Cu; and 5% and 15% of the Cd; respectively (Mulligan et al. 1999). Another applicability of this lipopeptide was investigated by Maity et al. (2018), with an association to hydroxyapatite nanoparticle adsorption aiming the withdrawal of fluoride from water. Uniform particles of bacterial-surfactin mediated nano-hydroxyapatite (HAp) were synthesized by the hydrothermal method without any impurities and uniform morphology. The adsorption process is processed in two-steps, which first occurs as fast adsorption during the first 1.5 h and after that, the equilibrium was slowly reached. The higher adsorption level of 7.004 mg/g was achieved at pH 3, which affirms HAp nanoparticle mediated by bacterial-surfactin as a remarkable option for environmental pollution control by removing fluoride from water.

Nevertheless, the high production and purification costs of surfactin restrict the wide range of utilizations. In this sense, fermentation modes have been extensively studied (Chen et al. 2015). Genetic modification to obtain recombinant and indigenous strains is an alternative to produce large amounts of surfactin through various cheap nutrients (Mulligan et al. 1989; Carrera et al. 1992; Ohno et al. 1995; Qingmei et al. 2006; Gong et al. 2017). Other approaches include the substitution of regular culture medium by agro-industrial residues, which contain a high content of fermentable sugar with important macro and micronutrients essentials to microorganism growth and bioproducts production (Andrade et al. 2016). Nitschke and Pastore (2004), reported the surfactin production using a residue from cassava flour as an alternative culture medium at 150 mL working volume by *B. subtilis* LB5a. Gudiña et al. (2015) evaluated the corn liquor as a culture medium for *Bacillus subtilis* #573 achieving approximately 1.3 g/L of surfactin production. Zhu et al. (2013) have obtained values above than 1.56 g of surfactin in which gram of dry substrate of bean cake, cornmeal, rapeseed meal, rice straw, soybean flour, and wheat bran through *B. amyloliquefaciens* XZ-173 culture.

Optimized conditions of bioremediation using biosurfactants are also a usual subject, for instance, Liu et al. (2014) studied the influence of distinct medium for the fermentation by *Bacillus subtilis* BS-37 in the oil recovery and its removal from oil sand. At 0.3 g/L, both, glucose medium and Luria–Bertani (LB) medium obtained surfactin provided 96% removal rate of crude oil from oil sand. Considering 0.03 g/L surfactin obtained from LB medium presented a better efficiency at oil washing and displacement at a low concentration which combined with its lower surface tension indicates its possible utilization at enhanced oil recovery, and could enhance the oil recovery (MEOR).

A first evaluation of the pH impact in surfactin emulsification or surface activities was analyzed by Long et al. (2017) focusing on its application in MEOR, and the demulsification of previous stabilized surfactin through down-regulation of pH and its reuse for enhanced oil recovery. The emulsifying activity was better performed by pH beyond 7.4 presenting a rapid decrease at levels below 3.0 which have a direct influence on the dissolution–precipitation of surfactin promoting easily control by pH adjustments of oil emulsification and separation.

Andrade et al. (2016) studied the mannosylerithritol lipids-B (MEL-B) surface activity and surfactin at critical conditions to be applied in MEOR. The main parameter on the surface activity of surfactin was the ionic strength, besides that, it was also found a significant influence of pH.

Bayoumi et al. (2011) isolated 25 bacterial cultures from 20 samples of contaminated soil with crude oil. The 10 bacterial isolates were analyzed in concern of capability to surface-active compounds (SACs) biosynthesis by oil spread and blood agar lysis techniques in a liquid culture media which carbon and energy source was crude oil. Through the measure of surface tension, the most potent bacterial isolate (*Bacillus subtilis-KG82-KSA*) was chosen and showed the highest reduction of surface tension. The SAC was identified based on ultraviolet, infrared, and high-performance liquid chromatography (HPLC) analysis techniques as iturin, which has a great capability to be utilized as an agent for the remediation of soil and water that were contaminated with oil. Its optimized synthesis process conditions were also determined.

Statistical optimization of iturin A production was proposed by Kumar et al. (2017) by analyzing 100 bacterial isolates from the soil. The *Bacillus amyloliquefaciens* RHNK22 strain owns the best emulsification index and assay. The biosurfactant produced was identified by HPLC and FTIR. Then, alternative culture media were tested as medium culture using response surface methodology, which results highlighted that sunflower oil cake presented threefold higher production of biosurfactant.

Bezza and Chirwa (2017) studied the polycyclic aromatic hydrocarbons (PAHs) bioremediation on a heavily contaminated soil sample from an aged wood treatment plant by biosurfactant produced by *Bacillus cereus* SPL-4. The main concerns about PAHs are related to their teratogenic, mutagenic, and carcinogenic properties, high hydrophobicity, low water solubility, and hard sorption to the soil. At laboratory scale, Bezza and Chirwa (2017) performed a batch with 6.7455 g/kg—a total of 13 PAHs, in which 55% and 79% of 5- and 6-ring PAHs were eliminated, using microorganisms supplement with 0.2 and 0.6% (w/w) of lipopeptide, respectively. The analysis of mass spectrometry indicated that the biosurfactant studied was a mixture of surfactin and iturin.

Liu et al. (2012) isolated over a hundred microorganisms capable of biosurfactant production from petroleum-contaminated soil and oily sludge. In the investigation, 16 of out all bacterial isolates reduced the surface tension of the growth medium from 71 to 30 mN/m with more than 72 h (fermentation). Nevertheless, the *Bacillus amyloliquefaciens* strain produced biosurfactant resulted from four different homologs of fengycin A that shown the best efficiency to separate the three phases of oily sludge (oil, sediment, and water), achieving 88% separate level after 24 h.

Etchegaray et al. (2017) developed a first biorefinery concept study on the production of biosurfactants. The inoculation in modified Landy's medium formed three principal metabolites: acetoin (which enhances plant growth), fengycin, and surfactin. Glycerol was used to increase surfactin-specific origination; arginine improved, significantly, the yields of biomass, fengycin, and surfactin. It was observed an increase of fengycin specific production at approximately ten times, which can be associated with a connecting pathway involving ornithine and arginine. The process of adding value to biomass and crude extracts shown to be useful for biodiesel production and the *p*-xylene elimination from contaminated water, respectively.

According to Farias et al. (2018) the NaCl concentration (2.7, 66, and 100 g/L) interferes with the surface activity and composition of cyclic lipopeptides (CLPs) from *Bacillus* strains regarding MEOR. Through 16S rDNA, rpoB, and gyrB sequences analysis, the strains were identified as *Bacillus amyloliquefaciens*, *Bacillus subtilis*, and *Bacillus vallismortis*. Concentrations higher than 100 g/L NaCl were tolerated by all strains, nevertheless, *B. amyloliquefaciens* was not able to decrease surface tension. *Bacillus subtilis* exhibited emulsification activity at 66 g/L NaCl concentrations. High NaCl concentrations assisted the synthesis of fengycins and/or surfactins that is compatible with the surface activities of *B. vallismortis* and *B. subtilis*, while low concentration assisted the iturins production. These results, when analyzed together, propose that the definition of CLP under a known and expected oil reservoir condition could guide the definition of the strain to MEOR.

Lichenysin is a monoanionic lipopeptide with the same properties as surfactin but presents better effectiveness in chelating properties and surface activity. It can complex divalent cations in a relation of 2:1 and, associated with Ca^{+2} and Mg^{+2} (Grangemard et al. 2001).

Amodu et al. (2014) isolated a new strain from rotting wood for biosurfactant production, which posteriorly was identified as *Bacillus vulgaris*, being the first report of this strain in surfactant production. The synthesized biosurfactant presented a high propensity for hydrocarbon emulsification and surface tension reduction of water to lower than 30 mN/m. Based on the FTIR analysis report, the biosurfactant was associated with lichenysin cyclic LMW lipopeptide.

Ngwenya (2016) developed a study to upgrade the yield of biosurfactant from this *Bacillus* sp., by optimizing bioprocess conditions with supplementation of a broth of biocompatible nanoparticles synthesized from *B. vulgaris* agro-waste extracts, which was used as a culture medium for biosurfactant production, to reducing production costs. The supplementing of the biocompatible Ca-based nanoparticles in the reaction media by *Bacillus licheniformis* STK 01 promoted an improvement in the emulsification index of the biosurfactants to 50% using kerosene. Biochemical tests confirmed the ability of strain STK 01 to generate lichenysin biosurfactant. This research indicated the high production yield, the emulsification activity of the lichenysin biosurfactant produced, and the influence of the biocompatible Ca-based nanoparticles.

The evaluation of n-alkanes and polycyclic aromatic carbons biodegradation was taken by Xia et al. (2014) that isolated *Pseudomonas* sp. WJ6 from soil contaminated by oil and tested its performance on long-chain alkanes and PAHs degradation. The crude biosurfactant was analyzed through HPLC that proposed a mix of surfactin, fengycin, and lichenysin which efficiency to remove heavy oil from quartz sand reached 92.46% of heavy oil washing.

Therefore, lipopeptides are biodegradable, eco-friendly, more biocompatible, and less toxic than chemical surfactants. Due to their extensive variety and interesting functional properties, lipopeptide biosurfactants can be applied for many purposes. They can decrease the interfacial and surface tension which promotes their application to hydrocarbon mobilization and solubilization—enhanced biodegradation and enhanced oil recovery from petroleum well. It is observed their participation in the heavy metal remediation is due to their sequestering characteristic, biodegradability, and low toxicity. Furthermore, biosurfactant production using agro-industrial wastes as alternative culture media which makes their production economically competitive.

3.3.2 Rhamnolipids

3.3.2.1 Remediation of Metal Contamination

Over the years, industrial activities have led to heavy metal contamination of the environment (aquatic and terrestrial) (Yang et al. 2018). According to Sarubbo et al. (2015), activities such as incineration, mining, galvanization, and production of vehicle batteries are some examples of processes responsible for the contamination of the environment by heavy metals, since these are not biodegradable, leading to the destruction of biological systems, soil, and underground due to leaching.

These pollutants, especially Pb^{2+}, Zn^{2+}, Cr^{3+}, Cd^{2+}, and Hg^{2+}, are potentially reactive, toxic, and motile in the soil, being easily disseminated into the environment (Aşçi et al. 2008). Furthermore, heavy metals have recalcitrant behavior more accentuated compared to oil derivatives and other organic pollutants (Sarubbo et al. 2015). Classical remediation techniques for these compounds include chemical oxidation, electrokinetics, excavation, thermal extraction of volatile metals, solidification/stabilization, and soil washing (Aşçi et al. 2008). For these pollutants to be removed, physical removal or modification of their redox state to a less toxic form is required (Franzetti et al. 2014).

Bioremediation involves biological processes in the elimination of pollutants through solubilization or chemical mineralization, being a promising method for the recovery of contaminated environments (Jimoh and Lin 2019). In this sense, biosurfactants stand out due to the ability of metals removing from the soil by bio-extraction or biosurfactant washing, in which the mechanisms involved are counter ion binding, electrostatic interactions, and ion exchange (Liu et al. 2018). In addition, biosurfactants show higher selectivity by metallic compounds when compared to synthetic surfactants (Aşçi et al. 2008).

For removal of metals from water bodies, biosurfactants act as ion collectors through the foam flotation process, in which the biosurfactant adsorbs the metals from the liquid medium, followed by separation by foam flotation, allowing the contaminant material to be separated (Franzetti et al. 2014).

Rhamnolipids are biosurfactants from the glycolipid class with a negative charge, being able to form stronger stabilizing bonds between the cationic metal and the biosurfactant than between the metal and the soil. According to Singh and Cameotra (2004), biosurfactant soil bioremediation efficiency is influenced by soil composition, particle size, ion exchange capacity, and contamination time.

The mechanisms of metals removal from soil by rhamnolipids consist of three stages, whereas the first one is the formation of the rhamnolipid–metal complex. On the surface, which represents the interface between the matrix and the soil solution, there is the accumulation of rhamnolipid molecules due to their amphoteric characteristics, favoring the formation of the complex (Liu et al. 2018). In the second stage, the complex dissolves, allowing the metal to be released into the solution. Finally, in the third stage, the metal is bonded to the polar group of rhamnolipid micelles through electrostatic interactions (Sarubbo et al. 2015; Liu et al. 2018). This process of removing metals allows recycling and reuse of the soil (Rocha Junior et al. 2018).

The technologies involved in heavy metal soil remediation can be divided into two categories. The first one consists of ex situ washing of the soil with a biosurfactant solution on a glass column. Contaminants are removed due to interfacial tension reduction, allowing the pollutant mobilization along the column. Then, the contaminant is recovered at the bottom of the column (Kumar et al. 2017). The second is the installation of a pipe and drainage system used to introduce and collect biosurfactant during the process. Initially, injection wells are drilled into contaminated soil where solutions containing biosurfactants will be injected. After the solution is injected into the wells, the metal–biosurfactant complex is formed and directed to the extraction wells. Pollutants are collected from extraction wells and treated. Subsequently, the biosurfactant is recovered by precipitation (Sarubbo et al. 2015; Das et al. 2017; Kumar et al. 2017).

The removal of metals from aquatic environments by biosurfactants is possible with the addition of oppositely charged biosurfactant considering the metal contaminant, causing the synthesis of the biosurfactant–metal complex. After the complex formation, air bubbles are introduced into the system, causing foaming. Due to the presence of the hydrophobic and hydrophilic portion in the biosurfactant molecule, the complexes are collected by the bubbles due to the interaction between the hydrocarbon chains and the air bubbles. As a result, the contaminant is separated by foam flotation at the solution interface, which is removed at the process termination (Franzetti et al. 2014; Peng et al. 2019).

Many studies of remediation by rhamnolipid of soil and water contaminated by metals have been reported in the literature, in which the technologies involved are mostly soil washing and flotation (Slizovskiy et al. 2011; Venkatesh and Vedaraman 2012; Wan et al. 2015; Lee and Kim 2019).

Salmani Abyaneh and Fazaelipoor (2016) investigated the rhamnolipid (RL) property to eliminate Cr (III) from aqueous solutions. The authors verified through a Full Factorial Design (24), the effect of airflow rate, pH, molar ratios Fe/Cr and RL/Cr on the percentage of chromium removal, concluding that all factors had a significant effect for the response variable, with the highest removal of 96.1%, and around 90% removal for the central point assays. In the study of interfering ions in removal, the authors found that NaCl had little effect on Cr removal, and the presence of $CaCl_2$ negatively impacted removal, reducing it by 36%. According to the authors, Ca ions interact with the biosurfactant carboxyl group, decreasing removal efficiency. Furthermore, the authors concluded that the biosurfactant significantly remediated Cr.

Chen et al. (2017) investigated bioremediation of sediments containing high amounts of Cu, Cd, Pb, and Cr by using rhamnolipids. Seven concentrations of rhamnolipid were evaluated, ranging from 0.2 to 3% (w/v). Cd presented the highest percentage of washing efficiency, between 75 and 86.87% for concentrations between 0.8 and 3.0%. Lower efficiency was observed in chromium removal, reaching the highest percentage of 47.85% for the 3.0% rhamnolipid treatment. Pb and Cu had the maximum removal of 80.21 and 63.54% for a 3.0% rhamnolipid treatment. The washing time was also an important factor in the washing efficiency for all studied metals. There was a rapid increase in efficiency in the first 12 h and higher efficiencies were obtained after 24 h of batching, remaining constant up to 40 h for all metals studied. When investigating the effect of pH, the authors verified that basic medium favored the washing efficiency for all metals evaluated. The higher impact was observed in the removal of Pb and Cu, reaching efficiencies between 70 and 90% approximately, for pH values between 7.0 and 11.0. In an acid medium, for the same metals, the removal efficiency was below 50%. The authors report that the different efficiency values are due to biosurfactant structure modification. The structural differences of rhamnolipid as a function of the pH medium is associated to the rise in the carboxyl group charge density, conducting to the formation of a hydrophilic head group with more repulsive characteristic, and an increase in the dimensions of the head group, culminating in micelles with high curvature.

Mn nodules are widely distributed on the deep-sea and have valuable metals such as Cu, Ni, and Co, which are used in many industrial segments. Thus, ocean mining has become increasingly attractive due to the gradual depletion of land resources (Lee and Kim 2019).

Lee and Kim (2019) reported an unprecedented study on heavy metals removal from Mn nodules by rhamnolipids. The nodules were taken from Clarion-Clipperton

Fracture Zone, presenting high concentrations of Ni and Cu, and also composed of Al, Fe, Cr, Zn, As Cd, and Pb. The authors concluded that Cu removal is affected by rhamnolipid concentration, and by the reaction time of the treatment. In Ni removal, the reaction time had a greater effect on removal compared to biosurfactant concentration. After 7 days of reaction time, Cd removal was the most efficient (approximately 100%) using 0.3% rhamnolipid, also being mainly influenced by the biosurfactant concentration used.

Tang et al. (2017) studied the elimination of heavy metals from sewage sludge from a wastewater treatment plant in Qun Li (China). For this, an improved electrokinetic decontamination treatment combined with rhamnolipid and Tetrasodium of N, N-bis (carboxymethyl) glutamic acid (GLDA) was performed. Higher removal was observed by replacing rhamnolipid as an electrolyte when compared to the use of GLDA. The metal with the highest removal efficiency was Mn (69.9%), followed by Cu (64.8%) and Ni (60.4%). For Zn, Cr, and Pb, the removal efficiencies were 56.8, 49.4, and 46.6%, respectively. The authors also report a synergistic effect between GLDA and rhamnolipid, since higher removals were obtained in the electrokinetic process, with the highest removal percentage for Cr (89.0%) and the lowest for Pb (60.0%). The chelating action of GLDA was favored by the simultaneous addition of rhamnolipid and chelating agent, allowing greater removal efficiency of heavy metals.

3.3.2.2 Remediation of Organic Contamination

Industrial and technological developments have been increasing energy demand, intensifying oil exploration, and processing. These compounds are toxic to the environment, requiring efficient remediation actions due to the low recovery through physicochemical and oxidative treatments, and also limited bioavailability to hydrocarbon degradation bacteria (Liu et al. 2018). Spills and leaks from refineries, factories, and oil product distribution depots are examples of potential sources of environmental contamination (Befkadu and Chen 2018). In this sense, biosurfactants may be remedial agents due to their ability to solubilize hydrocarbons and toxic polyaromatic compounds from contaminated soil and aquifers (Joy et al. 2017).

According to Liu et al. (2018), rhamnolipids increase the uptake of organic compounds by degrading bacteria, due to the variation of cell surface hydrophobicity by the surfactant, however, the concrete mechanisms for these types of effects are still not elucidated (Zhong et al. 2017). Rhamnolipids also present a strong potential to modify the properties of porous media, being capable to enhance bacterial transport efficiently. This can be useful for bioaugmentation, which is a remediation technique responsible for the improvement of the degradative capacity of contaminated soil, through the introduction of specific microorganisms (Mrozik and Piotrowska-Seget 2010; Tahseen et al. 2016). Instead, higher permeabilization of the plasma membrane can be promoted by rhamnolipids, allowing the passage of hydrocarbons into bacterial cells (Zeng et al. 2018).

At low concentrations, rhamnolipid monomers stand themselves at the interface between the organic contaminant and the liquid phase, allowing the formation of microdroplets due to interfacial tension reduction, decreasing the repulsive forces between the two phases. Values above the critical micellar concentration, organic pollutants are captured in the hydrophobic nucleus of the micelles, facilitating the mobilization and availability of organic contaminants, and the next steps of pollutant remediation (Zeng et al. 2018).

Soils contaminated by metal can also be recovered by phytoremediation, encouraging researchers to explore metal resistant microorganisms capable of biosurfactants production and plant-growth stimulating compounds to the efficiency intensification of metal phytoextraction (Franzetti et al. 2014). In this context, Zhen et al. (2019) reported the synergic action of biochar (BC) and rhamnolipid (RL) on phytoremediation of oil-contaminated soil using *Spartina anglica*. According to the authors, the biochar and rhamnolipid effects on phytoremediation of soil with oil contamination by *Spartina anglica* were reported for the first time. Different treatments were carried out for petroleum-contaminated soils, which are rhamnolipid modified biochar (RMB), BC, and BC + RL for the respective contaminant concentrations of 50, 10, and 30 g/kg. The maximum removal rate of total petroleum hydrocarbons (TPHs) at a concentration of 30 g/kg was 35.1% for cultivated soil with the RMB addition.

Câmara et al. (2019) investigated rhamnolipids production by *P. aeruginosa* followed by its application on MEOR, where retained oil is extracted from the pores due to the interfacial tension reduction between water and oil, caused by biosurfactant injections during treatment. Rhamnolipid was efficient in contaminated soil remediation, since the maximum recovery was 50.45%, with 11.91% resulting from MEOR. This value corresponded to the treatment of 2× critical micellar concentration (CMC) for API grade oil of 21.90 and represented almost twice the recovery factor when the biosurfactant concentration was only 30% above CMC. The authors also reported that the high biodegradability of the biosurfactant did not impair oil recovery, since remediation was possible even after 2 months of biosurfactant production, although the time may influence the surface activity of the surfactant.

Zhao et al. (2020) analyzed the *P. aeruginosa* potential of rhamnolipid production using soybean oil or glucose as a carbon source. The biosurfactant obtained from glucose presented better superficial activity, while the biosurfactant from oil presented better emulsifying activity. On the other hand, the authors investigated the removal of oil present in sludge by using rhamnolipids. Sludge containing 22.91% of the oil was treated with 200 mg/L of the rhamnolipid solutions obtained from both carbon sources, achieving total petroleum hydrocarbon (TPH) removal of 35.81% for the biosurfactant obtained from soybean oil, and 32.06% from glucose.

Petroleum exploration produces different kinds of waste, including drill cuttings, which is a major waste produced mainly due to the huge amount of volumes generated. In addition, the mixture of oil-based drilling fluids and excavated materials may become a potential long-term pollutant (Olasanmi and Thring 2019). In this scenario, Olasanmi and Thring (2019) investigated the use of rhamnolipids in the improved rinsing of drill cuttings and oil-contaminated soil samples from British Columbia (Canada). The authors used the Taguchi method to optimize the process parameters in petroleum hydrocarbon remediation, such as temperature, rhamnolipid concentration, time of washing, and agitation, in order to evaluate its effect on the independent variable (Petroleum Hydrocarbon Reduction, %). The authors concluded that the ideal process parameters, which led to the best reduction of pollutants for both soil and drill cuttings, corresponded to a concentration of rhamnolipid of 500 mg/L at 23.5 °C during 30 min of washing. Regarding agitation and solution-to-sample ratio, a higher agitation (200 rpm) and ratio (4:1) were required for a higher drill cutting washing efficiency. The agitation and solution-to-sample ratio to contaminated soil were 100 and 1:1, respectively. The higher value of petroleum hydrocarbon fractions reduction was 85.4% for drill cuttings and 63.5% for soil with petroleum contamination. The authors suggest that the optimized technique is an efficient primary step in the bioremediation of drill cuttings and oil-contaminated soils.

Pi et al. (2017) studied the remediation of crude oil (Haierzhan) through a simulated spill. Dispersants and biosurfactants have been evaluated by the Box–Behnken design of RSM, in order to analyze their ability to decrease the total petroleum hydrocarbons percentage in water. The authors report that rhamnolipid effectively improved pollutant removal and that biosurfactant concentration has a significant impact on the removal rate. The maximum petroleum hydrocarbon removal achieved was 39% for rhamnolipid (B). For rhamnolipid (L), the removal percentage achieved was 31%, probably due to the lower biosurfactant concentration, which was 10 times lower than rhamnolipid (B).

3.3.3 Mannosylerythritol Lipids

The most studied applications of MELs are in food, cosmetic and pharmaceutical industries, medical uses, and antimicrobial agents. However, they can also be used for environmental applications due to their low toxicity, biodegradability, and ability to solubilize low solubility contaminants, enhancing their biodegradation (Yu et al. 2015). Few studies have explored MELs for remediation, and the most is for oil contamination or contaminants derived from the oil industry, such as aromatic hydrocarbons (Souza et al. 2014), alkanes, and kerosene (Hua et al. 2004). Some studies also show that MELs can be utilized for heavy metals remediation in contaminated soil and wastewater (Arutchelvi et al. 2008) and pesticide residues, such as lindane (Salam and Das 2013).

Some studies have shown that MELs can be great alternatives to chemical surfactants since they are able to emulsify solutions with equal or better performance than some chemical surfactants commercially available, besides presenting lower toxicity. According to Kitamoto et al. (2001), MEL-A showed much higher emulsifying activity to n-tetradecane and soybean oil when compared to Tween 80 (polyoxyethylene sorbitan monooleate), and both MEL-A and MEL-B showed similar activity to that of Tween 80 towards a hydrophobic phase containing the polycyclic aromatic hydrocarbon 2-methylnaphthalene. This occurred because the MELs obtained by Kitamoto et al. (2001) had much lower CMC (below 3 μg/mL) than Tween 80 (13 μg/mL). Kim et al. (2002) compared the toxicity of MEL and two commercial surfactants (dodecylbenzene sulfonate—LAS and sodium lauryl sulfate—SDS) through a Neutral Red (NR) test to transformed mouse fibroblast L929 cells post 48h of contact. The results were expressed in terms of surfactant concentration that diminished the NR uptake by 50% when compared to control (untreated cells). The authors observed that the NR_{50} was 5 g/L for MEL, while LAS and SDS showed NR_{50} of 0.01 and 0.05 g/L, respectively. With this, the authors showed that the tested MEL presented much lower cytotoxicity than the chemical surfactants.

MELs can be produced in situ by microorganisms that use the contaminants as substrate, or by biological routes and then be used for remediation. The action of MELs, as well as other biosurfactants, is associated with the metabolism of the microorganism used for the remediation. Based on this, MELs can act through two possible metabolic vias in order to improve biodegradation: increasing the solubility of the substrates for the microbial cells, and/or promoting a better interaction between the substrate and the cell surface by increasing the hydrophobicity of the surface (Zhang and Miller 1992).

3.3.3.1 Microbial Conversion of Contaminants/Wastes to MELs

The carbon source generally used for the production of MELs is an oil, mainly soybean oil since it provides higher yields (Yu et al. 2015). However, one of the main drawbacks of using biosurfactants, including MELs, is the higher cost of production and purification. The culture medium can represent around 30% of total costs (Andrade et al. 2016). Based on this, some researches started to study the use of waste materials as the substrate, such as cassava wastewater (Fai et al. 2015; Andrade et al. 2017), waste cooking oil (Niu et al. 2019), wheat straw (Faria et al. 2014a), glycerol (Morita et al. 2007), and *n*-alkanes (Kitamoto et al. 2001). The use of waste substrates favors the reduction of production costs, and also adds value to a material that would have to be treated or properly discarded. Thus, this economic technology can decrease the costs of industrial/municipal waste management and ease the pressure on the environment.

Fai et al. (2015) and Andrade et al. (2017) investigated the generation of MEL by *Pseudozyma tsukubaensis* and using cassava wastewater as a culture medium. Fai et al. (2015) reached a surface tension of 26.87 mN/m using 80% (v/v) of cassava wastewater at 200 rpm and 30 °C for 48 h. The MELs showed good thermal, pH, and ionic strength stability, and excellent emulsifier activity. Andrade et al. (2017) obtained a MEL-B production yield of 1.26 g/L using 100% cassava wastewater in a bioreactor (100 rpm, 3.0 L of working volume, 0.4 vvm of aeration rate in the first 24 h, and then 150 rpm and 0.8 vvm for more 60 h). According to the authors, the cassava wastewater is a promising alternative to conventional synthetic culture mediums.

Niu et al. (2019) studied the use of waste cooking oil as carbon source for the synthesis of MELs by *Pseudozyma aphidis*. By using a culture medium composed of 95 mL/L of waste cooking oil, 29.95 mL/L of inoculum size, 48.65 mL of medium per 250 mL, at 5.76 of initial pH, the MEL production reached 61.50 g/L. The authors also compared the use of waste cooking oil with conventionally used soybean oil and concluded that MELs produced in the medium containing waste cooking oil had better surface activity, performance, and application stability.

Faria et al. (2014b) evaluated the growth and MEL production ability of three yeasts from the genus *Pseudozima* (*P. antarctica*, *P. aphidis*, and *P. rugulosa*) using pure lignocellulosic sugars (arabinose, glucose, and xylose) as carbon source. All the strains were able to grow in mediums containing the three sugars, although the one with glucose provided a higher growth rate. MEL was produced from both glucose and xylose, but no production was detected from arabinose. The authors observed that between the microorganisms tested, *P. antarctica* was the most promising strain for MEL production from lignocellulosic sugars with a yield of 5 g/L. The same research group investigated the conversion of hydrothermally pretreated wheat straw into MEL (Faria et al. 2014a). The production yield reached 2.5 g/L of MEL using cellulolytic enzymes (Celluclast 1.5L® and Novozyme 188®) and *P. antarctica* in the fed-batch saccharification and fermentation process. Thus, the authors suggested that the yeasts have the potential for valuable biosurfactant production from lignocellulosic biomasses. The use of lignocellulosic material for MEL production decreases the spending of the substrate but requires the adding of hydrolytic enzymes, which may not yet be cost-effective, besides increasing the process complexity (Beck et al. 2019).

Morita et al. (2007) studied the microbial conversion of waste glycerol into MELs by *Pseudozyma antarctica*. The MEL yield reached 16.3 g/L after 21 days at 30 °C. The authors used a fed-batch reactor with a working volume of 1 L, to which, every seven days, 100 g/L of glycerol and 20 mg/L of mannose were added. The same research group also investigated the production of MELs by *Pseudozyma churashimaensis* from cuttlefish oil (Morita et al. 2013). This oil contains high amounts of polyunsaturated fatty acids and, because of this, can permit the synthesis of MELs containing unsaturated fatty acids such as MEL-A. The MEL-A from cuttlefish oil showed a CMC and surface tension at CMC of, respectively, 5.7×10^{-6}M and 29.5 mN/m, while MEL-A from soybean oil presented a CMC of 2.7×10^{-6}M sand surface tension of 27.7 mN/m. Thus, according to the authors, the produced MEL-A could be an attractive new functional surfactant with excellent surface-active properties.

Kitamoto et al. (2001) investigated the use of *n*-alkanes as an alternative for vegetable oils in the production of MEL by *Pseudozyma antarctica* resting cells. The authors used *n*-alkanes fluctuating from C_{12} to C_{18} and the maximum yield of 0.87 g/g of the substrate was found using an initial pH of 5.7 and 6% (v/v) of *n*-octadecane after 7 days. The production of MEL using 16.1 g/L of resting cells reached 140 g/L after 4 weeks using a fed-batch system, to which, every 7 days, 1.8 mL of *n*-octadecane was added. Thus, MELs show a great potential to be applied in bioremediation of long-chain alkanes since they are less volatile and generally remain as main contaminants in environments contaminated by oil.

Dziegielewska and Adamczak (2013) evaluated the use of several wastes (glycerol, free fatty acids, post-refining waste, post-refining fatty acids, soapstock, and waste cooking oil) in the synthesis of MELs by *Pseudozyma antarctica*, *Pseudozyma aphidis*, *Starmerella bombicola*, and *Pichia jadinii*. The highest yield (107.2 g/L) was obtained by *P. antarctica* grown in a medium with post-refining waste, followed by *S. bombicola* (93.8 g/L) and *P. aphidis* (77.7 g/L) cultivated in a medium containing soapstock, and *P. jadinii* (67.3 g/L) grown in a medium with waste cooking oil.

As can be noticed, there are several processes reported in the literature on the production of MELs using agro-industrial wastes that are very promising to be applied on a large scale once optimized. The use of inexpensive fermentation substrates is expected to have an important influence on the production costs of MEL, turning its commercialization economically feasible.

3.3.3.2 Direct Use of MELs for Remediation

After production, MELs can be directly applied to enhance the degradation of contaminants present in water or soil. They can be used to increase the contaminant solubility, that is, they assist the assimilation of contaminants by the microorganisms. Biosurfactants, such as MEL, can be used as energy and carbon backup molecules remaining as a defensive deposit for the microorganisms at harsh environmental conditions and can act as a sequestrant, forming complexes with the contaminant and reducing its toxicity, as in the case of heavy metals (Arutchelvi et al. 2008).

For remediation purposes, MELs can be purified before their application or can be used mixed with the culture broth. Sajna et al. (2015), for example, compared the use of MELs purified by chromatography with the use of culture broth containing MELs produced by *Pseudozyma* sp. in the crude oil biodegradation. According to the authors, the culture broth enhanced crude oil degradation by approximately 46%, which was a higher increase than that obtained when using purer biosurfactants. Therefore, as the extraction and purification steps represent 60% of the total production costs (Desai and Banat 1997), the utilization of MELs with no purification can considerably increase the interest in their uses for bioremediation processes.

Hua et al. (2004) studied the effects of MEL produced by *Candida antarctica* on some petroleum compounds' biodegradation in an aqueous medium. They found out that the insert of 1% of MEL to the culture medium increased the degradation of crude oil from 53.0% to 74.1%. It also increased the degradation of kerosene from 80% (800 mg/L initial concentration) to 87% (4785 mg/L initial concentration) in 15 h. The addition of MEL to the culture medium enhanced the emulsification of the kerosene, enabling the use of a higher initial concentration, besides increasing its biodegradation rate.

Salam and Das (2013) showed that the use of MELs for the stabilization of oil-in-water microemulsion increased the solubility and the biodegradation of lindane, an organochlorine pesticide. *Pseudozyma* sp. was used for the MELs production and lindane biodegradation assays. The produced MEL showed excellent surface-active properties, reducing water surface tension to 29 mN/m, exhibited a CMC of 25 mg/L, and was stable over a wide range of temperature, pH, and salinity. The use of MEL in the preparation of the oil-in-water microemulsion increased the lindane solubility up to 40-fold and enhanced biodegradation by 36% in two days compared to 12 days with no MEL addition. The authors also evaluated lindane biodegradation in a soil slurry, and the assay containing MEL showed an increase of approximately 40% in the degradation.

Park et al. (2002) used MEL produced by *Candida antarctica* as an additive to enhance the efficiency of phenanthrene removal from soil using an electrokinetic method. The role of the biosurfactant, in this case, was to enhance the desorption ability and movement of the contaminant on the soil surface. The removal efficiency in two weeks increased from 4.23% to 16.2% with the use of MEL. They also compared the biosurfactant with the synthetic surfactants alkyl polyglycosides (APG), polyoxyethylene-4 lauryl ether (Brij30), and SDS that reached removals of 11.1%, 6.31%, and 9.97%, respectively. Thus, besides increasing the phenanthrene removal from contaminated soil, MEL showed to be more efficient than commercialized chemical surfactants.

3.4 Conclusion and Future Perspectives

Biosurfactants can be applied as a bioremediation agent. Nevertheless, their cost of production needs to be reduced for an economical competition with synthetic surfactants at an industrial scale. In this sense, the group and also the subgroups of biosurfactants should be related to their applications (bioremediation), in which the current literature is scarce; however, some trends can already be spotted, as below:

- When compared to other lipopeptides, iturin presented a solid potential to be utilized as an agent for remediation of oil spills in soil and sea;
- When compared to surfactin, lichenysin, a monoanionic lipopeptide, shows better effectiveness in chelating properties and surface activity, in particular with divalent cations (e.g., Ca^{+2} and Mg^{+2});
- A mixture of surfactin and iturin seems to be more effective to remediate 5- and 6-ring PAHs;
- The concentration of rhamnolipid significantly affects the Cu remediation, whereas the retention time affects Ni removal;
- Rhamnolipids can be used to bioremediate drill cuttings and oil-contaminated soil, in particular at 500 mg of rhamnolipids/L, 23.5 °C for 30 min;
- There are few studies on MELs for remediation, and the majority of them is for oil contamination or contaminants derived from the oil industry, such as aromatic hydrocarbons, alkanes, and kerosene;
- When compared to purified MEL, the culture broth containing MEL can enhance the crude oil degradation by $\approx$46%;
- MEL can increase the biodegradation of lindane, an organochlorine pesticide.

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Biosurfactant Mediated Remediation of Heavy Metals: A Review

4

Ruchira Malik and Savita Kerkar

Abstract

Heavy metal contamination has become a serious issue in recent decades. These heavy metals are lethal even at trace amounts. They can bio-accumulate for a long time and can become strongly inhibitory to all the living forms. Various remediation strategies have been developed over the past few decades. However, there is still an ongoing search for alternate tools that are equally effective as well as eco-friendly. This review lays particular emphasis on the use of biosurfactants as a tool for heavy metal removal. Biosurfactants are amphiphilic molecules produced extracellularly by different microorganisms. These molecules have gained interest in the last few decades due to its biodegradable and eco-friendly nature. The properties like emulsification, solubilization, and complex formation with metal ions make it an excellent tool for heavy metal remediation. This chapter explores the various classes of biosurfactants produced by microorganisms and their applications in heavy metal remediation.

Keywords

Biosurfactants · Bioremediation · Heavy metals · Microbes

4.1 Introduction

Heavy metals are naturally occurring elements classified by their higher atomic weight and atomic number and are found throughout the earth's crust. They are known to have high density, i.e. above 5 g/cm^3. Some of these metals are essential in minute quantities as nutrients for microorganisms, plants, animals, and humans.

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They function as cofactors in a wide array of enzymatic and metabolic pathways, however, are capable of being toxic in increased concentration or in specific molecular structures. Some heavy metals are poisonous even at very low concentrations (Mishra et al. 2019). They accumulate in the soft tissues and can develop into emphatically inhibitory to the entire living forms. They can originate from both natural and anthropogenic processes. Under certain environmental circumstances, natural emissions of heavy metals occur, which include volcanic eruptions, forest fires, rock weathering, and many more. The anthropogenic activities include agricultural waste, livestock waste, industrial waste, pesticides, fertilizers, mining, automobile exhaust, smelting, and burning of fossil fuels. Once the metals are released from their endemic spheres they penetrate into different environmental compartments such as soil, water, and air and ultimately enter the food chain. Moreover, these can penetrate into the living system through the air, water, or food and bio-accumulate for quite a while (Tchounwou et al. 2012; Selvi et al. 2019). An elevated amount of metals in loam can cause damaging effects on the quality and lushness of the soil. In the human body, the accumulation of these toxic metals causes extreme health impacts such as growth deformities, carcinogenesis, damaged liver and kidneys, abnormalities, infertility, and pregnancy (Jaishankar et al. 2014; Ayangbenro and Babalola 2018). Nowadays rapid urbanization and industrialization are resulting in unprecedented heavy metal contamination in the environment, thus, their exclusion has become obligatory in favor of environmental well-being. This has given rise to discover and develop innovative approaches that are equally effectual at the same time eco-friendly. One such strategy explicitly attaining importance is using biosurfactant for remediation.

4.2 Biosurfactants

Biosurfactants are structurally diverse groups of surface-active agents produced by diverse microorganisms, for instance, bacteria, fungi, and yeasts on the cell surface or excreted extracellularly. They are naturally amphiphilic, i.e. they have both hydrophilic (water-loving) and hydrophobic (water-hating) moieties. They possess an ability to accrue between liquid segments, capable of lowering surface and interfacial tension. Biosurfactants are produced by inexpensive raw materials which increase its effectiveness towards the increasing demand. In recent years they are widely used for various applications from household detergents to pharmaceuticals. Also, biosurfactants can be customized based on the applications by modifying the genes or by optimizing the production conditions (Thernmozhi et al. 2011).

Table 4.1 List of biosurfactants produced by different microorganisms

Class	Source	References
Glycolipids		
Rhamnolipids	*Pseudomonas* sp., *Pseudomonas aeruginosa*	Guerra-Santos et al. (1986), Hisatsuka et al. (1971), Koch et al. (1988), Rashedi et al. (2005), Robert et al. (1989), Suzuki et al. (1965)
Trehalose lipids	*Rhodococcus erythropolis, Nocardia erythropolis, Arthrobacter sp., Mycobacterium sp.*	Abu-Ruwaida et al. (1991), Bryant (1990), Cooper et al. (1981), MacDonald et al. (1981), Robert et al. (1989), Rosenberg et al. (1979)
Sophorolipids	*Candida bombicola, Candida apicola, Rhodotorula mucilaginosa, and Candida rugosa*	Daverey and Pakshirajan (2009), De Oliveira et al. (2014), Desai and Banat (1997), Deshpande and Daniels (1995)
Mannosylerythritol lipids	*Pseudozyma (Candida) sp, Ustilago sp*	Arutchelvi et al. (2008), Morita et al. (2015), Yu et al. (2015)
Lipopeptides		
Surfactin/iturin/ fengycin	*Bacillus subtilis*	Arima et al. (1968), Bernheimer and Avigad (1970), Cooper et al. (1981), Rosenberg et al. (1988), Wei et al. (2004)
Viscosin	*Pseudomonas fluorescens*	Neu and Poralla (1990)
Lichenysin	*Bacillus licheniformis*	Grangemard et al. (2001), Madslien et al. (2013), Nerurkar (2010)
Serrawettin	*Serratia marcescens*	Matsuyama et al. (1991), Thies et al. (2014)
Subtilisin	*Bacillus subtilis*	Bernheimer and Avigad (1970)
Gramicidins	*Bacillus brevis*	Marahiel et al. (1977)
Polymyxins	*Bacillus polymyxa*	Suzuki et al. (1965)
Arthrofactin	*Arthrobacter* sp.	Morikawa et al. (1993)
Bamylocin A	*Bacillus amyloliquefaciens*	Lee et al. (2007)
Fengycin S	*Bacillus amyloliquefaciens*	Lee et al. (2010)
Phospholipids/fatty acids/neutral lipids		
Phospholipids	*Acinetobacter sp., Corynebacterium lepus, Thiobacillus thio-oxidans*	Beeba and Umbreit (1971), Dehghan-Noudeh et al. (2007), Kaeppeli and Finnerty (1979), Knoche and Shiveley (1972), Rosenberg and Ron (1999), Rosenberg et al. (1988), Zosim et al. (1982)
Fatty acids	*Corynebacterium lepus*	Chandran and Das (2011), MacDonald et al. (1981)
Neutral lipids	*Nocardia erythropolis*	MacDonald et al. (1981)
Corynomicolic acid	*Corynebacterium insidibasseosum*	Nitschke and Costa (2007)

(continued)

Table 4.1 (continued)

Class	Source	References
Polymeric surfactants		
Emulsan	*Acinetobacter calcoaceticus*	Cirigliano and Carman (1984), Cirigliano and Carman (1985)
Biodispersan	*Acinetobacter calcoaceticus*	Nitschke and Costa (2007)
Liposan	*Candida lipolytica*	Bernheimer and Avigad (1970), Bryant (1990)
Particulate biosurfactants		
Vesicles	*Acinetobacter calcoaceticus*	Gutnick and Shabtai (1987), Kaeppeli and Finnerty (1979)
Whole microbial cells	*Cyanobacteria,* variety of bacteria	Fattom and Shilo (1985), Nitschke and Costa (2007), Rosenberg et al. (1988)

4.3 Classification of Biosurfactants

They are classified following their molecular structure and microbial source (Table 4.1). In general, they are composed of a hydrophilic moiety (polysaccharides or peptides or amino acids) and hydrophobic moiety (saturated or unsaturated fatty acids) (Desai and Banat 1997). They can also be classified as based on the molecular mass. Glycolipids, lipopeptides, and phospholipids are low molecular mass surfactants while polymeric and particulate surfactants are high molecular mass surfactants (Rosenberg and Ron 1999). Biosurfactants are moreover anionic or neutral (Nitschke and Costa 2007).

4.4 Properties of Biosurfactant

4.4.1 Self-Aggregation

As biosurfactants are amphiphilic in nature with hydrophilic and hydrophobic moieties they have self-aggregation properties. In the solution, they form molecular aggregates termed as micelles beyond critical concentration which gives it excellent detergency and solubilization properties. They can be used as detergents, emulsifiers, wetting agents, dispersants, and foaming agents. Micelles act as emulsifiers allowing a compound to dissolve which are usually insoluble. They are an important component of pharmaceutical chemistry and have several applications. Biosurfactants increase the bioavailability of the compounds or act as a mobilizing agent which can be used in the removal of the hydrocarbon contaminants by pseudo-solubilization.

4.4.2 Specificity

They are multifarious organic molecules with precise functional groups, which frequently make them more specific in their action which would be quite persuasive in detoxification of contaminants (Kosaric 2001).

4.4.3 Biodegradability

Biosurfactants are biodegradable as they are produced from natural sources. So they have an advantage over synthetic surfactants that are lethal to the environment owing to their recalcitrant and persistent nature.

4.4.4 Stability

They are stable over a range of temperature, pH, and salinity.

4.4.5 Low Toxicity

They are less toxic in comparison to synthetic surfactants (Juwarkar et al. 2007).

4.5 Role of Biosurfactants in the Remediation of Heavy Metals

Several studies have been executed to evaluate the possibility of metal removal by biosurfactants from the soil as well as from aqueous solutions due to their anionic characteristics and properties like emulsification, solubilization, and complex formation with metal ions. Biosurfactants are capable of modifying the metal surfaces and form aggregate at interphases that favor the separation of metals from contaminated soils. Bacterial cell and exopolymers are capable of remediating metals from waste streams such as industrial effluents, mine water, and sewage sludge. Nonetheless, metal–cell and metal–exopolymer complexes would be filtered out by the soil during washing or flushing due to the large size of bacterial cells and exopolymers (Aşçı et al. 2007). Also, numerous aspects that influence and edge bioremediation efficiency using microbes include pH, temperature, nutritional status, redox potential, moisture, and composition of heavy metals (Shukla et al. 2013). The utilization of microorganisms unaided has revealed limited efficiency due to several aspects including poor competitiveness and excessive heavy metal concentrations. Therefore, biosurfactants have a discrete advantage over the use of the entire cell and exopolymers, as they are small in size and stable over a wide range of temperature, pH, and salinity.

4.6 Mechanism of Action

- In solid phases, desorption of heavy metals endorsed according to Le Chatelier's principle, which occurs in the course of electrostatic interactions or formation of the metal complex with biosurfactants, decreasing the activity of the metal in aqueous phase (Miller 1995).
- Accumulation of biosurfactants at the interface will possibly allow undeviating contact between the biosurfactant and the metal to form a metal–biosurfactant complex. The bonds between metal and biosurfactant are stronger than the bond between metal and soil. Under conditions of decreased interfacial tension, these complexes are further desorbed from the soil matrix to the soil solution succeeding in its removal by flushing. (Gomaa and El-Meihy 2019).
- In aqueous solutions, biosurfactants will adsorb heavy metals and will chelate with the heavy metals to form an insoluble metal—biosurfactant co-precipitate (Das et al. 2009).

4.7 Biosurfactants Used in the Remediation of Heavy Metals

4.7.1 Rhamnolipids

Among biosurfactant classes, rhamnolipids are the most characterized biosurfactant for its potential to remove heavy metals. They are anionic in nature so they are useful to remediate cationic metal ions, such as cadmium, nickel, lead, copper, zinc, and iron (Dahrazma and Mulligan 2007). They are said to be the successive generation of biosurfactants to achieve the market. Rhamnolipids are produced by *Pseudomonas aeruginosa* and are classified as mono and di-rhamnolipids (Parra et al. 1989; Rashedi et al. 2005; Robert et al. 1989; Siegmund and Wagner 1991). They comprise of β-hydroxy fatty acid and a rhamnose sugar molecule attached by carboxyl end. They are also produced by *Pseudomonas fluorescens, Pseudomonas chlororaphis, Pseudomonas plantarii, and Pseudomonas putida* (Sekhon Randhawa and Rahman 2014). They have a wide array of applications in various industries. Though so far, the bioremediation potential of rhamnolipids has been extensively studied and is the major topic for publication.

In 2007, Juwarkar et al. reported remediation of Cd and Pb from artificially contaminated soil using rhamnolipid biosurfactant produced by *Pseudomonas aeruginosa* strain BS2. The study showed that the remediating efficiency reached 92% of Cd and 88% of Pb after 36 h. when the soil was washed with the rhamnolipid. Also, the treatment with rhamnolipid solution enabled the soil to regain its fertility and soil microflora which were lost due to the inhibitory and toxic effect of heavy metals. Thus the study showed that biosurfactant technology is an efficient method for bioremediation. The feasibility of rhamnolipid foam to remediate nickel (Ni) and cadmium (Cd) from sandy soil was evaluated by Wang and Mulligan (2004). The rhamnolipid solution (0.5%) was able to generate foam which removed 73.2% of Cd and 68.1% of Ni with an initial pH value of 10.

Rhamnolipid-mediated desorption of heavy metals from representative soil components was also examined. In 2007, Asci et al. assessed the potential of rhamnolipid to remove Cd(II) from kaolin (soil component). Herein study, the effects of pH and rhamnolipid concentration on desorption efficiency were also evaluated. The maximum removal of Cd(II) was observed to be 71.9% with 80 mM concentration of the rhamnolipid at pH 6. An additional study by Asci et al. reported the removal of zinc from Na-feldspar (a soil component). It was found that the utmost removal efficiency was 98.83% of the sorbed Zn (II) from Na-feldspar using 25 mM rhamnolipid concentration at optimal pH 6.8. The recovery of Cd(II) from sepiolite and K-feldspar (soil components) using rhamnolipid was also accounted for by Asci et al. (2008). The desorption efficiency from K-feldspar was approximately 96%, whereas only 10.1% from sepiolite.

In 2011, Venkatesh and Vedaraman found that 2% of rhamnolipids produced by Pseudomonas aeruginosa MTCC 2297 were able to remove 71% of 474 ppm copper and 74% of 4484 ppm copper from the soil using batch washing experiment. Akintunde et al. (2015) reported remediation of Fe using rhamnolipid from aqueous solution. In this study potential of the biosurfactant to remove iron was investigated. The rhamnolipid was able to remove 60.34% of iron indicating it as an efficient iron remediating agent.

4.7.2 Lipopeptides

Lipopeptides are the most popular biosurfactants as they have a broad range of applications in de-emulsification, food-processing, and crude oil recovery. They also exhibit antimicrobial antiviral, anti-adhesive, and antitumor activities (Cao et al. 2009; Lee et al. 2010; Donio et al. 2013; Pereira et al. 2013; Varadavenkatesan and Ramachandra 2013; Alvarez et al. 2015). They consist of a peptide moiety in combination with fatty acid. The isoform differs from the peptide moiety, the length of the fatty acid chain with the linkage among the two groups (Mnif and Ghribi 2015). *Bacillus sp*. is reported to produce lipopeptide surfactants which have wide applications. Surfactin produced by *Bacillus subtilis* on the whole is the most potent lipopeptide type biosurfactant among the lipopeptides (Wei et al. 2004; Wei et al. 2003; Yeh et al. 2005). It consists of four isomers, Surfactin A–D which displays various physiological activities (Arima et al. 1968). Due to its anionic character, they are capable of forming a complex with the positively charged metal which makes them a metal sequestering candidate for remediating heavy metals.

The efficiency of a biosurfactant in removing heavy metals from solutions was detailed by Das et al. (2009). Biosurfactant derived from a marine bacterium was able to remove 42.74% and 76.6% of 100 ppm of cadmium and lead at a 0.5× critical micelle concentration (CMC). At the same time as the concentration of biosurfactant was increased to 5× CMC, there was an almost complete removal of cadmium and lead. The efficiency of metal removal depended on the concentration of biosurfactant and that of the metal. In 2013, Singh and Cameotra studied the ability to remediate heavy metals from contaminated soil using fengycin and surfactin produced from *Bacillus subtilis* A21. Heavy metals such as zinc cadmium, iron, copper, lead, cobalt, and nickel were present in high concentrations in the soil. Washing of the soil was carried out with a mixture of surfactin and fengycin at a concentration of 50 CMC. It was able to remove copper (26.2%), lead (40.3%), cadmium (44.2%), zinc (32.07%), nickel (32.2%), and cobalt (35.4%) in a period of 24 h. Further biosurfactant washed soil was for mustard seed germination to check its ability for plant growth. The soil treated with biosurfactant showed 100% germination of seed as compared to the soil washed only with water where no germination was seen.

Bioreduction of Cr (VI) using surfactin was also reported by Swapna et al. (2016). Chromium solution (100 ppm) was treated with surfactin (10 mg/ml) over the period of 72 h. There was 38% removal of Cr (VI) at 12 h which was increased to 74% on incubation up to 72 h.

The advantage of biosurfactants is that they can be produced by using cheap raw materials which can be cost-effective. Hisham et al. (2019) accounted production of biosurfactant by *Bacillus* sp. HIP3 using used cooking oil. The produced lipopeptide biosurfactant was able to remove 12.71% lead, 2.91% zinc, 1.68% chromium, 0.7% cadmium, and 13.57% copper, respectively, from artificially contaminated water, stressing its bioremediation prospective.

4.7.3 Sophorolipids

Sophorolipids consist of disaccharide sophoroses linked to a long-chain hydroxy fatty acid. They are produced by yeasts such as *Candida bombicola*. They are a mixture of 6–9 different hydrophobic sophorosides (Desai and Banat 1997). They can be classified as anionic (acidic) or non-ionic (lactonic). Among all the biosurfactants, the yield of sophorolipids is reported to be the highest. They are considered among promising biosurfactants and are used for commercial production and applications.

The potential sophorolipids from *Torulopsis bombicola* were utilized in the metal ion remediation such as copper and zinc from contaminated sediments. The study confirmed that 4% of sophorolipids were able to remove zinc (60%) and copper (25%) with a single washing (Mulligan et al. 2001). The efficiency of sophorolipids in the removal of lead and cadmium from artificially contaminated soil was also deliberated by using sophorolipids derived from *Starmerella bombicola* CGMCC 1576. Crude acidic sophorolipid was able to remediate 44.8% of lead and 83.6% of cadmium at a concentration of 8%. The removal efficiency of sophorolipids was better than the synthetic surfactants. Moreover, the study also showed that the efficiency of acidic sophorolipid to remediate heavy metals was higher than the lactonic sophorolipid (Qi et al. 2018).

4.7.4 Other Biosurfactants

Heavy metal bioremediation was explored using biosurfactant produced from *Rahnella* sp. RM isolated from chromium-contaminated subsurface soil. The biosurfactant was able to remove 74.3%, 72.5%, and 70.1% of 100 mg/L of Cu, Cr, Pb, respectively, at 48 h. The study showed the purified biosurfactant can be used as a potential candidate in the removal of the metals from contaminated environments (Govarthanan et al. 2017). The biosurfactant extracted from *Candida guilliermondii* UCP 0992 was able to remove 98.6% Fe, 99.9% Zn, and 93.8% Pb from the soil comprising of initial metal concentrations of 1470, 1877, and 3038 mg/l of Zn, Fe, and Pb, respectively. Further, the toxicity of this biosurfactant was also studied on the germination of seeds of cabbage (*Brassica oleracea*). The study showed that the biosurfactant had no toxic effect on seed germination. (Sarubbo et al. 2018).

Recently, Gomaa and El-Meihy (2019) described the efficiency of biosurfactant derived from *Citrobacter freundii* MG812314.1 to remediate heavy metals from the wastewater. The biosurfactant was able to remove 80% aluminum, 67% lead, 66% zinc, 55% cadmium, 45% iron, 44% copper, and 41% manganese, respectively, from wastewater with a concentration of 10% (w/v) after 3 days. Interestingly, the results also showed that when wastewater was treated with 5% biosurfactant with increasing contact time the removal efficiency was increased.

4.8 Conclusions and Future Perspectives

The biosurfactant industry has revealed significant growth over the past few decades. Through recent years numerous studies have shown a wide range of microorganisms capable of producing different types of biosurfactants. The properties like biodegradability and lower toxicity significantly reduce the environmental impact and offer an advantage over their synthetic counterparts. They have an ample range of uses in a range of industries and are on the verge of replacing synthetic surfactants. Despite the immense potential of biosurfactants, their use remains limited, owing to their high production and purification cost. Research needs to focus on the production of biosurfactants on a large scale at a minimum operational cost, which will step forward to a new age of biosurfactants. Even though several studies have accounted for the bioremediation efficacy of biosurfactants, many questions are yet to answer. Generally, studies illustrated are performed under laboratory conditions. There is a requirement for structuring more effective as well as cost-efficient bioremediation strategies using biosurfactants.

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Surface-Active Agents from *Pseudomonas* Emulsify *n*-Hexadecane: Past, Present, and Future Trends

5

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Abstract

This chapter highlights the importance and the devastating irreparable damage it could have on the various ecosystems, especially in the marine realm. In the past, various ways have been adopted to counter the effect of oil pollution by both chemical and physical means, however, they themselves pose either harm to the ecosystem or are highly expensive/involve high-end infrastructure for the operations. Hence a most inexpensive and an ecofriendly approach using microorganisms have been thought of to reduce or mitigate the effects of oil pollution for the last five decades. The chapter concentrates on the non-marine as well marine-sourced bacterial groups those were/are employed for bioremediation purpose and the importance of bioemulsifiers in such operations. The chapter details the remediation strategies for hexadecane, a 16-C aliphatic hydrocarbon and the usage of bioemulsifiers for such purpose. Work from the authors' laboratory gives insights into the isolation of a bacterium, *Pseudomonas guguanensis* and the role of its bioemulsifier in hexadecane removal. A detailed pathway is proposed for the biosynthesis of the emulsifier by the bacterium and how that is being used to emulsify hydrocarbon so that a link is established between the feed and the product. Conclusive statements on the future of use of this organism for hexadecane removal and the possible approaches are listed.

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Bioemulsifier · Bioremediation · Microbes · Petroleum hydrocarbons

5.1 Introduction

One of the major resources in this modern industrial world is oil and its products. Hence it is certain that there is a huge danger of oil spillage as long as oil is being used. Oil spills impose serious concerns in the environment (Kingston 2002). Oil spillage is a type of pollution wherein as a result of accidents or anthropogenic actions, there is a release of liquid petroleum into the surroundings, mainly in the marine environment (Briggs and Briggs 2018). Oceanic oil spills became a serious environmental problem in the 1960s (Fig. 5.1).

There are four major sources for oil pollution: 1. urban runoff, 2. atmospheric fall outs, 3. natural seeps, and 4. oil spills. In the urban areas, oil from the vehicles build-up on the roads is washed off due to rains or melting of snow and enters the sewer systems and the water sources. The U.S. Environmental Protection Agency (EPA) states the major causes of runoff oil pollution to be vehicular leaks, fuel station spills, and oil which is not disposed properly. During rains or melting of snow, the oil which floats on the water is forced to flow out of the city and thus enters the rural areas polluting its water resources and natural elements. Oil from vehicles and planes which pollutes the air is called atmospheric fallout. In the long run, this oil tends to drop down from the air and settles on oceans or on land. Based on the site and the pollution load in the air, the fallout can be heavy or light. For instance, as vehicles run, a part of the oil is burned which produces not only energy but also emit gases into the atmosphere. Thus, this oil travels in the air or drops down from the air. The oil is pushed from the air and settles onto the water or land to cause pollution during rains or snow. Natural seep is a type of pollution which occurs naturally and is unavoidable. The oil oozes from the ground and causes pollution in the surrounding area. La Brea Tar Pits in California seepage of oil and gas forming tar maybe

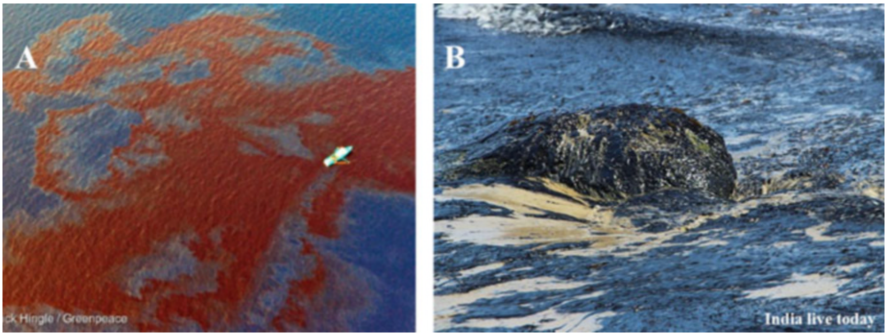


Fig. 5.1 Oil spill (**a**) April 2010, Gulf of Mexico and (**b**) January 2017 Ennore, Tamilnadu

considered as one of the well-known natural seeps. Oil spill is the most serious type of oil pollution out of all the types mentioned above. This may occur due to several reasons such as damage to an oil ship or any transport issues, equipment malfunctions at oil refineries. Among these, oil spills mostly take place during the transportation of oil. For example, an oil spill occurred on April 20, 2010 in the Gulf of Mexico due to an explosion which caused 205 million gallons of oil to be spilled into the sea as reported by "The Huffington Post" (Mayank 2019; www.newindianexpress.com). Around 0.33 million tonnes of petroleum lubricant spilled into the sea when two cargo ships collided in the Ennore coast in Chennai (Tamil Nadu, India) on January 28, 2017. These oil spills resulted in serious damage to the beaches and the marine environment. More recently, there was an oil spill in Russia on May 29, 2020 when a fuel tank collapsed and released around 21,000 tonnes of diesel oil into the Ambarnaya River, turning it crimson red, which now has a risk of spreading into the Arctic Ocean (BBC News 2020).

5.2 Biological Impact of Oil Pollution

Oil pollution damages the ecosystems and causes contamination of water. The oil coats the marine animals and also the birds' feathers and fur (Fig. 5.2).

The animals cannot protect themselves from the cold water and the birds experience trouble flying once they are covered in oil. The animals ingest some of the oil during the process of cleaning themselves. Due to the thick oil deposit on the water surface, fishes can be suffocated, and also prolonged exposure to oil can result in liver, reproductive and growth-related disorders in bottom-dwelling fishes (NOAA 2020). Oil pollution can harm the plants which grow in or near the water. Sunlight needed for the plants to carry out photosynthesis can be blocked by an oil spill and as a result the plants growing in oil spilled water cannot survive and hence a huge loss in primary productivity in localized areas may occur. Oil spills can cause closure of beaches and harbors. Certain areas are more susceptible than the others to oil pollution. For instance, when compared to the sandy beaches and sea-grass beds, the more easily affected areas are the coral reefs, mangroves, and marshes (ITOPF 2011a). The oil at times can be carried off for a long distance from the site of the spill by the water and wind currents and along the way causes harm to the plants, birds and marine animals.

5.3 Oil Pollution Clean-up Methods

Depending upon the kind and the quantity of the spilled oil, the location of the water source and the weather conditions of that area, there are various clean-up strategies that can be recommended. The recovery period can vary from weeks to decades. Recovery may occur within several weeks along the bedrock shorelines due to the high-energy waves. Usually, exposed beaches recover in a few months. Although, recovery could take several years or even decades in marshes and salt flats. Recovery

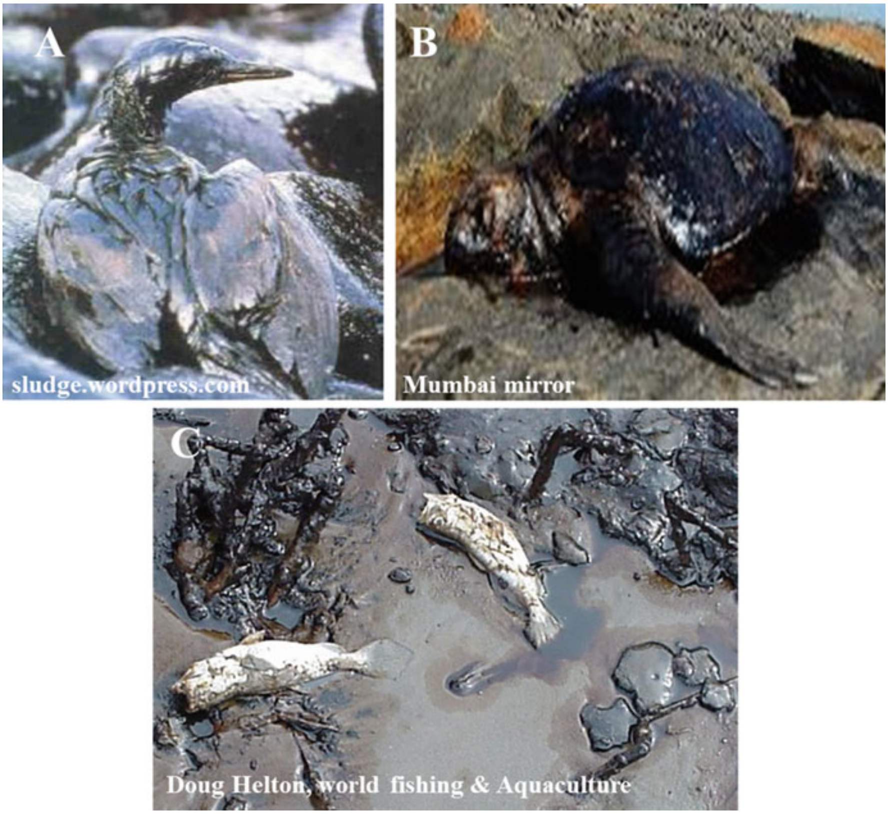


Fig. 5.2 (**a**) Birds soaked in oil after Exxon Valdez oil spill, Alaska, (**b**) dead turtle after Ennore oil spill, and (**c**) dead fish in an oil spill

can take up to 50 years in the Mangroves, which are claimed to be the most productive yet sensitive coastal regions in the tropics and subtropics.

A list of commonly used clean-up methods to treat oil spilled areas is summarized below (Safe Drinking Water Foundation 2017).

5.3.1 Booms

One of the most commonly used tools is the booms as they contain the oil and prevent the spread. There are three common kinds of booms extant: hard, sorbent and fire booms (NOAA 2019c). Booms are highly efficient when the oil slicks are thin and light. There are four basic characteristics a boom possesses: a freeboard which is above the water and this helps in containing the oil; a device for floatation; a skirt that is below the water surface which helps in containing the oil and reduces the quantity of oil which goes under the boom; a longitudinal support which goes along the skirt bottom and this helps the boom to withstand wind and wave action offering stability. Once the oil is contained, the boom is fastened to a vessel at the end points in order to form a pocket which is U- or J-shaped in which the oil is collected. This confined oil is pumped out into storage tanks and taken for appropriate disposal to the shore (US EPA 1999b; ITOPF 2011b).

5.3.2 Chemical Dispersants

The usage of chemical dispersants in the clean-up of oil spills has been successful. These are chemicals which are applied by a low-flying plane to the water surface. Many a times, hydrocarbons can also breakdown naturally. Chemical dispersants are those which speed up this natural process. Once the dispersants are applied, the oil is dispersed in the water, that is, the oil and the dispersant are bound and have moved down the water column. The concentration of the oil is diluted by the water so that there is less danger to the marine life (US EPA 1999a; ITOPF 2011c).

5.3.3 Skimmers

The oil can be skimmed from the surface of water with the aid of boats called skimmers (NOAA 2019a). The physicochemical properties of oils are not quite changed by the skimmers. Thus, the oil can be refined if it is relatively fresh, whereas, in other instances, the oil is burned. The kind and the denseness of the oil spill, the debris load in the water, the site and its weather conditions decide the success rate of skimming (calm weather is best suitable for skimming) (US EPA 1999b).

5.3.4 Sorbents

Sorbents are also applied as powders to the surface of water as it has the ability to absorb small quantities of oil. Thus the final step of clean-up is mostly sorbents. Natural as well as synthetic organic materials are used as sorbents. Peat moss and sawdust are some of the natural organic materials and polypropylene, polyester foam or polystyrene are some of the synthetic organic materials that are commonly used as sorbents. Generally, these are applied manually, and nets and rakes are used for recovery (US EPA 1999b; ITOPF 2012).

5.3.5 Burning

Burning is a frequently used method for the removal of oil from the surface of water. Following the deployment of skimmers for the removal of oil from the surface of water, the oil can be burned. Although the removal of oil from the water surface occurs rapidly and efficiently by burning, there is release of oxides of nitrogen and sulfur due to burning of oil which leads to acid rain and causes further pollution (NOAA 2019b; National Research Council 2013).

5.3.6 Beach Clean-Up

Manual clean-up with the help of shovels and trucks is often carried out in oil contaminated beaches and shores. The oiled beach sand and gravel can be removed manually from the beach and transported to another location to carry out treatment. The oil may be vacuumed off the beach with the help of vacuum trucks. Oil can then be washed off of the beaches with the help of pressurized hoses into the water. Here, the oil will be dispersed and diluted (NOAA 2019a; US EPA 1999c).

These methods have various disadvantages, for example, booms are efficient only in cleaning of thin oils, burning of oil causes acid rain and dispersants per se cause detergent pollution. Not only that, all of these methods increase the Chemical Oxygen Demand (COD) and the Biological Oxygen Demand (BOD) thereby lowering the amount of available Dissolved Oxygen (DO). Higher aquatic organisms are affected by the chemical substances by inhalation through respiratory tracts. It can either be external gills or regions of specialized cells on the body surface as in the case of invertebrates such as crustaceans or epithelial membranes as in the higher organisms such as fish. When exposed to emulsifiers there may be destabilization of the epithelial membranes which causes changes in membrane permeability, cellular lysis and cellular respiration impairment (Dicks 1998). Thus on top of oil pollution the recovery methods also pose significant challenges to the biota and hence there has been a shift from chemical to biological way of cleaning up oil spills, which may be eco-friendly.

5.4 Biosurfactants and Bioemulsifiers Could Be an Eco-Sustainable Solution?

Contaminants from the water and soil are efficiently removed by the microorganisms. Certain microorganisms which occur in the environment are able to break down many toxic chemicals, especially hydrocarbons, such as gasoline and oil. In order to enhance the rate at which the microorganisms work, often, there is an addition of nutrients like nitrogen or phosphorus. The process by which a contaminated site is cleaned up or remediated with the help of microorganism is called bioremediation. The oil which is difficult to remove is broken down by this biological process. Sensitive areas such as coral reefs and mangroves are also cleaned up by this process. Bioemulsifiers are amphiphilic compounds that contain both hydrophobic and hydrophilic moieties and make emulsions by dispersing oil in water or water in oil. This can be achieved by reducing the surface-active forces of both the oil as well as water thus making both the aqueous and non-aqueous phases either fully or partially miscible.

5.4.1 Bioemulsifiers

Microorganisms which produce bioemulsifiers are omnipresent. They are present both in aquatic and terrestrial environments and also in extreme environments (for example, in hypersaline sites and in oil reservoirs as well). They are able to survive in a broad range of temperatures, pH and salinities. Bioemulsifier produced by microorganisms solubilizes the hydrophobic compounds in the surroundings and helps in its utilization as sources of energy and nutriment (Floodgate 1978; Margesin and Schinner 2001; Olivera et al. 2003). At times, a bioemulsifier is produced on substrates which are water-soluble by few microorganisms (Turkovskaya et al. 2001; Gunther et al. 2005). This indicates that the bioemulsifier molecules present on the cell surface of the microorganism tends to increase the cell's hydrophobicity and aids for its survival in the hydrophobic setting (Abraham et al. 1998; Perfumo et al. 2009). The bioemulsifier produced may either be localized on the surface or released extracellularly into the environment. In the case when the bioemulsifier is in association with the cell, the cell membrane of microorganism acts as a bioemulsifier and controls the property of adherence to the substrates which are insoluble in water (Maneerat and Dikit 2007). The isolation and characterization of microorganisms which produce bioemulsifier has mostly been carried out from the polluted (petroleum or its byproduct and oils) marine and terrestrial environments. Different types of bioemulsifiers with various molecular structures are produced by a broad range of genera which are linked with the marine environment.

5.4.2 A Short Review on Bioemulsifiers from Marine and Non-Marine Microbes

Bioemulsifiers which are produced by marine microbes, in addition to having properties such as tolerance to temperatures (20–100 °C), pH (3–12), and salinities (0.5–2.0%), have certain other unusual properties as well. Due to the lack of infrastructure to culture marine bacteria, there is very limited bioemulsifiers produced from marine microbes. *A. calcoaceticus* RAG-1 when cultured on hexadecane produces bioemulsifier (Rosenberg and Ron 1997). An anionic glucose lipid was produced by *Alcanivorax borkumensis* that contained a tetrameric oxyacyl side chain (Abraham et al. 1998), while an *Alcaligenes* sp. produced a glucose lipid (Poremba et al. 1991). An extracellular polysaccharide bioemulsifier was produced from *Rhodococcus rhodochrous* and has been characterized in Japan (Noriyuki et al. 2002). A complex of lipid, carbohydrate, and protein which was isolated from *Yarrowia lipolytica* was identified to function as a bioemulsifier at National Chemical Laboratory (NCL), Pune, India (Zinjarde and Pant 2002). A commercial bioemulsifier was produced by *Acinetobacter* sp. which is a predominant group of Gram-negative bacteria in the marine environment (Haleem 2003). A flavolipid bioemulsifier was produced by *Flavobacterium* sp. strain MTN11 of Arizona, Texas and its structure and some of its selected properties have been identified and reported for the first time (Bodour et al. 2004). *Pseudomonas aeruginosa* produced rhamnolipid bioemulsifier in larger quantities (Wei et al. 2005). Lipoproteins such as Ornithine lipids with bioemulsifier like function were isolated from *Myroides* sp. SM1 in the coasts of Okayama, Japan (Maneerat et al. 2006). A glycolipid bioemulsifier was partially characterized (Thavasi et al. 2008) at the Centre for Advanced Study in Marine Biology, Parangipettai, Tamil Nadu. The preliminary characterization of the bioemulsifier products was performed for the isolates *B. megaterium, C. kutscheri* and *P. aeruginosa* and it was identified to be glycolipid, glycolipopeptide, and lipopeptide, respectively (Thavasi et al. 2010). A marine Actinobacterium, *Brevibacterium aureum* MSA13 produced a lipopeptide which was optimized to bioemulsifier production at the Bharathidasan University, Tiruchirappalli, Tamil Nadu, India (Kiran et al. 2010).

From the petroleum contaminated sites and oil reservoirs, the bacteria producing bioemulsifiers have been isolated (Batista et al. 2006). There are numerous emulsifiers produced by terrestrial bacteria and fungi. *Bacillus* strain FE-2 produced a lysozyme-sensitive bioemulsifier (Patel and Gopinathan 1986). *Acinetobacter radioresistens* KA-53 produced an anionic alanine-containing heteropolysaccharide—protein bioemulsifier called Alasan. *A. junii* SC14 produced a proteoglycan bioemulsifier (Patil and Chopade 2004). An extracellular polymer bioemulsifier was produced through continuous fermentation by *Corynebacterium hydrocarboclastus* when the carbon source used was kerosene (Shilo et al. 1993). *Pseudomonas putida* ML2 was reported to produce a bioemulsifer and an extracellular polysaccharide with emulsifying and flocculating activity (Bonilla et al. 2005). In the fungal groups, a liposan emulsifier was produced by *Candida lipolytica* and a mannoprotein type of bioemulsifier was produced by *Saccharomyces cerevisiae.* An extracellular polysaccharide was isolated and characterized from *Penicillium citrinum* (Morais et al. 2003). *Pseudozyma* sp. or *Ustilago* sp., *Pseudomonas aeruginosa* and *Bacillus subtilis* YB7 produced mannosylerythritol lipids, glycolipid, and cyclic lipopeptide, respectively (Arutchelvi et al. 2009; Arutchelvi and Doble 2010).

5.4.3 Bioemulsifier Classification

The classification of emulsifiers is on the basis of their hydrophilic—lipophilic balance (HLB). Predominantly, an emulsifier is lipophilic when its HLB is low and has a water-soluble property when its HLB is high. A biosurfactant has two major components: a hydrophobic tail and a hydrophilic head, wherein the hydrophilic region consists of amino acids/peptides; mono, di/polysaccharides while the hydrophobic part consists of either unsaturated or saturated fatty acids which may be hydroxylated, in most of the cases. Glycolipids, lipoprotein, lipopeptides, phospholipids, fatty acids and polymeric bioemulsifiers are the major classes of bioemulsifiers (Desai and Banat 1997). This chapter generally confines to the glycolipid-type of emulsifiers because similar compounds were isolated by us.

5.4.3.1 Glycolipid Bioemulsifier

These are basically low molecular weight bioemulsifiers. Their structure includes carbohydrates and a long chain composed of aliphatic hydroxyl/aliphatic acids. Rhamnolipid, trehalolipid, and sophorolipid are the well-studied glycolipid bioemulsifiers. *Arthrobacter paraffineus* when grown on hydrocarbon substrates produced a trehalose lipid which was confined to the emulsion layer of the culture broths (Suzuki et al. 1969). *Rhodococcus erythropolis* is generally known to produce trehalose dimycolates (Wagner et al. 1983). It is said to have interfacial activities which could be widely applied for enhanced oil recovery (Kim et al. 1990). The trehalose lipid bioemulsifiers produced by *R. erythropolis* are mostly cell bound (Kretschmer et al. 1982). Extracellular sophoroselipids which consists of two glucose units each linked with 6` hydroxyl moieties are produced by different species of yeast. *Torulopsis bombicola* when grown on glucose and oil produced sophoroselipids which was obtained from the extracellular fluid (Itoh and Inoue 1982). Sophoroselipids are produced by *T. bombicola* ATCC 22214 when substrates such as glucose and vegetable oil were used in the medium. Because of the lower surface tension, sophorose lipids are not considered as very potent emulsifying agents (Cooper and Paddock 1983).

5.4.3.2 Rhamnolipid Bioemulsifier

The glycolipid bioemulsifier “Rhamnolipids” stands apart amongst the different categories of bioemulsifiers. *Pseudomonas* sp., produces these rhamnolipids predominantly which are classified as mono and dirhamnose containing lipids. It has been reported that *P. chlororaphis*, *P. aeruginosa, P. putida, P. plantarii,* and *P. fluorescens* are those species in this genus which produce rhamnolipids. Some of these bacteria are recognized producers of mono-rhamnolipids, while some produce both mono and di-rhamnolipids together. By the production method, the ratio of mono and di-rhamnolipids can be manipulated. The conversion of mono-rhamnolipids into di-rhamnolipids are mediated strictly by certain enzymes.

Rhamnolipid was initially discovered on 1946 (Bergström et al. 1946) and it was reported that *P. aeruginosa* when grown on glucose produced a glycolipid which was named as pyolipic acid. The production of glycolipids which contain rhamnose from *Pseudomonas aeruginosa* and the structure of rhamnolipid was elucidated (Jarvis and Johnson 1949). In general, two β-hydroxydecanoic acid groups are bound to two rhamnose groups with glycosidic linkages. When two of the β-hydroxy fatty acids are joined by ester linkages, the disaccharide portion possessed 1,3-glycosidic bonds. However, the bond between the two rhamnose groups was identified as an α-1,2-glycosidic, the linkage was predominantly ascertained by periodate oxidation and subsequent methylation (Edwards and Hayashi 1965). Thus, 2-*O*-α-1,2-*L*-rhamnopyranosyl-α-L-rhamnopyranosyl-*β*-hydroxydecanoyl-*β*-hydroxydecanoate was the chemical description given for this rhamnolipid (Fig. 5.3).

After this discovery, α-*L*-rhamnopyranosyl-*β*-hydroxydecanoyl-*β*-hydroxydecanoate, a monorhamnolipid was isolated from *P. aeruginosa* when grown on *n*-paraffin. It was also hypothesized that this monorhamnolipid is the

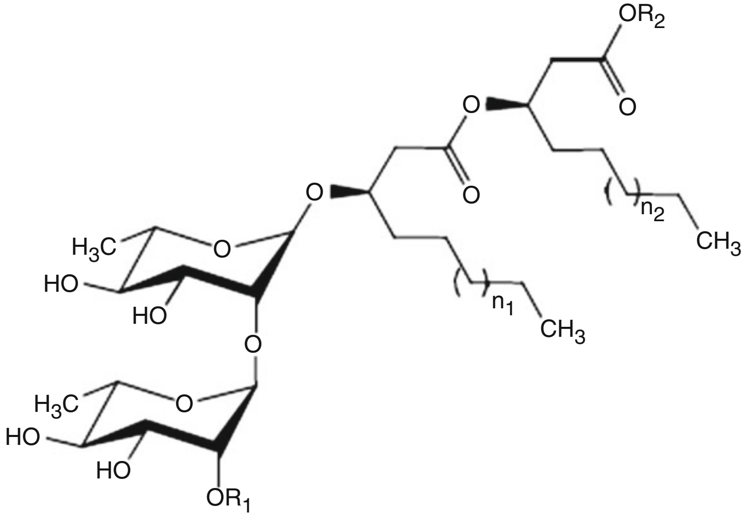


Fig. 5.3 A di-rhamnolipid from *Pseudomonas aeruginosa*

major precursor for di-rhamnolipid (Itoh et al. 1971). Two additional rhamnolipid congeners were produced by *Pseudomonas* sp. DSM 2874 when cultivated on glycerol. It was found that these two are very similar to the previously identified rhamnolipid with the difference being that it has only one *β*-hydroxydecanoic acid side chain (Syldatk et al. 1985). Different compositions of the rhamnolipid produced in the batch culture of *Cellulomonas cellulans* were reported by Arino et al. (1998). It was identified to be a mixture of 67% of di-rhamno-di-lipid, 22% of mono-rhamno-di-lipid and slightly lesser amounts of di-rhamno-mono-lipid (9%) and still a lesser amount of mono-rhamno-mono-lipid (3%).

In 1980s, a set of four other rhamnolipid congeners were identified. Two unusual di-lipidic rhamnolipids were produced by a *Pseudomonas* sp. when the sole carbon source used was *n*-paraffin. Acylation reaction with a 2-decenoyl group at the 2-hydroxyl moieties of the rhamnose molecules and a clear description of the congeners was also reported (Yamaguchi et al. 1978; Lang and Wagner 1987). These two congeners have been reported only by a very few teams since then. This may be an indication of their strain-specificity (Yamaguchi et al. 1978; Ishigami et al. 1987). Two novel rhamnolipids were found to methyl esters of the free carboxylic ends of two di-lipidic rhamnolipids were also identified previously. The only known nonionic rhamnolipids are these two methylated congeners (Hirayama and Kato 1982). The isolated rhamnolipids were found to include rhamnolipid homologues such as, RL1, RL2, RL3 and RL4 (Abdel-Mawgoud et al. 2010).

A clinical isolate of *P. aeruginosa* produced five new di-rhamnolipid congeners which was found to have aliphatic chains of variable lengths (C_8-C_{10}, C_{10}-C_8, C_{10}-C_{12}, C_{12}-C_{10}, and C_{10}- $C_{12:1}$) (Rendell et al. 1990). A total of 28 rhamnolipids, the di-rhamnolipid congeners which contain C_8-C_{10}, C_8-$C_{12:1}$, $C_{12:1}$-C_8, $C_{12:1}$-C_{10},

$C_{12:1}$-C_{12}, C_{10}-$C_{14:1}$, C_{12}-C_{12}, C_8, $C_{12:1}$, and C_{12} moieties, and also certain new monorhamnolipid congeners with C_8-C_8, $C_{12:1}$-C_{10}, C_8, and C_{12} moieties which was secreted by *P. aeruginosa* when nourished with mannitol or for that matter even naphthalene (Deziel et al. 1999; Deziel et al. 2000). New monorhamnolipid congeners ($C_{8:2}$ and $C_{12:2}$) which are polyunsaturated with β-hydroxy-fatty acid chains was identified from *P. aeruginosa* cultures (Abalos et al. 2001). *P. aeruginosa* (AT10) also produced the same congeners in significant amounts (Haba et al. 2003). In the cultures of *Pseudomonas chlororaphis*, a monorhamnolipid with C_{10}-$C_{14:1}$, C_{12}-$C_{12:1}$, and C_{10}-C_{14} were detected (Gunther et al. 2006). Other monosaturated di-rhamnolipid congeners were also identified (Sharma et al. 2007). *P. aeruginosa* LBI produced new monorhamnolipids containing C_8-$C_{10:1}$, C_{10}-$C_{10:1}$, and $C_{12\text{-}C12}$ chain lengths (Nitschke et al. 2010). Monorhamnolipid congeners containing $C_{14:2}$ and $C_{10:1}$-C_8 moieties were produced by a *P. aeruginosa* mutant (MIG-N146) (Guo et al. 2009).

Apart from *P. aeruginosa*, other *Pseudomonas* spp. reported to produce rhamnolipids are the following: *P. alcaligenes* (Oliveira et al. 2009), *P. cepacian* (Onbasli and Aslim 2009), *P. chlororaphis* (Gunther et al. 2006), *P. fluorescens* (Onbasli and Aslim 2009; Wilson and Bradley 1996; Vasileva-Tonkova et al. 2006; Husain 2008; Abouseoud et al. 2008), *P. luteola* (Onbasli and Aslim 2009), *P. putida* (Tuleva et al. 2002; Martinez-Toledo et al. 2006; Onbasli and Aslim 2009), *P. stutzeri* (Onbasli and Aslim 2009; Janiyani et al. 1992; Celik et al. 2008). Mono and di-rhamnolipids production in *P. clemancea*, *P. collierea,* and *P. teessidea* has been identified (Rahman et al. 2009).

5.4.3.3 Rhamnolipids from Non-Pseudomonads

Non-*Pseudomonas* sp. also has the ability to produce rhamnolipid bioemulsifiers. A rhamnolipid was isolated from *Acinetobacter calcoaceticus* (Rooney et al. 2009). Although *Pseudomonas* and *Acinetobacter* belong to different families, they come under the same Phylum: Gammaproteobacteria. Examples include *Pseudoxanthomonas* sp. (Nayak et al. 2009), *Enterobacter* sp., and *Pantoea* sp. (Vasileva-Tonkova and Gesheva 2007; Rooney et al. 2009).

The rhamnolipid synthesizing bacteria those do not come under the class Gammaproteobacteria have also been found. A new di-rhamnolipid which was produced by a *Pseudomonas glumae* was identified (Pajarron et al. 1993) and the organism was renamed thereafter as *Burkholderia glumae* (Urakami et al. 1994). Congeners with C_{14}-C_{14}, C_{12}-C_{14}, C_{14}-C_{12}, C_{14}-C_{16} and C_{16}-C_{14} have been discovered. Yet another species of *Burkholderia* that produced dirhamnolipids is *B. pseudomallei* (Haussler et al. 1998; Howe et al. 2006). Dirhamno-C_{14}-C_{14} congener and a few other rhamnolipid congeners with β-hydroxytetradecanoic acid: Dirhamno-C_{14} and Dirhamno-C_{14}-C_{14}-C_{14} (unpublished datum) was secreted by *Burkholderia plantarii* (Andra et al. 2006). *Burkholderia thailandensis* when cultivated on glycerol or vegetable oil and different combinations of fatty acids was found to produce new mono- and di-rhamnolipid homologues. *B. pseudomallei* produced a range of di-rhamnolipid congeners which was found to carry the same mixtures of C_{12}, C_{14}, and C_{16} fatty acids as found in *B. thailandensis* (Dubeau et al. 2009).

Myxotyrosides, an unusual glycolipid which contains rhamnose (rhamnoside) was produced by *Myxococcus* sp. (class Deltaproteobacteria). It consists of a core structure which is tyrosine-derived. The basic skeletal structure is glycosylated and acylated with rhamnose and unusual fatty acids, respectively, such as (Z)-15-methyl-2-hexadecenoic and (Z)-2-hexadecenoic acid. Although these are not the usual rhamnolipids, the authors claim that the rhamnolipids and the similarly acylated amino acids are the only molecules related to myxotyrosides (Ohlendorf et al. 2008).

Interestingly, bacteria such as *Cellulomonas cellulans* (Arino et al. 1998), *Nocardioides* sp. (Vasileva-Tonkova and Gesheva 2005), and *Renibacterium salmoninarum* (Christova et al. 2004) which belong to a different phylum other than *Pseudomonas* have the ability to produce rhamnolipids. These bacteria come under the phylum *Acetinobacteria*. *Tetragenococcus koreensis,* belonging to the Phylum-Firmicutes. New congeners are still being reported regularly (Lee et al. 2005).

5.5 How Difficult is Hexadecane Biodegradation?

Hexadecane (which is also known as cetane) is a hydrocarbon (Chemical formula: $C_{16}H_{34}$). It contains a 16 carbon chain wherein the three hydrogen atoms form bonds with two carbon atoms at the ends and two hydrogen atoms to each of the remaining 14 carbon atoms. Pollution caused by petroleum oil and its by-products pose a widespread ecological hazard (Kumar et al. 2018). Thus, the breakdown of hydrocarbons by microorganisms, in general, bacterial groups remain as a top priority among many researchers (Cameotra and Singh 2009). Hexadecane is also one of the constituents of crude oil which is categorized as water-immiscible. To evaluate the biodegradation and bioavailability of aliphatic compounds, most importantly and to understand the metabolic pathways, hexadecane (*n*-C16) is generally used as a reference standard (Dombrowski et al. 2016). Fuels which are used in most combustion engines, such as gasoline and diesel contain more amounts of aliphatic than aromatic compounds (Chenier et al. 2003; ITRC 2014; TOXNET 2016). In hydrocarbon-polluted sites, microbial degradation has been utilized as an alternative remediation technique. Based on the biochemical and microbiological aspects of a specific site, the rate of petroleum degradation takes place (Varjani and Upasani 2017). Soil polluted by hexadecane has notably known to pose danger to the terrestrial and marine ecosystems. Production of biosurfactants is a key mechanism, a process which is greatly exploited by organisms that degrade hydrocarbons, especially bacteria to use and assimilate such substrates. In natural ecosystems, the process of biodegradation of hexadecane is much complex owing to the long duration which is mainly because of its bulk size. Generally speaking, hexadecane or for that matter any hydrocarbon is utilized by a variety of microbial process as a carbon source which results in the breakdown of higher molecular weight compounds to lesser ones during the process of biodegradation. On the basis of

Table 5.1 Bioremediation of hexadecane by marine bacteria reported from the beginning till date

S. No	Microorganisms	Studies carried out in vitro	References
1	*Acinetobacter calcoaceticus subsp. anitratus*	Ethanol precipitation; stability studies; emulsification activity; emulsifies hexadecane	Phetrong et al. (2008)
2	*Acinetobacter calcoaceticus* (BS); *Alcanivorax dieselolei* (PG 12)	Crude oil removal assay –82% and 71%; n-alkanes (C9-C25) degradation by these two organisms C16 degradation - 48% and 100%; biosurfactant production: Drop collapse, oil displacement; emulsification activity; bacterial adhesion to hydrocarbons; surface tension reduction assays; presence of alkB gene	Hassanshahian et al. (2012)
3	*Phormidium* sp	Biodisks of Phormidium sp. in 150 ml of media with hexadecane (0.3%) and diesel (0.5%); ethanol extraction; gas chromatography; emulsification index; hexadecane removal - 45%	Morales and Paniagua-Michel (2013)
4	*Bacillus amyloliquefaciens*, *Staphylococcus epidermidis*, *Micrococcus luteus, Nitratireductor aquimarinus*, and *Bacillus pumilus*	Hexadecane biodegradation screening; biodegradation analysis; biodegradation index above 97%	Ferrari et al. (2019)
5	*Bacillus cereus* (J3), *Staphylococcus haemolyticus* (J5) and *Pseudomonas aeruginosa* (J12)	Hemolytic activity, oil spreading, emulsification activity, surface tension measurement; crude oil removal assay –66%, 53%, and 43%; J3 degrades C9-C25 n-alkanes. In consortia, n-alkane degradation increases. Removal of 60% of n-alkanes in crude oil residues	Tanzadeh et al. (2020)

the details known from alkane oxidation, generally these reactions are enhanced by alkane mono/di-oxygenases and invariably these reactions produced the respective alcohols. Thereafter further oxidation happens with a formation of an aldehyde and its associated fatty acid by respective alcohol and aldehyde dehydrogenases. In general, primary alcohols and fatty acids of the similar chain lengths for the bacterial cultures grown on *n*-hexadecane is a clear-cut indication that there happens oxidative attack specifically at the methyl groups of such hydrocarbons.

A thorough review is being done here to understand which non-marine and marine bacterial species could utilize hexadecane as their carbon source and listed in Tables 5.1 and 5.2. From both the tables it is very clear that only a hand full of bacteria could utilize hexadecane both from marine (Phetrong et al. 2008;

Table 5.2 Bioremediation of hexadecane by non-marine bacteria reported from the beginning till date

S. No	Microorganisms	Studies carried out in vitro	Studies carried out ex-situ	Type of biosurfactants	References
1	*Flavobacterium sp.* strain MTN11 isolated from soil	Reduces surface tension; strong and stable emulsifier; solubilizing agent and enhances hexadecane mineralization		Flavolipid	Bodour et al. (2004)
2	*Pseudomonas aeruginosa* isolated from oil contaminated soil	70% hexadecane degradation		Rhamnolipid	Cameotra and Singh (2009)
3	*Acinetobacter beijerinckii* ZRS isolated from an oil-contaminatedsoil sample	Emulsification activity—diesel, hexadecane, aromatic hydrocarbons; optimization of medium for BE production; stability studies; extraction and characterization of BE	Oil spill bioremediation simulated experiment: The beach-simulating tank system; crude oil degradation—58.3%	Glycolipoprotein complex	Zhao et al. (2016)
4	*P. aeruginosa* PG1 isolated from hydrocarbon contaminated garage soil	Degradation of crude oil (and n-alkanes - C16); degrades 81.8% of total petroleum hydrocarbons (TPH); biosurfactant production, extraction, characterization; emulsification activity -emulsifies hexadecane; reduces surface tension		Rhamnolipid	Patowary et al. (2017)
5	*Bacillus* sp. L30 isolated from contaminated groundwater	Degradation of n-alkanes (C10-C27) in diesel; biosurfactant production: Drop collapse test; emulsification activity - for hexadecane 19.4 ± 1.91; presence of alkane hydroxylase alkB gene (group III)			Lima et al. (2019)

Hassanshahian et al. 2012; Morales and Paniagua-Michel 2013; Ferrari et al. 2019; Tanzadeh et al. 2020) and non-marine sources (Bodour et al. 2004; Cameotra and Singh 2009; Zhao et al. 2016; Patowary et al. 2017; Lima et al. 2019) and almost all the works are limited to in vitro experiments only. Among the bacterial groups only *Bacillus, Pseudomonas* and *Acinetobacter* could effectively utilize hexadecane. The mostly stated biosurfactant types are rhamnolipids followed by a lipoprotein and a flavolipid. In the following section works from our laboratory with respect to screening of hexadecane consumers and the potent bioemulsifiers produced are discussed.

5.6 Works from Our Laboratory

5.6.1 Isolation and Evaluation of Bacteria for Bioemulsifier Production

While in the previous section an extensive review has been made emphasizing the role of the genus: *Pseudomonas* and its species in producing biosurfactants and utilization of aliphatic hydrocarbons, this section will focus on a particular species, *guguanensis*. A wide range of sampling sites were chosen and microbiological screening was huge isolation programme was conducted at six different locations in the Indian coast, particularly in the Southeast border: 1. Tuticorin, 2. Olaikuda boat jetty, 3. Fishing boat jetty at Gulf of Mannar and three points of Chennai harbor, ie., 4. Signal station, 5. Container and 6. Sailing regions. The first three sites are designated as "highly biodiversified areas" under the Gulf of Mannar Biosphere Reserve. Hence it can always be hypothesized that bacterial species prevalent in these areas to be highly competent owing to the rich biodiversity. Three types of media: Minimal Salt medium, Bushnell and Haas Medium, and ZoBell Marine Medium were used for isolation process. Different hydrocarbons like, crude oil, tributyrin, diesel, and *n*-hexadecane were supplemented to the aforementioned media for recovery of maximum isolates as shown in Fig. 5.4. More than 849 bacterial isolates were isolated and all of them were put to rigorous screening for hydrocarbon utilizing capacities by employing assays, such as hydrocarbon dispersion (Morikawa et al. 1993) and Emulsification Index$_{24}$ [EI_{24}] (Cooper and Goldenberg 1987). As a preliminary check, the expended medium of the bacterial isolates alone were used for these assays. Both oil spread and emulsification assays showed only 0.0023% of the total isolates to be positive, i.e., only two isolates. They were identified as *Pseudomonas aeruginosa* and *Pseudomonas guguanensis.* Since there are numerous reports to quote the oil degrading properties of *P. aeruginosa,* the latter was chosen to mention in detail in this section.

The identity of *P. guguanensis* was established by 16S rRNA gene sequencing and the blast sequences were submitted to GenBank with the accession number: KU302611]. The results of the *e*mulsification activities on the different types of hydrocarbons by the spent broths of *P. guguanensis* are illustrated as Fig. 5.5. In a large-scale cultivation of this potent bacterium in a 40 L fermentation vessel, it was

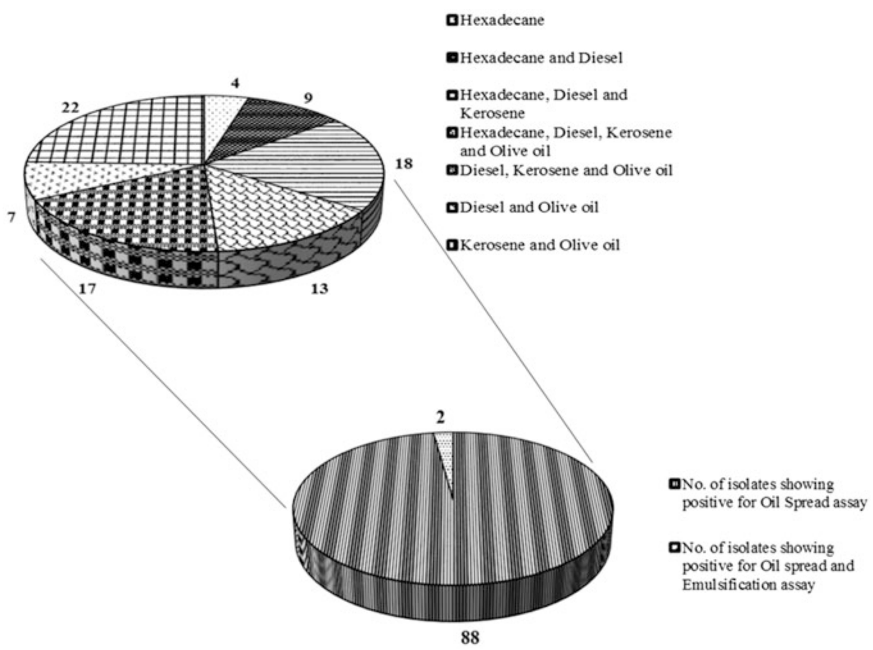


Fig. 5.4 Bacterial population [90 amongst 849 isolates] possessing oil spreading [up] and oil emulsifying (2.2% of oil spreaders) [down] abilities

found that the yield of the bioemulsfier was only 2 g and that too at day 7. The emulsifier was categorized as a rhamnolipid that possessed three compounds, i.e., a rhamnose sugar and two aliphatic hydrocarbon chains. The molecular weight of this compound was higher than 1000 Da (close to 1250 Da) and hence it is better named emulsifier and not as surfactant. The following section will give information on the chemical and biological properties of this bioemulsifier.

5.6.2 Chemical Properties of the Bioemulsifier from *P. guguanensis*

The emulsifier was identified as an unusual mono-rhamnolipid which is composed of three compounds: The combination of all the three molecules synergistically possessed emulsification activity. In contrast, the individual or combination of two compounds not showed the emulsion activity. The chemical structures of compounds 1–3 are given as Fig. 5.6.

The compound 1 appeared as dark yellowish waxy oil and isolated in 24 mg. The FT-IR analysis of compound 1 indicated the intramolecularly bound alcoholic hydroxyl (-OH) groups, C-H stretching vibration from long alkyl chains and also the presence of aliphatic ester carbonyl and C-O stretching vibration. The structure of palmitic acid-glycerol ester has been identified with the support of fragmentation pattern of mass spectrum obtained from GC-MS. In addition, ^{1}H and ^{13}C NMR

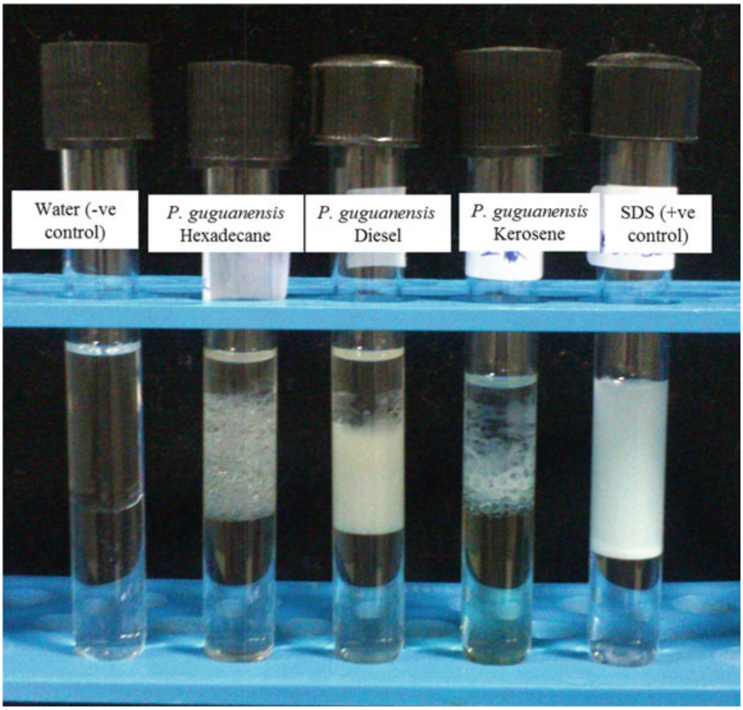
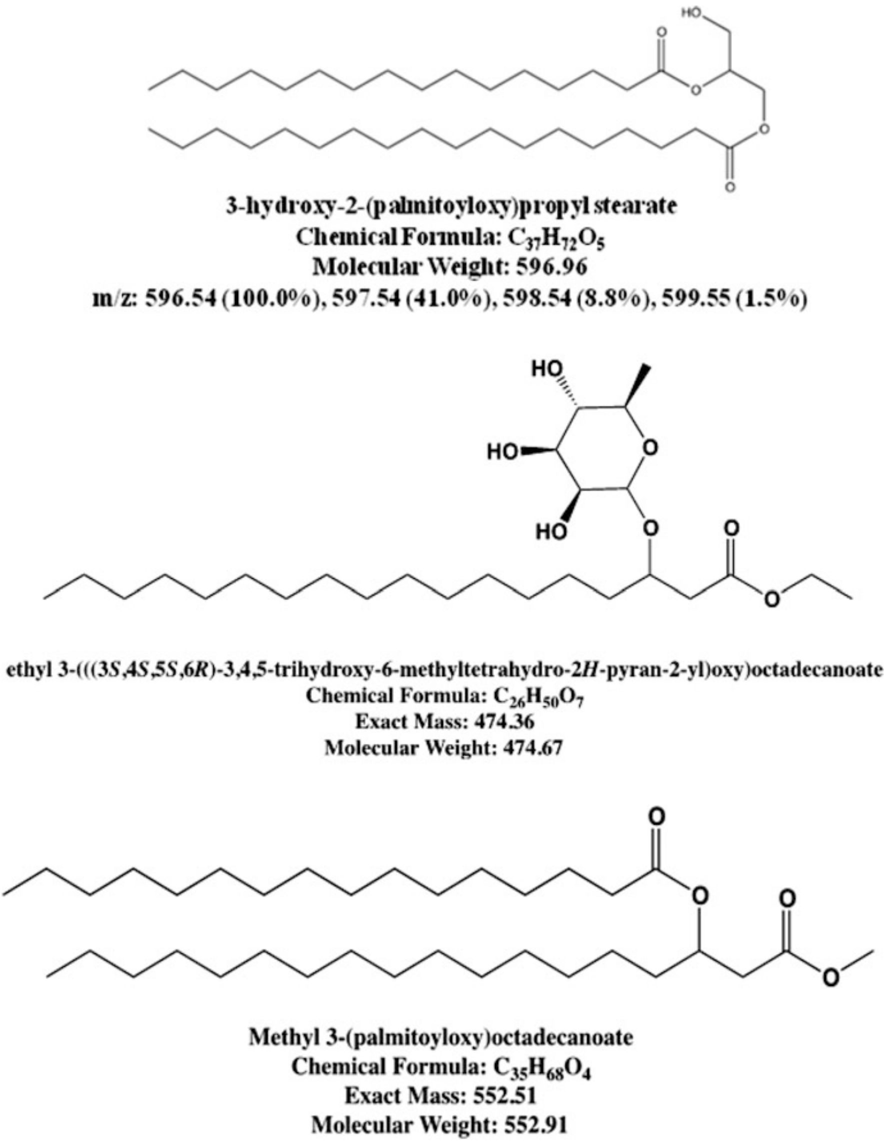


Fig. 5.5 Bioemulsifier containing expended media [≈1 OD at Abs660] of *P. guguanensis* emulsify different types of hydrocarbons

studies confirmed the presence of long hydrocarbon chain of fatty acid, ester group as well as glycerol ester groups in the compound 1. Hence, compound 1 is named as 3 hydroxy-2-(palmitoyloxy) propyl stearate with a molecular formula $C_{37}H_{72}0_5$ and molecular weight of 596.96 g. mol^{-1}.

Compound 2 was isolated as yellow oily shiny soft crystalline semi-solid and the yield was found to be 41 mg. In FT-IR spectrum, the presence of broad peaks in 3500–3000 cm^{-1} range revealed hydrogen bonding of the alcoholic groups present in Rhamnose sugar. The study revealed the presence of alkyl chain C-H vibration and ester carbonyl groups from the respective FT-IR peaks. Further, the structure of compound 2 is ascertained to be a rhamnose sugar attached with 3-hydroxy hexadecanoic acid ethyl ester. Further, the study also revealed rhamnose sugar connected to hydroxy group of hexadecanoic acid. The carbon skeleton of Compound 2 contained an ester carbonyl, hydroxy carbon and C=O was confirmed by 13C NMR while the presence of fatty acid and rhamnose sugar was confirmed using ^{1}H NMR. Based on the spectral studies, compound 2 was confirmed to be a ethyl ester of 3-((Rhamnosyl)-2-oxy)octadecanoate.

Compound 3 was purified as an oily substance with dark yellowish-brown color weighing 8 mg. The compound was subjected to FT-IR study which showed the



3-hydroxy-2-(palmitoyloxy)propyl stearate
Chemical Formula: $C_{37}H_{72}O_5$
Molecular Weight: 596.96
m/z: 596.54 (100.0%), 597.54 (41.0%), 598.54 (8.8%), 599.55 (1.5%)

ethyl 3-(((3*S*,4*S*,5*S*,6*R*)-3,4,5-trihydroxy-6-methyltetrahydro-2*H*-pyran-2-yl)oxy)octadecanoate
Chemical Formula: $C_{26}H_{50}O_7$
Exact Mass: 474.36
Molecular Weight: 474.67

Methyl 3-(palmitoyloxy)octadecanoate
Chemical Formula: $C_{35}H_{68}O_4$
Exact Mass: 552.51
Molecular Weight: 552.91

Fig. 5.6 Structural details of compounds 1, 2 and 3 of the rhamnolipids of *P. guguanensis*

presence of alcoholic hydroxyl groups, alkyl chain and ester carbonyl functional groups. Mass fragmentation pattern confirmed the presence of palmitic acid and α-hydroxy palmitic acid. Additionally, the confirmation of fatty acid chain, ester group, and other alkyl chains connected alcoholic group of palmitic acid was obtained using ^{1}H NMR and ^{13}C NMR. Thus compound 3 was identified to be a methyl 3-(palmitoyloxy) octadecanoate.

5.6.3 Biological Properties of the Bioemulsifier

Among the hydrocarbons, n-hexadecane preferentially emulsified by the extracellularly secreted monorhamnolipids with Emulsification Index (EI_{24}): 56 ± 1.42% using 2 mL of the used medium. The ethyl acetate partitioned extract possessed an EI_{24} value of about 65%, while the purified rhamnolipid product showed 78% and the concentration of the samples used were 12.5 mg/mL concentration. It is interesting to observe that individual or combination of any two components not showed any emulsifying activity on n-hexadecane in water but mixture of all the three components showed emulsifying activity.

Surface-active property of the isolated mono-rhamnolipid from *P. guguanensis*, the reference compound (*n*-hexadecane) (to which it showed maximum emulsification), control (water) and reference control (SDS) were all estimated by GBX 3S tensiometer [Dublin, Ireland] by employing Wilhelmy plate technique (Wilhelmy 1863). Water as well as the used up broth had surface tension of 70–72 mN/m, whereas the purified mono-rhamnolipids of *P. guguanensis* was at 32.98 ± 0.3 mN/m, indicating better surface-active property.

Scanning Electron Micrographs of the bacterial cultures revealed an increasing pattern of extracellular secretion of mono-rhamnolipids that reached maximum on the sixth day (as observed in Fig. 5.7) of the investigation period. When the bioprocess parameters for obtaining maximal emulsification efficiencies were standardized, the sixth day yet again showed maximum results which is concordant with the SEM results. There was a striking difference between the amount of *n*-hexadecane present in the uninoculated and inoculated culture tubes at the end of the experimentation period as seen by the peak area obtained from GC-MS analysis (data not shown). We were able to observe a 77.2% removal of hexadecane and degradation of C_{10}-C_{18} fatty acids as compared with library of references, preloaded in the software. These fragments overlap with the components of the monorhamnolipids produced by this bacterium which suggest that these fragments may be used in the production of rhamnolipids and this idea is discussed below.

5.6.4 Biosynthesis of Rhamnolipids of *P. guguanensis* as Compared with *P. aeruginosa*

Hexadecane is opted as a reference substrate to investigate crude oil degradation and diesel (Schoefs et al. 2004). Based on the analytical results, we recommend the possible pathway on synthesizing mechanism of the reported three compounds present in *P. guguanensis,* which together worked as an emulsifier. We have arrived at a biosynthetic pathway for the production of this emulsifier based on the spectral and chromatographic on the substrate and the products formed (as given in Fig. 5.8). We have observed that the degradation begins with conversion of the methyl group of n-hexadecane to give hexadecan-1-ol as reported in *Pseudomonas aeruginosa* previously (Meng et al. 2017; Nie et al. 2017). Further, the hexadecan-1-ol is oxidized to palmitic acid, which supported by other reports (Meng et al. 2017;

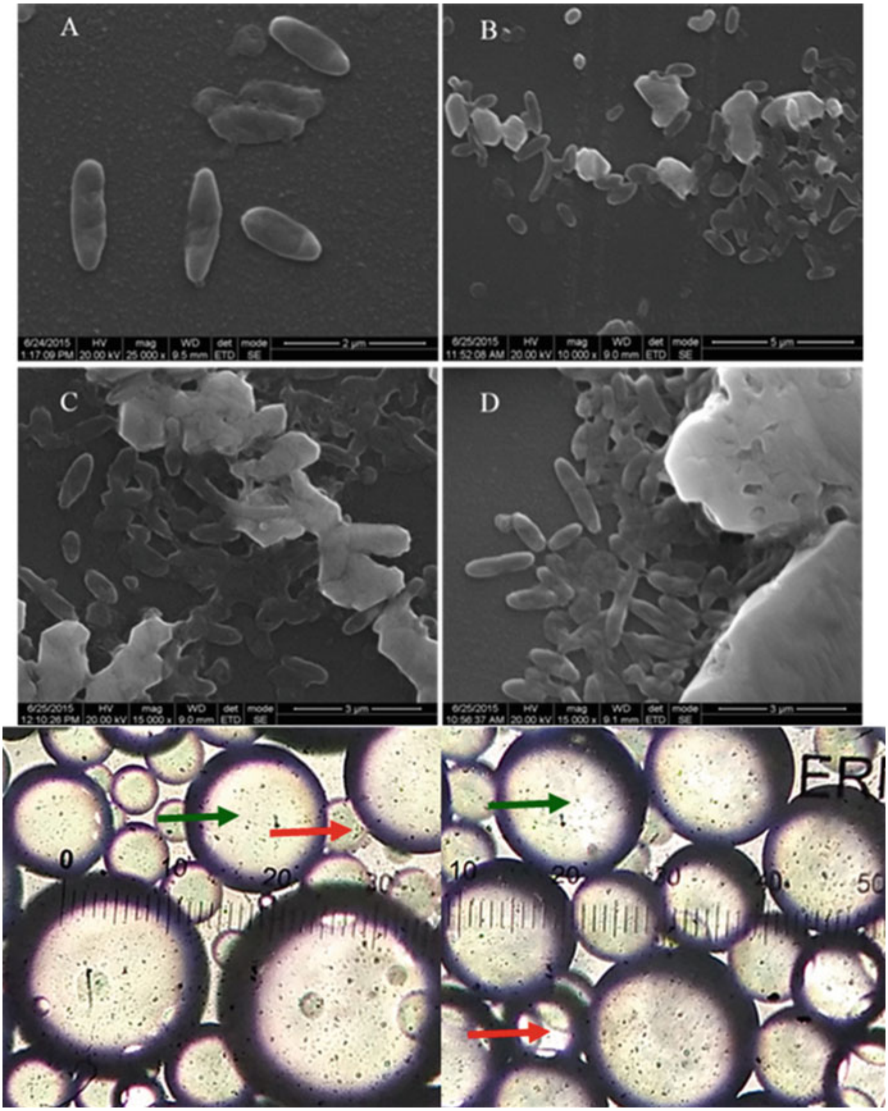


Fig. 5.7 Oiled cultures of *P. guguanensis* showing extracellular secretion of monorhamnolipids on the 2nd [B], 4th [C], and 6th day [D] of the experimental trials as against unprovoked controls [A] given as Scanning Electron Micrographs (SEMs). Micrographs of water-hexadecane emulsions formed by mono-rhamnolipids (left) and SDS (right) both at 5 mg/mL concentration as exactly viewed in 10X magnification in an optical Nikon Eclipse 200 binoculars (green and red arrows indicate water and hexadecane droplets, respectively)

Zhu and Rock 2008). Oxidative transformations promoted by alkane hydroxylase and hexdecan-1-ol dehydrogenase usually occur in the extracellular region to aid the uptake of the available carbon by the bacterial consortium. The palmitic acid

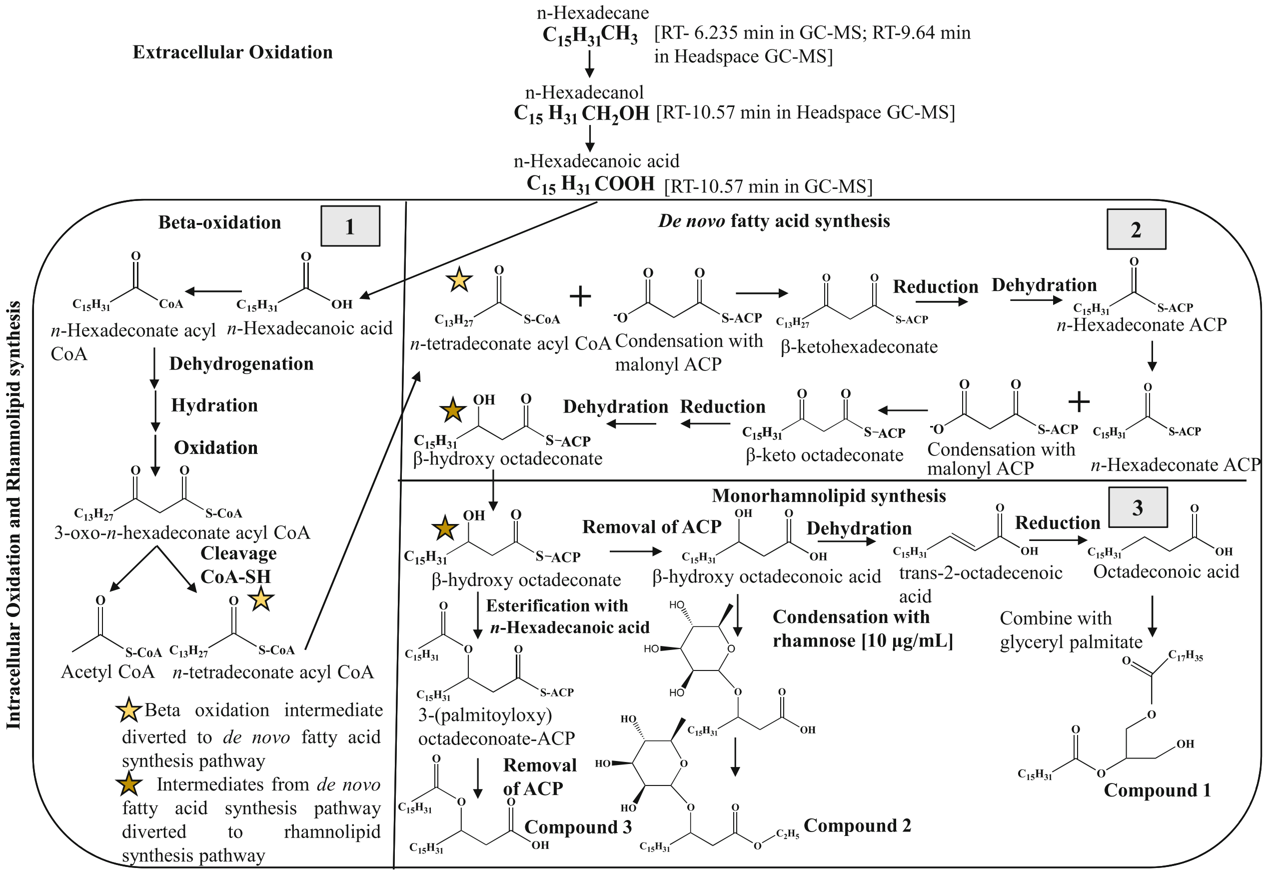


Fig. 5.8 Proposed de novo synthetic pathway of monorhamnolipids in *Pseudomonas guguanensis*

transported through the bacterial membranes inward the cell to form a conjugate with coenzyme A (CoA). A study using isotope tracing method and assays of gene expression reported that *n*-tetradeconate acyl CoA undergoes fatty acid synthesis de novo that led to the production of rhamnolipid precursors (Yuan et al. 2012), which was catalyzed by β-ketoacyl ACP synthase (Zhang et al. 2012). Further, the reduction of the keto group to alcoholic group formed 3-hydroxystearic acid and subsequent elimination of water to form trans-2-hexadecenoyl ACP. Similar cycle has been repeated to form β-hydroxyoctadeconate. The precursors obtained for the biosynthesis of compounds, 1, 2, and 3 obtained from three different routes to attribute a synergistic role to the bioemulsifer are proposed herein.

De-esterification of β-hydroxyoctadeconate led to β-hydroxyoctadeconoic acid (HAA) followed by the removal of water to give trans-2-octadecenoic acid and conversion to stearic acid is by hydrogenation reactions. Thus, compound 1 can be formed by esterification of octadecanoic acid with glyceryl palmitate. The mechanism of compound 2 formation followed the condensation of β-hydroxyoctadeconoic acid with a rhamnose sugar containing octadecenoate. Further, it may be also possible that due to the presence of hydroxyl group in β-hydroxy octadeconate, formation of 3-(palmitoyloxy) octadecenoate (compound 3) is achieved because of the availability of free fatty acids in the cell, followed by the removal of ACP. Based on our studies, the most plausible synthetic route for the bioemulsifiers is thus proposed.

5.7 Conclusion

Generally, it is believed that only a narrow niche of bacterial species produce biosurfactants because of a few reasons: 1. It is hard to utilize bulk hydrocarbons as they do not diffuse easily through the cell walls. 2. Production of biosurfactants is a cumbersome and energy expending in principle. Both these factors put together during a hydrocarbon stress, give the organisms all the more difficulty to get evolved and be fit enough to express those genes that are particularly involved in the biosynthetic pathway of biosurfactants. Moreover, biosurfactants are produced in minimal amounts and released out of the cell in a time and concentration-dependent manner and hence large-scale cultivation of biosurfactant producers depend on a lot of factors, including temperature, pH, salinity, nutrients supplied, and many other culture conditions. However, permutation studies involving computerized reactions using a variety of software for the purpose, most importantly, Response Surface Methodology (RSM), can certainly increase the yield of biosurfactants. *P. guguanensis* listed in this section was permuted for various bioprocess factors like carbon and nitrogen sources, pH, and time courses, all of which were validated using RSM tools. When the results obtained from the permutation experiments were used as the base for fixing the conditions for cultivation and growth of the bacterium under laboratory conditions, close to a three-fold more rhamnolipid production was reported by the authors. Despite the small amounts of production of biosurfactants in nature, certainly these amphiphilic molecules are considered as better choices than chemical dispersants. The price of a 10 g quantity of any rhamnolipid (90% purity) is around Rs. 10,000/− and there is a huge market for the same. Hence let us look forward to biological means of hydrocarbon degradation by way of relying on microorganisms, especially bacterial systems, which offers a steadfast and a safe way to bioremediation.

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Application of Bio-Nanoparticles in Biotechnological Process Focusing in Bioremediation

6

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Abstract

Environmental contamination is a problem that currently faces the world-wide population due to extensive industrialization, urbanization, and new agricultural practices. Several and different pollutants profoundly alter water, soil, and air, producing biodiversity extinction, the decline in soil condition, and harming human health. Hence, various environmental remediation systems have been investigated, using biological and physicochemical approaches. This chapter examines new techniques for the remediation of contaminated systems using nanotechnology. General concepts about nanoparticles such as, types, methods of production, properties, and distinctive characteristics. It focuses in particular on the use of green synthesis nanoparticles for the bioremediation of soils and water.

Keywords

Bioremediation · Bio-nanoparticles · Synthesis mechanism · Microbes

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6.1 Introduction

Environmental contamination is a problem that currently faces the world-wide population due mainly to technological progress and demographic growth. Especially contamination with heavy metals is of great concern due to their high toxicity. Mercury (Hg), lead (Pb), arsenic (As), nickel (Ni), cadmium (Cd), zinc (Zn), copper (Cu), and chromium (Cr) are among the most common pollutants (Hansda et al. 2014).

Even though it is natural to find metals in the ground, when the values are above a certain limit they are seen as sources of environmental pollution. Metals are considered important even in trace concentrations since they cannot degrade and consequently cause physiological effects in living organisms. Contamination of the soil by heavy metals can cause disorder in their structure. Besides, metals accumulate in plants, joining finally, into the cycle of the food. Thence it is of great importance to protect soil and ensure its stability. The tendency of heavy metal accumulation in the soil is growing and its impact will be evidenced after years (Esmaeilzadeh et al. 2019). Numerous methods have been used to approach this problem, for example, ion exchange, chemical precipitation, reverse osmosis, dialysis, and solvent extraction (Xu et al. 2017). Nevertheless, such techniques have high costs and low efficiency, in addition to showing adverse effects on the soil structure, changing their natural composition (Azimi et al. 2017). To get over these inconveniences, alternative ecological methods have been developed (Uqab et al. 2016). Researches are increasingly promoted for the development of green strategies to speed up decontamination of soil and water, in addition, to cheapen pollutant removal. Biologically based methods known together as bioremediation have shown great potential (Philp and Atlas 2005).

Bioremediation is able to eliminate smaller concentrations of pollutants in comparison with environmental clean-up physical or chemical methods. These methods offer a profitable remediation technique and environmentally friendly (El-Kassas et al. 2016).

Amongst the newer methods, the use of nanomaterials and their field applications have been the objective of several laboratory studies, mainly in North America and Europe.

The combination of bioremediation with nanomaterials has a huge potential because of efficiency and sustainability (Cecchin et al. 2016).

The fundamental component of nanomaterials is nanoparticles (NPs). They are particles from 1 to 100 nm which most important characteristic lies in the high surface area (Bhardwaj and Kaushik 2017). Amongst the different existing NPs, metallic NPs composed of pure metal atoms (zinc, silver, gold, cerium, thallium, and iron) or their compounds (oxides, hydroxides, sulfides, phosphates, fluorides, and chlorides) stand out. So far, they are the most promising types of nanomaterials due to their diverse applications, highlighting those related to the field of bioremediation (Salvadori et al. 2018).

There are different forms to synthesize NPs. The most innovative and eco-friendly of such methods use biomolecules from microorganisms or plants to reduce a metallic precursor, resulting in the obtention of NPs (Singh et al. 2016c). The use of biosynthesized NPs in the area of bioremediation implies the combination of two green technologies as a sustainable alternative for cleaning different polluted environments.

6.2 Nanotechnology

Nanotechnology is considered a multidisciplinary science responsible for the understanding and manipulation of materials involved in the manufacture, development, and study of nanomaterials. In recent years, nanotechnology has acquired great global interest because their development represents important progress in different areas such as optics, mechanics, foods, environmental, space industries, biomedicine, healthcare, tissue engineering, among others (Sudha et al. 2018). This will make possible to achieve important scientific advances oriented to the manufacture of new materials with extraordinary properties or, to the development of those already existing, with a significant improvement of their characteristics (weight, density, conductivity, resistance, hardness, etc.) (Saratale et al. 2018).

6.2.1 Nanoparticles

The fundamental component of nanomaterials is nanoparticles (NPs). Nanoparticles can be defined as any particle from 1 to 100 nm, and that behaves as a unit in terms of structural properties, functionality, transport, and interaction with other species and with the environment (Bhardwaj and Kaushik 2017).

One of the most important characteristics of NPs which makes them more advantageous compared to their precursor material lies in their high surface-volume ratio. The shape and structure of NPs are important parameters that must be taken into account for possible applications in the area of nanotechnology. These distinctive features are responsible for their various electronic, optical, electrical, magnetic, chemical, biological, and mechanical properties. Thus, spherical, cylindrical, flat, cubic, icosahedral, triangular, etc., NPs can be found (Khan et al. 2019).

6.2.2 Organic Nanoparticles

Conforming to the chemical nature, NPs are classified into two main groups. Organic NPs involve organic polymers such as lipids, proteins, and membranes, among other biological materials. Micelles, dendrimers, ferritins, liposomes are some of the organics NPs that can be mentioned. This kind of NPs is characterized as being non-toxic, biodegradable, being sensitive to thermal and electromagnetic radiation such as heat and light (Ealias and Saravanakumar 2017). Organic NPs are one of the most used in the biomedical area, for example, in the system of directed administration of medications, since they can be injected into specific parts of the body, reaching good drug stability (Moeinzadeh and Esmaiel 2017).

6.2.3 Inorganic Nanoparticles

Inorganic NPs are composed of pure or combined atoms forming a crystalline structure when they are interacting. This type of NP is characterized by excellent chemical and physical properties, which convert them into very important candidates for the manufacture of optical, electronic, and magnetic devices. Inorganic NPs are also recognized for their great catalytic power, which allows classifying them into two groups: non-metallic and metallic. Non-metallic NPs are generally based on carbon atoms. This atom is very versatile for the formation of different structures due to its allotropic character (Moeinzadeh and Esmaiel 2017).

The metal NPs are composed of pure metal atoms (zinc, silver, gold, cerium, thallium, and iron) or their compounds (oxides, hydroxides, sulfides, phosphates, fluorides, and chlorides). From a practical point of view, metal NPs are very important at present, since they represent the most promising kinds of nanomaterials because of their electrical, magnetic, optical, catalytic, and thermal properties, antimicrobial activity, and applications in bioremediation (Slavin et al. 2017). Some examples of metallic NPs are:

-quantum dots: semiconductor NPs that are generally used as imaging probes, since they have high quantum yields of fluorescence, high photostability, and a fluorescent emission that can be variable according to their size (Namdari et al. 2017).

Iron oxide nanoparticles (FeO NPs): biocompatible and easily biodegradable. They are widely used for the purification of contaminated water. They also have great potential in biomedicine given their intrinsic ability to be monitored in vivo by nuclear magnetic resonance techniques (Ali et al. 2016).

6.3 Nanoparticles Synthesis

The development of methods to obtain NPs with controlled chemical composition, shapes, and sizes became a field of great interest for research. The numerous methods of synthesis of NPs that have been proposed involve two types of strategies: the “top-down” or the “bottom-up” paths (Hu and Shaw 1999). The term “top-down” refers to the obtaining of NPs from micromaterials, such as the mechanical crushing of the microcellulose by a grinding process to obtain nanocellulose. In the “bottom-up” strategy, structures are constructed atom by atom. An example is the chemical production of AuNPs or ZnNPs by reducing agents. The selection of the procedure is related to the specific characteristics of the desired NPs and their chemical composition (Al-Kassas et al. 2017).

The NPs obtention can be carried out by different physical, chemical, or biological methods.

6.3.1 Physical Methods

Physical methods consist of the use of high radiation or mechanical pressure, electrical or thermal energy for NPs obtention. This causes the abrasion, fusion, evaporation, or condensation of the material, thus generating the NPs (Ealias and Saravanakumar 2017). Generally, these methods follow a "top-down" strategy and have certain advantages such as avoiding the use of solvents and producing uniform monodispersed NPs. On the other hand, the abundant residues produced during the synthesis make these methods more expensive (Abbasi et al. 2016). Some examples of physical synthesis to highlight are electrospraying, laser ablation, laser pyrolysis, physical vapor deposition, and ash spray pyrolysis (Ealias and Saravanakumar 2017).

6.3.2 Chemical Methods

Techniques such as hydrolysis, condensation, precipitation, emulsification, among others, together with chemical reducing agents and organic and inorganic solvents are used. Some reducing agents currently used are polyethylene glycol, ascorbate, sodium citrate, N, N-dimethylformamide, sodium borohydride, elemental hydrogen, etc. (Ealias and Saravanakumar 2017). This type of synthesis has advantages with respect to physical methods such as greater control in the morphology and structure of the NPs, higher speed of production, and greater control of the process. However, chemical methods have unfavorable characteristics because of the use of harmful chemicals as stabilizing and/or reducing agents for the NPs produced and the extremely stringent conditions of pH, temperature, and pressure that must be taken into account to synthesize certain NPs.

Some of the most commonly used chemical methods are hydrothermal synthesis, sol–gel method, chemical vapor synthesis, and microemulsification (Abbasi et al. 2016).

6.3.3 Biological Methods

It has been explained that different plants and organisms can perform as "bio-nano-factories" for the fabrication of metal oxide and pure NPs using biomimetic methods. It has been recognized that biomolecules from these organisms (microorganisms, bacteria, and fungi) and plants perform an operating role in NPs production with different sizes and shapes (Sharma et al. 2019). Bio-NPs are synthesized when metal particles are reduced by means of the bioreductors synthesized by the cells themselves (Gour and Jain 2019).

Microorganisms can detoxify heavy metals because they have a variety of biomolecules, among which are different reductase enzymes with the capacity of reducing metal salts and form metal NPs with low polydispersity. Proteins, metal-resistant genes, enzymes, peptides, organic materials, and reducing cofactors act as reducing agents and provide a natural capping to the synthesized NPs, giving additional stability (Singh et al. 2016c).

Biological methods have a great number of advantages over traditional chemical methods. They are environmentally friendly, energy saving, and cheaper. The synthesized NPs does not demand extra stabilizing agents because the biomolecules from plants and microorganism act as capping agents (Makarov et al. 2014).

In comparison with NPs obtained by chemical methods, this layer that covers its surface makes them biocompatible (Tripp et al. 2002; Hakim et al. 2005). The NPs biocompatibility offers notable applications in the biomedicine ground (Huang et al. 2015). For instance, when biological NPs interact with complex biological fluids, adsorb biomolecules gradually and selectively on its surface, developing a corona that participates in interactions with biological systems. The corona coat offers extra effectiveness over comparing with naked NPs (Monopoli et al. 2012; Mukherjee et al. 2012). The biogenic procedures allow the obtention of NPs with diverse sizes and interesting morphologies (Schröfel et al. 2014). Besides, green methods of synthesis can reduce significantly the toxicity of NPs and their synthesis process consumes a shorter time in comparison with physicochemical methodologies (Gour and Jain 2019). Biosynthesis of NPs applied in processes of bioremediation is a technique that promises to cope with the increasing demands for wastes treatment, particularly in relation to the activity of the heavy metal industry (Salvadori et al. 2018).

6.4 Bio-Nanoparticles Producing Organisms

6.4.1 Microorganisms and Algae

There are many examples of microorganisms, such as bacteria (Raliya et al. 2014; Wypij et al. 2017) fungi (Raliya and Tarafdar 2013; Bhargava et al. 2016), and algae (Arockiya Aarthi Rajathi et al. 2012; Zhang et al. 2016) acting as microbial-nanofactories of NPs.

Gold NPs of uniform size were obtained using *Penicillium rugulosum*, a bacterium frequently used in several industrial processes (Mishra et al. 2012). Platinum NPs of regular size and shape have been synthesized with the cell-soluble protein extract of sulfate-reducing bacteria (Riddin et al. 2010). In both cases, yields of NPs fabricated by enzymatic processes surpassed those obtained by traditional chemical methods.

The culture of *Verticillium* sp. in the presence of an aqueous solution of Ag^+ ions resulted in the synthesis of AgNPs. NPs were observed to be produced on the surface of the mycelia due to the electrostatic interaction between the carboxylate groups of negatively charged enzymes present in the cell wall and the Ag^+ ions. (Mukherjee et al. 2001).

The biosynthesis of NPs using algae is an emergent area of research. Different morphotypes of algae are being used as models for the synthesis of NPs, especially useful in bioremediation (Patel et al. 2015).

Fawcett et al. (2017) communicated that different bioactive chemicals, such as proteins and polysaccharides, present in the cell membrane of marine algae can play a role not just as reducing, but also as capping agents. The formation of stable, polycrystalline, spherical Au and Ag NPs was carried out using extracts of the brown macroalgae *Palmaria decipiens* and *Desmarestia menziesii* (González-Ballesteros et al. 2018).

6.4.2 Plant-Mediated Biosynthesis

Plant biomass submerged in water can be used for the synthesis of NPs (Gour and Jain 2019). Different parts of the plant (fruits, leaves, roots, stems, and their biomolecules) have been utilized to obtain metal NPs (Murugan et al. 2015; Naseem and Farrukh 2015). Although the mechanisms are not yet fully elucidated, it was suggested that organic acids, amino acids, vitamins, proteins, and secondary metabolites, like alkaloids, polysaccharides, flavonoids, heterocyclic compounds, polyphenols, and terpenoids, have an important function in the reduction of metal salts to obtain NPs.

Additionally, plant biomolecules may have a role as protection and stabilizing agents for the synthesized NPs (Duan et al. 2015). Nanoparticles of Au and Ag have been produced successfully employing leaf extract and root of the medicinal plant *Panax ginseng* (Singh et al. 2016a, b). Studies suggest that the different mechanisms used for the plant to synthesize NPs depend on the plant species (Baker et al. 2013). For example, cyperoquinone and remirin present in mesophytic plants are convenient, in general, to synthesize metal NPs. Emodin, a purgative resin present in xerophyte plants is specifically responsible for the synthesis of AgNPs (Makarov et al. 2014). Dicotyledonous plants have a great number of secondary metabolites that can participate in the NPs synthesis (Singh et al. 2016c).

6.4.3 Mechanisms of Nanoparticles Biosynthesis

As a result of the development of different defense mechanisms that microorganisms use to decrease environmental toxicity, appear diverse ways of NPs production (Bansal et al. 2012). Nevertheless, independent of the biosynthesis mechanism, it is imperative to optimize the conditions of NPs production to achieve monodispersity and to control the particle size. These are important considerations for its subsequent use in biotechnology (Jain et al. 2015).

6.4.3.1 Intracellular Synthesis

First, metallic ions are absorbed into the cell wall as a consequence of the attraction to the negatively charged functional groups along the cell surface (Erasmus et al. 2014). The second process comprises the passage of the metal ions into the cell through ATP-dependent pumps. Cellular enzymes reduce metallic ions and occasionally cap them, and consequently, the synthesis of NPs begins. Then, capping proteins neutralize NPs surface charge, binding to these through open amine groups and cysteine residues (Dávila Costa et al. 2020). Furthermore, these capping proteins prevent the agglomeration, playing an essential role as a site for bio-conjugation with other molecules (El-deeb et al. 2013). Stability decreases the toxicity of the NPs, making them more environmentally friendly (Stark et al. 2013).

6.4.3.2 Extracellular Synthesis

This synthesis of NPs can happen in two ways. The first one might be comparable to the intracellular mechanism: oxide-reduction enzymes perform the production of NPs when metal ions pass into the cell as described above. The capping and reducing proteins bind to the NPs during the reductive process. NPs are transported to the outside of the cell after configuring their size and shape. (Bansal et al. 2012). The second way consists of the expulsion of the reducing proteins to the solution of the exterior. This process is a result of the change in pH because of the presence of the metallic ions. At the moment that this signal is received, the cell activates the secretion of oxidoreductase enzymes that produce the reduction reaction and form NPs (Huang et al. 2015).

6.5 Methods for NPs Characterization

A very important step after the biosynthesis of NPs is their characterization. Because NPs of varied shapes and sizes can be obtained, which in turn will define their possible applications, various techniques are used to characterize them in depth. Some important parameters that can be known in this way are the morphology, size, elemental composition, and dispersion of the NP.

Ultraviolet-visible (UV-vis) spectrophotometer, energy dispersive X-ray spectroscopy (EDX), transmission electron microscopy (TEM), atomic force microscopy (AFM), scanning electron microscopy (SEM), and Fourier transform infrared spectroscopy (FTIR) are some of the most used methods for the characterization of NPs.

Surface plasmon resonance is what dominates the optical absorption spectra of metallic NPs. The wavelength at which the characteristic peak of the plasmon resonance is presented depends on each NP (Vaghari et al. 2016). For example, a peak near 400 nm indicates the presence of AgNPs. Also, the position and shape of the peak can give us an idea of the NPs concentration (Mahmoudi et al. 2009; Xu and Sun 2013).

UV spectroscopy is a type of absorption spectroscopy in which the light from the UV region (200–400 nm) is absorbed by the molecule. It produces the excitation of electrons from the fundamental state to a state of greater energy. The energy of the UV radiation that is absorbed is equal to the difference in energy between the fundamental state and the higher energy states.

Complete UV-visible absorption happens at a determinate wavelength in each molecular structure (Xu et al. 2014). In the NPs field, UV-visible spectrometry is a widely used technique. It is a consistent and very simple method to know the shape, size, and polydispersity of the NPs.

FTIR is a simple, adequate, convenient, non-invasive, and cost-effective technique, frequently used to detect biomolecules associated with the NPs surface and possibly involved in their synthesis and stabilization (Dávila Costa et al. 2020).

SEM, TEM, and AFM are imaging methods by which morphology, size distribution, dispersion, and aggregation of a NPs sample can be identified (Liu 2006). The ability to perform analytical measurements and give a better spatial resolution are two of the advantages that TEM has over SEM (Chauhan et al. 2016). AFM can be used to characterize the interaction of nanomaterials with compatible lipid bilayers in real-time and measurements can be performed in aqueous fluids. The downside is that particles not attached to a substrate will float and leading to imaging artifacts (Al Juraifani and Azzah 2015).

The NPs elemental composition can be analyzed by the blend of two techniques: SEM and X-ray spectroscopy (EDX). This can also provide important information about the degree of the particles aggregation and purity. XRD is utilized to determine the crystal structure of the NPs (Shi et al. 2015).

Dynamic light scattering (DLS) is a widely used technique employed to quantify size distribution and surface charges of NPs on a simple solvent or biological environment (Wen et al. 2016). Measurements are non-invasive and very fast when a sample is in its native colloidal state (Xue et al. 2016).

6.6 Nanoparticles Applications.

The applications of NPs have become very important in all areas of science (Singh et al. 2016c). Biomedical, agricultural, environmental, and physicochemical are just some of them (Pereira et al. 2015). For example, AuNPs have been used for drug delivery, tumor and genetic disease detection, photoimage, and photothermal therapy. AgNPs have been utilized for anti-cancer, antimicrobial, wound treatment, and anti-inflammatory purposes (Ahamed et al. 2010). Because of their non-toxic, self-cleaning, biocompatible, antimicrobial, and dermatological behavior, zinc and titanium NPs have been applied in cosmetic and biomedical areas (Ambika and Sundrarajan 2015). Palladium and copper NPs have been used in polymers, batteries, optical limiting devices, and plastic plasmon waveguides (Momeni and Nabipour 2015).

Amongst the most innovative and promising applications of NPs, those related to the recovery of contaminated environments are highlighted. Nano-remediation is a novel potential solution to clean up the environment. Nanoparticles play an important paper in the prevention, sensing, supervising, and remediation of polluted systems (Rajan 2011). The properties of the nanoparticles allow both catalysis and chemical reduction to attenuate the contaminants of interest. Nanoparticles can penetrate very tiny nooks in the subsoil and remain suspended in the groundwater, allowing them to travel faster than macro-size particles achieving wider distribution. Besides, the elevated relation surface/volume of NPs is beneficial for technologies that depend on reactions at the water–solid and gas–solid interfaces. Such is the case of the adsorption mechanisms used to treat wastewaters, exhaust gases, or photocatalytic processes for the degradation of pollutants. In the case of ex-situ remediation, NPs can be easily maintained in suspension reactors to treat contaminated soil and sediment. Alternatively, to improve water treatment, they can be anchored in a solid matrix such as carbon (Bhandari 2018).

6.6.1 Bioremediation

Contamination with heavy metals produces world-wide concern due to their high toxicity and great dispersion capacity. Consequently, bioremediation of heavy metals using biogenic NPs is a topic of great interest. One of the most hazardous metals is Pb since it is quickly accumulated by fishes (Ribeiro et al. 2010) entering into the cycle of the food (Crist et al. 1992). El-Kassas et al. (2016) biosynthesized iron oxide NPs (Fe_3O_4-NPs) to remove Pb by employing a fully green method. Seaweed extracts of the algae *Padina pavonica* and *Sargassum acinarium* were employed for the reduction of a ferric chloride solution, resulting in the synthesis of Fe_3O_4-NP. Biosynthesized Fe3O4-NP was stabilized on calcium alginate beads and utilized in experiments of adsorption of Pb. The authors observed the NPs biosynthesized through *P. pavonica* removed 91% of Pb while NPs from *S. acinarium* removed 78% of Pb, after 75 min. The utilization of FeNPs to remove chlorinated solvents (PCE, TCE, DCE), arsenic, pesticides (lindane, DDT), and for the transformation of other organic compounds such as nitrates from water and soil have also been reported (Karn et al. 2009). Kanel et al. (2005, 2006) informed the elimination of As(III) and As(V) using FeNPs. These are two of the most toxic and predominant species of arsenic in groundwater.

Another example of the use of biogenic NPs for bioremediation is the case of AuNPs. López-Miranda et al. (2019) were able to synthesize AuNPs of fairly homogeneous size (40–60 nm) using aqueous extracts of *Aloysia triphylla*. When evaluating their catalytic properties to degenerate organic dyes (Congo red and Methylene blue), short degradation periods were obtained. These results suggest that AuNPs produced by *A. triphylla* can be used for remediation of water.

Different studies show that the use of NPs as white rot fungi (WRF) supports can have a synergistic effect, improving the stability of WRFs in the bioremediation of wastewaters. Nanoparticles could contribute by increasing the practical yield of the WRF biomass or acting as supports in the immobilization of enzymes from WRF that participate in the removal processes (i.e., laccases) (Chen et al. 2013; Xu et al. 2013; Hu et al. 2016).

Because of their single qualities, biogenic NPs are suitable for the design of nanobiosensors (Peng and Miller 2011). Nanosensors were used for the determination of mycobacteria, algae, mercury toxins in drinking water (Selid et al. 2009). As well, nanosensors can be useful to detect viruses, crop pests, stress factors, and soil nutrient levels, and hormonal regulation. For example, Koren et al. (2015) detected levels of oxygen and auxin distributed in the seagrass rhizosphere using optical O_2 nanosensors with built-in NPs.

Biogenic AgNPs were used for the manufacturing of a cost-effective fiber optic-based sensor for H2O2 detection that can be applied in different industrial processes (Tagad et al. 2013).

6.7 Conclusions

The environmental damage produced because of the exponential increase in industrialization is a reason for great preoccupation. In this context, nanotechnology is presented as an alternative with an enormous prospect to improve actual technologies used in different areas. Regarding the remediation of polluted systems, nanotechnology can provide ecological and effective solutions. In this chapter, updated data about the biological synthesis of metallic NPs and some of the most used techniques for their characterization are presented in summary form. In addition, some of its main applications are described, emphasizing its use in bioremediation processes.

Nano-bioremediation is an efficient and sustainable focus to provide a remedy for global contaminated sites. It can proportionate profitable and timesaving cleanup procedures for extensive contaminated places.

Because of its great potential, it is estimated that NPs uses will enhance in the future and they would be key to a sustainable development. For this reason, more researches on aspects fundamental and practical of nano-bioremediation are needed.

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Plant–Microbe Interactions in Attenuation of Toxic Waste in Ecosystem

7

Monday Ubogu and Ejiro Akponah

Abstract

As a result of rapid human population growth and increased industrial activities, the world ecosystems more than ever before are perpetually inundated with anthropogenic toxic waste releases at levels and frequencies higher than natural recovery rates. To achieve sustainable development, timely, efficient, environmentally friendly, and cost-effective approaches are required for environmental pollution abatement. Phytoremediation technique involving plant–microbe synergy provides a simple plausible remediation alternative to existing intrusive and costly physicochemical and engineering-based decontamination techniques. Although plant and microorganisms can independently attenuate some toxic wastes, without microbial collaboration, this technique will not be a viable option for the remediation of most pollutants. This review examines the mutual relationship between microorganisms and plant within rhizosphere and phyllosphere and exploitation of their synergy for toxic organic and inorganic wastes attenuation in the ecosystem. Possible mechanisms and reasons for accelerated removal of pollutants within the vicinity of plants (rhizosphere and phyllosphere) are presented. The prominent role played by root-endophytes in toxic waste attenuation in soil ecosystem is highlighted.

Keywords

Bioremediation · Microbes · Plant · Phytoremediation · Toxic compounds

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7.1 Introduction

The world ecosystems have intrinsic ability to recover from toxic waste contamination. However, this remarkable recovery ability has been overstretched in the last few decades as a result of accelerated industrialization in order to keep gait with demands of ever-increasing human population. Consequently, world ecosystems are inundated perpetually with anthropogenic toxic waste releases at levels and frequencies higher than natural recovery rates. Globally, from moderate levels of 1.7×10^6 tons in the 1950s, plastic production rose astronomically to 3.22×10^8 tons in 2016 (Revel et al. 2018). Annually, over 4.0×10^9 tons of plastics are generated globally, most of which remain unaltered for a long period in refuse dump, landfills, and as litter in the environment (Madigan et al. 2012). Across the world, an estimated 5.6 billion pounds of pesticides are discharged yearly in the environment (Donaldson et al. 1999). In the past 50 years, approximately 1.3×10^7 barrels of crude oil have been discharged into Niger Delta environment (Federal Ministry of Environment (FME) 2006). India and China have witnessed astronomical rise in air pollution in the last three decades due to speedy economic growth accompanying rise in energy consumption (Wei et al. 2017a, 2017b).

Globally, air, soil, surface, and groundwater contamination has remained a serious issue due to its adverse health and environmental effects (Kuiper et al. 2004). Noxious environmental contaminants include various classes of inorganic and organic compounds including petroleum hydrocarbons, pesticides, chlorinated hydrocarbons, dyes, heavy metals, radionuclides, and gases (e.g. NO_x, CO_2, SO_2). Remediation of these contaminants using physicochemical and engineering-based decontamination techniques is usually inadequate (Dixon 1996). Besides, they are environmentally intrusive, complex, prohibitively costly, and lacking in public approbation (Niti et al. 2013). These obvious shortcomings have spurred up the involvement of bioremediation approaches. The trending plausible bioremediation strategy for toxic environmental waste attenuation is that which encompasses plant and microbial synergy, particularly at the rhizosphere (rhizoremediation) and phyllosphere (phylloremediation) (Bisht et al. 2014a, 2014b). Although delay in requisite critical biomass attainment, adverse climatic changes, and low tolerance of interacting plants and microorganisms to designated pollutants at certain threshold of concentrations may impede the effectiveness of this strategy; selection of well-adapted plants and microorganisms can help to address these challenges. Nonetheless, the preferential shift to plant-microbe synergy is anchored on several reasons: (1) sustainability, (2) viability, (3) cost-effectiveness, and (4) environmentally friendliness of this strategy. In this chapter, the relationship between plants and microbes in rhizosphere and phyllosphere for remediation of organic and inorganic toxic wastes in air and soil ecosystems is presented. The critical functions of root-endophytes in remediation of soil pollutants are also highlighted.

7.2 Microbe–Plant Relationship in Rhizosphere

Soil is a repository of intricate community of microorganisms where all the intrigues and battle for existence are brought to bear. The contention for survival among the constituent populations of microorganisms is invigorated within the rhizosphere (Parkinson and Waid 1960). The rhizosphere is the most influential ecosystem on our planet with immense energy flow rate (Barriuso et al. 2008), is defined as entire sphere of soil influenced by root and its exudations. Although this very crucial microbial hotspot in soil (Kuzayakov and Blagodatskaya 2015) stretches few millimeters to centimeters from the root (Pivetz 2001; Singleton and Sainsbury 2006; Prashar et al. 2013), its shape and size have no precise delimitation, rather encompasses a territorial gradient in physical, chemical, and biological properties that undergo radial and longitudinal change along the root (McNear 2013). The rhizosphere consists of three separately distinct but interacting components: ectorhizosphere (comprises soil immediately adjoining root); rhizoplane (actual root surface, along with tightly bound particles of soil and microbes), and endorhizosphere (the root tissue including cortex and endodermis) (Barea et al. 2005; Prashar et al. 2013; Brahmaprakash et al. 2017). Rhizosphere size is dependent on the specific plant root structural makeup in relation to its entire biomass. Although grasses offer enormous root surface area due to their fibrous nature in comparison to plants with tap root system (Atlas and Bartha 1987; Marshchner et al. 2002); trees generally have larger root biomass and penetrate deeper into soil than grasses, thus occupying larger volume of soil than grasses (Cook and Hesterberg 2013). Microbial assemblage and functions within rhizosphere are comparatively huge than unvegetated bulk soil. Beyond anchorage, plant roots depositions and exudates benefit root-associated-microorganisms enormously. Root exudations within rhizosphere which varies among species, genus, age, and cultivars of plant and other biotic and abiotic factors (Patkowska 2002) generally include organic materials such as dead fine roots and cell shelling, lysates, CO_2, O_2, ethylene, simple carbohydrates, plant hormones, organic acids, amino acids, sugar phosphate esters, phenolics, vitamins, proteins, enzymes, and mucilage (polysaccharides) (Bais et al. 2006; Prashar et al. 2013). These substances are utilized in the rhizosphere for growth and metabolism and it is utterly responsible for the elevated microbial populations and activities over regions devoid of root influence in the soil. Hence the rhizosphere effects (R/S) on microbial populations, particularly bacteria and fungi could be as high as 2 to 100-fold order of magnitude (Kołwzan et al. 2006; Jussila 2006; Ubogu et al. 2017; Ubogu et al. 2019). Mucilaginous substances and carbohydrate exudations aid huge microbial population growth during early stage of development. During maturity autolysis of some root substances occurs as part of the usual root development process with amino acids and simple sugar exudation (Atlas and Bartha 1987). Microorganisms gravitate toward the root zone in soil by chemotaxis induced by root exudations. Attachment of microorganisms to root surfaces (rhizoplane) is facilitated by agglutinin one of the plant root exudations (Kumar et al. 2007). Root exudation in rhizosphere also benefits plant itself. It promotes reduction of friction between soil and root tips, prevents root desiccation, and maintains soil structural stability (Rougier and Chaboud 1989). Conversely, microbial activities (which are also influenced by root exudation) alter the operation and pattern of root exudation (Prashar et al. 2013). Root exudate chemical makeup can be modified by soil microorganisms (e.g. rhizobia, fungi, and plant growth promoting bacteria (PGPB)) and hence plant physiology through liberation of different signaling molecules like exopolysaccharides, nod factors, microbe-associated molecular patterns (MAMPs), and volatile organic compound (VOC) (Goh et al. 2013). Many rhizosphere organisms benefit their associated plants in several ways. Some of these organisms which are dinitrogen fixers, legume nodulators, mycorrhizae, nutrient solubilizers, etc. are involved in the synthesis of antibiotics, vitamins, phytohormones, transmission molecules, etc. that either promote growth, suppress pathogens, or cushion abiotic stress in plants (Brahmaprakash et al. 2017). Microbial interactions in rhizosphere enhanced plant nutrients and water uptake by mycorrhizal fungi (e.g. *Acaulospora*, *Archaeospora*, *Entrophospora*, *Gigaspora*, *Glomus*, *Paraglomus*, *Scutellospora*, *Sclerocysts*, etc.), mobilize and solubilize phosphorus (e.g. by *Pseudomonas*, *Bacillus*, *Acinetobacter*, *Rhizobium*, *Penicillium*, *Aspergillus*, etc.), fix nitrogen symbiotically (e.g. *Frankia*, *Rhizobium*, etc.) and non-symbiotically (e.g. *Azotobacter*, *Beijerinckia*, *Derxia*, etc.) produce phytohormones (e.g. auxin, gibberellins, cytokinins, ethylene, abscisic acids) that regulate plant growth, promote plant immunity against pathogens and responses to abiotic stress (which includes drought, salinity, and low temperature), antagonize plant pathogens through antibiosis (e.g. *Pseudomonas fluorescence*) and mycoparasitism (e.g. *Trichoderma harzianum*), degrade soil toxicants, etc. (Spaepen et al. 2007; Krishnaveni 2010; Barat et al. 2016; Brahmaprakash et al. 2017).

7.3 Attenuation of Toxic Waste in the Rhizosphere

7.3.1 Rhizoremediation

Toxic wastes attenuation may occur naturally in the rhizosphere or may be facilitated through human mediation. The attenuation of toxic waste in the rhizosphere ecosystem which is termed rhizoremediation is a sort of phytoremediation that involves pollutants elimination or abatement through reciprocal interactions of root (exudates) and its accompanying microbes. The term rhizoremediation emphasizes the relevant functions of rhizosphere-competent microbes and root exudates in the waste attenuation process (Shukla et al. 2010). Irrespective of the fact that plants and microorganisms can on their own degrade a number of toxic wastes (Frick et al. 1999), rhizoremediation without microbial participation may not be a viable technique for the remediation of a vast array of organic contaminants that are naturally hydrophobic (Chaudhry et al. 2005). Rhizoremediation offers an attractive means of cleaning up polluted soils. Unlike other forms of phytoremediation, pollutant degradation is in situ with high possibility of mineralization. Translocation of toxic waste in plant or atmosphere is also a rarity. However, attenuation of toxic waste in the rhizosphere may have some setbacks as degradation may be hampered by rivalry for soil nutrient among plants and microorganisms. Plant exudations can also be a major source of carbon substitute for pollutants which can substantially limit the amount of pollutant degraded (Molina et al. 1995). Many plants also have short root systems, thus restricting the remediation process to depth of root area which is a major shortcoming (Pivetz 2001). These shortcomings notwithstanding rhizoremediation still remain one of the most effective, environmentally friendly, and economically viable means of pollutants attenuation in the ecosystem.

7.3.1.1 Rhizoremediation of Toxic Organic Wastes in Soil

Deliberate and accidental small chronic and huge sporadic releases of natural and synthetic toxic organic compounds into the environment particularly soil are regular occurrences across the world. These include petroleum hydrocarbons such as aliphatics, alicyclics, aromatics (e.g. toluene, benzene, ethylene, and xylene), polyaromatics (e.g. benzo(a)pyrene, pyrene, phenanthrene, naphthalene, etc.), chlorinated aliphatics, nitroaromatics, polychlorinated biphenyls, pesticides, herbicides, etc. Significant number of studies revealed elevated rates of attenuation of these organic pollutants occurring in rhizosphere of plants as compared to unvegetated soils. There are many reasons for the speedy breakdown of these organic toxicants in rhizosphere. First, nutrient-rich exudations promote astronomical rise in microbial populations in rhizosphere (Madigan et al. 2012). This swell in microbial populations provides the critical mass required to initiate and accelerate the degradation process. High microbial populations are needed to reduce the lag phase and accelerate bioremediation (Forczek et al. 2001). Second, some of the physicochemical factors limiting effective biodegradation of organic pollutants in soil are optimized within the rhizosphere. Microorganisms particularly mycorrhizae increase nutrients and water absorption in the rhizosphere proving the required moisture content for effective bioremediation. Furthermore, it has been revealed that environmental toxic wastes degradation drops off with soil depth (Olson et al. 2001). Required O_2 dispersion for efficient biodegradation takes place in the range of 30.0 cm soil vertical profile (Vidali 2001). Plant roots growth beyond this range of depth provide adequate aeration through their tilling actions as well as the direct release of O_2 into soil by particularized vas in root called aerenchyma (Muratova et al. 2003; Kuiper et al. 2004; Zalesny et al. 2005). Furthermore, O_2 released is also used for detoxification of some phytotoxic compounds generated under anoxic condition. For instance, *Beggiatoa* including other sulfur bacteria in rhizosphere of most swamp plant employ the released O_2 for the oxidation and detoxification of phytotoxic H_2S (Madigan et al. 2012). Besides N_2 fixation by rhizosphere microorganisms, exudates from roots harbor vast array of organic compounds that may function as reservoir of nitrogen and carbon for microbial growth and sustenance for organisms possessing the ability to degraded organic contaminants (Anderson et al. 1993; Pilon-Smits 2005). Third, exudate or lysates from roots may harbor lipophilic compounds that could improve water solubility of pollutants or stimulate growth of biosurfactant producing microbes (Read et al. 2003; Pilon-Smits 2005). Bioavailability through solubilization of organic pollutants can result from alteration of side groups mediated by plant and microbial produced enzymes

(Chaudhry et al. 2005). Fourth, microorganisms in the rhizosphere can secure accelerated remediation of organic contaminants via organic volatilization (e.g. PAH) or by facilitating organic pollutants humification (Salt et al. 1998), particularly the liberation of oxidoreductase such as peroxidase by microorganisms, similar to plant roots and catalyze contaminants polymerization into soil humic portion and root surfaces (Jussila 2006). Fifth, the liberation of degradative enzymes such as dehalogenase, peroxidase, laccase, nitroreductase, and nitrilase by plant which remains active over a period of time in the rhizosphere also contributes to the accelerated breakdown of organic pollutants in rhizosphere (Schnoor et al. 1995). Sixth, sizable number of organic constituents of root exudates can serve as co-metabolites in organic pollutants breakdown. Seventh, structurally some organic pollutants are related to some of the root exudates which are naturally utilized for growth and metabolism by rhizosphere microorganisms. Thus, microorganisms do not find it difficult to produce enzymes for the breakdown of such structural analogue (Hashmi et al. 2017). For example, organic pollutants having phenolic structure are easily degraded by rhizosphere microorganisms that readily utilize root exudates containing phenolic compounds. Eighth, there is a higher level of horizontal transfer of degradative genes in the rhizosphere. Conjugative plasmids that transfer genes responsible for bacterial adaption in the rhizosphere of polluted soils are stimulated by root exudations (Rohrbacher and St-Arnaud 2016).

There are current and overwhelming body of reports that lend credence to effective and accelerated diminution of petroleum hydrocarbons in root zones of plants over unvegetated contaminated soils (Euliss et al. 2008; Gaskin 2008; Phillips et al. 2009; Ezzatian et al. 2009; Tang et al. 2010a, 2010b; Soleimani et al. 2010; Zand et al. 2011; Ubogu et al. 2019). Ubogu et al. (2019) reported accelerated depletion of total petroleum hydrocarbon (TPH) in the rhizosphere of two wetland plants, *Phragmites australis* and *Eichhnornia crassipes* over unplanted mangrove swamp soil in Niger Delta. They reported a TPH loss of 74.7 and 82.3% in the rhizosphere of *P. australis* and *E. crassipes*, respectively, as against 67.5% loss in unplanted mangrove swamp soil receiving equivalent amount of NPK fertilization and inoculation of hydrocarbon utilizing bacteria and fungi within 120 days period; at a daily degradation rate of 44.64, 49.20, and 40.32 mg/kg/day, respectively. The higher degradative rate witnessed in the rhizosphere of *E. crassipes* was ascribed to increased populations of appropriate hydrocarbon utilizing fungi and bacteria stimulated by NPK fecundation (besides possible effects of root exudations) and ability of *E. crassipes* to absorb and metabolize some components of petroleum hydrocarbons (Nesterenko et al. 2012; Saleh 2016; Mishra and Maiti 2017; Gupta and Balomajumder 2018). Similarly, Gaskin (2008) reported elevated rate of TPH loss in contaminated soil cultivated with three Australian grasses, *Microlaena stipoides*, *Brachiaria decumbens*, and *Cymbopogon ambiguus* than uncultivated contaminated control. Tang et al. (2010a, 2010b) examined influence of fertilizer application together with inoculation of efficient microbial degrading agents along with plant growth-enhancing rhizobacteria in petroleum hydrocarbon contaminated soil planted with fescue, ryegrass, alfalfa, and cotton and reported higher TPH removal rate in planted soil than control. In this study, the rate of attenuation also varied among species of plant tested and this variation was attributed to the differences in root physiological functions. This further emphasizes the importance of selecting appropriate plants–microbe interactions for maximum attenuation of petroleum hydrocarbon in the rhizosphere ecosystem.

Around the world, past industrial production and use of polychlorinated biphenyls (PCBs) still constitute serious environmental challenges (Passatore et al. 2014). PCBs are persistent toxic xenobiotics that get easily adsorbed onto organic matter in soil rendering its remediation by traditional techniques inefficient or difficult (Willey et al. 2017). However, in addition to being economical and environmentally friendly, rhizoremediation promises to be an easier and efficient clean-up of PCBs in the environment. There are reports of successful attenuation of PCBs in sugar beet rhizosphere (Brazil et al. 1995), reed canary grass, alfalfa, switchgrass, flatpea, deertongue, sericea lespedeza, and tall fescue (Chekol et al. 2004). Chekol et al. (2004) reported increased PCB attenuation in rhizosphere of all the plants investigated. Attenuation rate of 62% was recorded in the rhizosphere against 18% in unplanted soil after 4 months of remediation studies. In this study higher degradation rate of PCB also correlated positively with increased population of microorganisms and enzyme actions in rhizosphere as compared to unplanted soil. Plant root exudations obviously played pivotal part in accelerated attenuation of PCB in rhizosphere ecosystem through induction of PCB-degradative genes among rhizobacteria. Bacterial populations capable of degrading PCB in the rhizosphere are stimulated by root exudations such as coumarins, flavonoids (Donnelly et al. 1994; Gilbert and Crowley 1997), phenolics (Fletcher and Hegde 1995), and *L*-carvone (Gilbert and Crowley 1997).

Pesticides is a generic name for a variety of chemicals used for the eradication or control of pests which include herbicides, fungicides, insecticides, etc. More than 1000 different pesticides are marketed worldwide (Madigan et al. 2012) and these group of chemicals appear to be the most widely spread environmental contaminants in the past century (Schwitzguebel et al. 2006). Persistent pesticides in soil are of great concern because of the dangers they pose to human and environmental health. Undegraded pesticides in soil may be washed into surface water or leashed into groundwater with a high tendency of bioaccumulation into living tissues, some of these pesticides have been linked to cancer, organ failure, and other health issues. These underscore the importance of their accelerated removal from the environment. Like most other organic contaminants, rhizoremediation of pesticides provides a more promising and acceptable offer for their elimination from the environment. Significant number of studies reported enhanced degradation of pesticides in contaminated rhizosphere compared to unvegetated soil. Rainbird et al. (2018) examined degradation of the herbicide sulfonylurea in contaminated agricultural soil planted with Lentils (*Len culinaris*) and unplanted soil and reported an enhanced rate of degradation in planted soil with the presence of higher population of chlorsulfuron-degrading bacteria (*Pseudomonas fluorescens*). Similarly, Bibi et al. (2019) reported enhanced attenuation of the pesticide hexachlorocyclohexane in soil planted with *Solanum nigrum* along with inoculation of effective rhizobacteria code strain ST47, over unplanted inoculated soil. In earlier studies, elevated pesticide-degrading populations and/or degradation of various pesticides were reported among different plants species over unplanted soil: atrazine in the rhizosphere of corn (Seibert et al. 1981); parathion in rhizosphere of rice (Reddy and Sethunathan 1983); 2.4-D (Sandmann and Loos 1984) and 2,4,5-T in rhizosphere of sugarcane (Boyle and Shann 1995); benthiocarb in rhizosphere of rice (Sato 1989); 1,4-dioxane in the rhizosphere of poplar (Schnoor et al. 1998; Kelley et al. 2001); and Chlorpyrifos in rhizosphere of ryegrass (Korade and Fulekar 2009).

7.3.1.2 Rhizoremediation of Heavy Metals and Radionuclides

Heavy metal is a poorly defined term consisting of transitional metals, metalloids, actinides, and lanthanides (Appenroth 2010), having specific density greater than 5.0 g/cm^3 (Ganesan 2012). These class of metals may also be grouped into three categories: the toxic metals which include Zn, Pb, As, Cu, Cd, Cr, Ni, Sn, Hg, etc.; the precious metals, Ag, Pd, Ru, Au, Pt, etc., and radionuclides, Am, Ra, Th, Cs, U, etc. (Nies 1999; Bishop 2002). Detrimental effects of heavy metal pollution on human health and ecosystems are well documented. Heavy metal tainting the environment is of much concern because of their remarkable toxicity at very minute concentrations (1.0–10.0 mg/L) (Ahemad 2014). Anthropogenic releases and mineral rock weathering are the main source of heavy metal pollution (Kumar et al. 2017). These releases may come from metalliferous mining and refining, atmospheric deposition, waste disposal, agricultural and industrial activities (Ross 1994). Soil is principally the sink for heavy metal releases in the environment (Kirpichtchikova et al. 2006). Unlike organic pollutants, heavy metals are non-biodegradable, therefor have to be taken out or contained within the contaminated site (Andreoni and Zaccheo 2010). Microorganisms have the capacity to remediate heavy metal pollution through a combine array of mechanisms such as metabolic uptake, precipitation, biosurfactant complexation, sorption, biofilm entrapment, and transformation (Parmar and Singh 2014). Siderophore production by rhizosphere microorganisms is known to chelate Fe^{3+}, this same mechanism may be applicable to other trivalent metals such as Cr, Ga, and Al (Schalk et al. 2011) and altering their bioavailability and reduction of toxicity (Mosa et al. 2016). Notwithstanding the fact that some species of plants have capacity to hyperaccumulate heavy metals, their application without microbial symbiotic involvement may not be effective in cleaning up sites with multiple contaminants hence, synergistic approach involving microbe–plant interaction in rhizosphere offers more effective remediation strategy (Wu et al. 2005). Karthika et al. (2017) reported improved root growth and reduction of toxicity in *Vigna mungo*, *Zea mays*, *Sesbania aculeata*, *Phaseolus vulgaris*, and *Vigna radiata* with the co-inoculation of Cr (IV) and resistant strains ARS6 of *Cellulosimicrobium funke* (PGPB). Bolan et al. (2016) evaluated rhizosphere-induced reduction of Cr (VI) among indigenous Australian plants: *Dichantheum sericeum*, *Acacia pubescens*, Enchylaena tomentosa, *Eucalyptus camaldulensis*, *Austrodanthonia richardsonii*, and *Templetonia retusa* and reported rhizosphere effect reduction of Cr (IV) in the range of 2.45–5.07 order of magnitude than unvegetated soil among tested plants. Significantly, increase in microbial activities correlated with Cr (VI) reduction in the rhizosphere. Wu et al. (2006)

reported 40 % improved cadmium accumulation in the root of sunflower and significant reduction of its phytotoxicity with the inoculation of genetically engineered rhizobacteria, *Pseudomonas putida* 06909. Similarly, increased uptake of nickel reportedly occurred in the shoot and leaves of *Alyssum murale* due to rhizospheric activities of three rhizobacteria: *Microbacterium arabinogalactanolyticum*, *Microbacterium liquefaciens*, and *Sphingomonas macrogoltabidus* in comparison with uninoculated control in a study by Abou-Shanab et al. (2006). Radioactive wastes are of great public concern. These types of waste are usually discharged into the environment as a result of nuclear weapon processing and testing, nuclear energy generation, and unintentional releases (Lloyd and Renshaw 2005). Radionuclides are elements that lack physical stability undergoing self-generated decay to emit energy either as electromagnetic waves, particles, or both (NABIR 2003). Many of the mechanisms for microbial remediation of heavy metals apply to radionuclides in soil environment. For instance, the bacterium *Microbacterium flavescens* has been shown to accumulate plutonium by the same mechanism used by microorganisms for iron uptake (siderophore-mediated accumulation) (NABIR 2003). Several bacterial such as *Kineococcus radiotolerans* sp. nov, *Deinococcus*, *Serratia*, *Geobacter*, and *Hymenobacter metalli* sp. nov. have been reported to act on radionuclides in radioactive wastes in the process altering solubility, bioavailability, and mobility of radionuclides (Lloyd 2003; Lloyd and Renshaw 2005; Lloyd and Gadd 2011a, 2011b; Dakora and Phillips 2002; Chung et al. 2010). Similarly, some plants have been recognized as proficient in remediating radionuclides (e.g. *Azolla imbricata*, *M. cordata*, and *P. australis* for phytoremediation of uranium-contaminated soil, *P. multifida* for ^{226}Ra-contaminated soil, and *P. australis* for thorium contaminated soil) based on their phytoremediation factor (PF) (Yadav and Kumar 2019). Although there is paucity of information on microbe–plant interactions in rhizosphere for radioactive wastes attenuation, metal resistant plant growth promoting rhizobacteria (PGPB) are known to enhance plant growth in heavy metal contaminated soils (Ahemad 2014). Therefore, synergistic effects of deliberate inoculation of wild or genetically modified rhizosphere-competent microbes able to remediate radionuclides into the rhizosphere of plants with high radionuclide-tolerance and phytoremediation factor could accelerate radioactive waste attenuation in the rhizosphere.

7.3.1.3 Root-Endophytic Attenuation of Toxic Wastes

One area that has attracted attention in recent years in toxic wastes attenuation in microbe–plant interactions in rhizosphere is the endorhizosphere. This microcosmic region is colonized by a set of soil microbes conjointly known as root-endophytes. Root-endophytes are non-pathogenic microorganisms (bacteria, fungi, and actinomycetes) which inhabit internal root tissue including cortex and endodermis (Schulz and Boyle 2006; Stepniewska and Kuzniar 2013; Kumar et al. 2018). These group of microorganisms are ubiquitous and nearly every species of plant on earth has one species of endophyte (Sessitsch et al. 2004; Germaine et al. 2006; Anyasi and Atagana 2016) and they are probably more abundant in tropical host plants due to their enormous biodiversity (Azevedo et al. 2000). Unlike ectorhizosphere

(Sessitsch et al. 2004; Germaine et al. 2006; Afzal et al. 2014) and rhizoplane microorganisms, they have profound intimate connection and enormous influence on the biochemical and genetic interactions with their host plants (Verma and Gange 2014; Kumar et al. 2018). Although endophytes are generally found in stem, leaves, seeds, and roots of plants, it has been incontrovertibly established that endophytes originate from soil environment (Compant et al. 2012). Except for seed endophytes, the primary point of entry into plant is the root and subsequently domicile in the root cortex or xylem or systematically colonize plant through movement via the vascular system or apoplast (Mahaffee et al. 1997; Quadt-Hallman et al. 1997).

Substantial part of the successes reported in toxic waste attenuation in the rhizosphere is attributable to root-endophytes. Bacteria degradation of recalcitrant pollutants occurs more with endophytes within the rhizosphere in contaminated soil (Siciliano et al. 2001). The increased removal of toxic waste is ascribed to the remarkable capacity of root-endophytes to generate plant growth promoting hormones, antagonize plant pathogens, increased plant nutrients uptake, fix nitrogen, assimilate, transform, and degrade environmental toxicants. These activities contribute to phytotoxicity reduction, improved plant health, growth, and adaptation to designated contaminants which is critical for effective and accelerated attenuation of toxic waste in the rhizosphere. Many endophytes in polluted sites have been reported to exhibit dual roles of pollutant degradation and plant growth promotion (Sheng et al. 2008; Dashti et al. 2009; Becerra-Castro et al. 2011). The involvement of large array of metabolic pathways by microbial endophytes makes them worthful tool in the bioremediation of environmental contaminants (Gai et al. 2009; Kim et al. 2012; Verma and Gange 2014). Numerous studies lend credence to the integral roles played by root-endophytes in the accelerated attenuation of soil pollutants in the rhizosphere. Soleimani et al. (2010) reported 72.0% total petroleum hydrocarbon (TPH) loss from contaminated soil cultivated with *Festuca* spp. infected with endophytic fungi as against 64.0 and 31.0% removal rate in uninfected *Festuca* spp. and uncultivated soil, respectively, from initial TPH amount of 47,400.0 mg/kg, and ascribed these differences to the rise in biomass of plant roots which consequently expanded root surface area and elicitation of microbial ameliorating metabolites like phenols that induced microbial activities in soil. Other reported cases of root-endophyte degradation of organic pollutants include BTEX and TCE degradation by *Acinetobacter lwoffi*, *A. nicotianae*, *Pseudomonas tolaasii*, *P. plecoglossicida*, *P. rhodesiae*, *P. fulva*, *P. jessenii*, *P. veronii*, *P. oryzihabitan*, *Paenibacillus amylolyticus*, and *Bacillus megaterium* in the root of *Populus* cv. Hazadens (Moore et al. 2006). Heavy metal bioremediation by root-endophytic microbes have also been reported. Karnwal (2018) investigated bioremediation of Cd, Cr, Ni, and Zn by biosurfactant producing *Pseudomonas fluorescence* RE1 and RE17 from the root of rice and reported reduced heavy metal concentration in medium by biosorption up to 90 % and above for all metal tested by both stains of *Pseudomonas fluorescence*. Similarly, Govarthanan et al. (2016) reported 59.4 and 51.4% removal rate of Cu and Zn, respectively, from medium by root-endophytic bacterium, *Paenibacillus* sp. RM isolated from *Tridax procumbens* root.

7.4 Microbe–Plant Interactions in Phyllosphere

Similar to rhizosphere, phyllosphere which is the aerial part of plants consists of four main distinct parts: the caulosphere (stem), phylloplane (leaf surface), anthrosphere (flower), and carposphere (fruit) (Bringel and Couee 2015). The phyllosphere microbiomes include bacteria, actinomycetes, molds, yeasts, and algae (Lindow and Brandl 2003; Willey et al. 2017). Bacteria are most dominants of these group of microorganisms. Bacterial population density on leaf surface is estimated to be as high as 10^6 to 10^8 cells per cm^2 (Leveau 2006; Willey et al. 2017). Among the fungi, ascomycetes are the most dominant prior to senescence (Abdelfattah et al. 2015). The orientation and cumulative large surface area offered by the phylloplane makes it the most significant zone for microbial activities and air-borne pollutants entrapment. The size of the phyllosphere varies among plant species. Generally, plants with broad leaves have the capacity to carry higher microbial populations than those with narrow leaves like grasses (Lindow and Brandl 2003). It has been estimated that overall planetary terrestrial leaf phyllosphere colonized by microorganisms could reach $6.\ 4 \times 10^8\ km^2$ (Morris and Kinkel 2002). Thus, the phyllosphere and its microbiome interactions exert significant influence on individual plant behavior and many important global processes (Lindow and Brandl 2003). The extent and pattern of microbial interactions in phyllosphere are critically determined by vicissitudes of environmental conditions. These include the level of humidity, ultraviolet radiation, temperature, and nutrients (Lindow and Brandl 2003; Vorholt 2012) which are extremely variable in time and space (Leveau and Lindow 2001; Monier and Lindow 2003). Leaves play crucial roles in aiding phyllosphere microorganisms (Bringel and Couee 2015) by providing anchorage and required nutrients, hence the phyllosphere microbial community structure is influenced by the leaf morphology, chemistry, and growth condition (Kembel and Mueller 2014). Phyllosphere microbiomes also benefit the plant. Substantial number of microbial interactions in the phyllosphere enhances plant health and improves growth via: fixation of nitrogen (Furnkranz et al. 2008), cytokinins (CKs) production which stimulate nitrogen conveyance to plant shoot tissues, indole acetic acid (IAA) production (Romero et al. 2016), protection against desiccation and UV radiation damage through extracellular polymeric substances (EPS) production (Bram et al. 2018), disease prevention through antagonism and competitive exclusion (Innerebner et al. 2011), and remediation of environmental pollutants (Bram et al. 2018).

7.5 Attenuation of Toxic Waste in the Phyllosphere

7.5.1 Phylloremediation

Air pollution is of serious global concern because of its probable trans boundary spread and its link to major health issues (e.g. respiratory and cardiovascular diseases) and environmental hazards. Significant reduction of air pollution can be achieved by cutting down anthropogenic releases of toxic emissions. However, released emissions may be substantially contained and degraded through phylloremediation process. Phylloremediation involves the trapping and attenuation/degradation of atmospheric pollutants by plants and its phyllosphere microbiomes. Anthropogenic releases of atmospheric pollutants include particulate matter (PM), organic compounds such as polyaromatic hydrocarbons (PAHs), volatile organic compounds (VOCs), formaldehyde and inorganic compounds (e.g. NO_x, CO_2, SO_2, $O_{3)}$ (Weyens et al. 2015). Huge amount of air pollutants is known to be scavenged by above-ground plants parts (Beckett et al. 1998; Popek et al. 2012; Weyens et al. 2015). Annually, approximately 772 tons of PM_{10} is reported to be taken off from the city of Beijing in China by trees (Yang et al. 2005). The long duration of leaves and its microbiomes exposure to atmospheric pollutants have been conjectured as a possible way of developing mechanisms for the adaptation of plant and microorganisms to air pollutants (Wei et al. 2017a, 2017b). Air pollution attenuation mechanisms in the phyllosphere include pollutant adsorption, absorption, sequestration, metabolic assimilation, transformation, and biodegradation by plant leaves and its associated phyllospheric and endophytic microorganisms (Weyens et al. 2015; Wei et al. 2017a, 2017b). For effective and successful remediation of atmospheric pollutants to occur, phyllosphere and rhizosphere synergy is required. Some of the scavenged, undegraded atmospheric pollutants in the phyllosphere are presented for rhizosphere degradation in soil via leaf falls and rain washout. Significant quantum of empirical evidences exists for the bioremediation of atmospheric pollutants in the phyllosphere. Forczek et al. (2001) reported trichloroacetic acid reduction in air sample was due to microorganisms inhabiting phyllosphere of spruce needles. Similarly, Charoenchang et al. (2003), reported pyrene, fluoranthene, and phenanthrene degradation by a consortium of microorganisms isolated from leaves of dried rain tress. Sandhu et al. (2007, 2009) also reported phenol degradation by *Alcaligenes*, *Acinetobacter*, and *Rhodococcus* isolated from bean and maize phyllosphere. Toluene degradation by *Pseudomonas putida* TVA8 from the phyllosphere of *Azalea indica* has also been reported (De Kempeneer et al. 2004).

7.6 Conclusion

Knowledge of the plethora of mutualistic interactions between microorganisms and plant in rhizosphere and phyllosphere and its exploitation provides a robust ground work for the effective attenuation of myriad of toxic organic and inorganic wastes in the ecosystem. While plant and microorganisms can independently remove pollutants from the environment, bioremediation involving the combined action of plants and colligate microbes proffers more viable mode of pollutant attenuation. The accelerated pollutant attenuation occurring within the vicinity of plant (rhizosphere and phyllosphere) is attributable to plant–microbial synergy as they interact with themselves and the pollutants in the ecosystem. Rhizoremediation and phylloremediation offer a viable, sustainable, cost-effective, and environmentally friendly means of attenuating toxic anthropogenic waste releases in the ecosystem.

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Biotransformation of Pollutants: A Microbiological Perspective

8

Jupinder Kaur and S. K. Gosal

Abstract

Microorganisms perform an important function in many of the biological processes that sustain ecosystem. Degradation or detoxification of toxic contaminants is one of such process which contributes towards sustainability of environment. Microorganisms such as bacteria, fungi, and actinomycetes can utilize wide range of substrates as their energy and carbon source. This attribute of microbes makes them suitable candidate in the remediation process of pollutants. The research interest in biotransformation of pollutants has been intensified recently, as mankind is looking for the sustainable ways to clean up the hazardous pollutants. The process of biotransformation harnesses the potential of diverse microbes to decompose, transform, or assimilate the broad spectrum of toxic materials like stiff alloys, hydrocarbons, pharmaceutical content, polychlorinated biphenyls, pesticides, etc. Natural transformation processes are non specific, time consuming and less productive. So, microbial transformations are very beneficial in bioremediation as they are more specific and productive.

Keywords

Bioremediation · Environmental pollutants · Microorganisms · Microbial transformation · Toxic contaminants

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8.1 Introduction

Presence of contaminants in soil, air, or water is one of the major problems of every country. Heavy metals, pesticides, and hydrocarbons are among the examples of commonly encountered pollutants. These harmful pollutants are not only a serious threat to our environment but these toxic contaminants will interfere in the functioning of natural processes also. The presence and persistence of these pollutants in natural system like soil or air cause extensive harm as these pollutants accumulate in the tissues of plants and animals leading to mutations and sometimes even death. So, management of these toxic contaminants is the major focus of researchers in these days. There are many methods like incineration, pump and treat systems, etc. which aim to reduce, remove, or mitigate the effects of toxic contaminants. But each of these conventional methods has risk associated with them apart from their drawbacks (cost and effectiveness).

The prominent organizations like USEPA "(United States Environmental Protection Agency)" prefer the process of biotransformation to control pollutants (US EPA 2006). The process of biotransformation uses microbes like bacteria, fungi, and actinomycetes for detoxification and degradation of pollutants. There are many studies which highlight the potential of microbes in treatment of contaminants in effective and economical way. Microbes with their activities lead to complete mineralization of toxic compounds to the end products which are not harmful to health and environment. There are many microbes which are able to degrade, assimilate, or consume hydrocarbons, heavy metals, pesticides, etc. resulting in non-toxic end products. So, this ability of microbes to manage toxic pollutants helps in cleanup of many contaminated sites. So, microbes are not only boon for the process of biotransformation of pollutants but also for the various other remediation techniques also. In this chapter, we will emphasize on the contribution of biotransformations in remediation of pollutants with microbes as our center of attraction.

8.2 Pollutants/Toxic Contaminants

Pollutants or contaminants are the substances which may be naturally present in the nature but they are serious hazard for the health of human and their surrounding if present in concentration greater than the permissible threshold limit. These contaminants when present in higher concentration pose a risk of toxicity and they even affect various non-target organisms also. The presence of these toxicants can lead to undesirable changes in physico-chemical and biological characteristics of air, water, and soil. So, elimination of the hazardous waste or toxic pollutants from the environment is very essential for sustainable functioning of environment and ecosystem.

Vast arrays of microorganisms are inhabitant of soil or other natural resources (Gosal and Kaur 2017). These microbes possess many functional activities like nitrogen fixation, phosphate solubilization, production of plant growth promoting hormones, etc. (Gosal et al. 2017). Apart from these activities, the diverse catabolic abilities of microbes (like their efficiency to harness xenobiotic composites as their carbon or energy source) act as boon in the bioremediation field as microbes can utilize diverse range of compounds as substrates leading to their decomposition or transformation to non-toxic end products.

8.3 Prominent Source of Toxic Compounds

There are number of ways by which environment can be polluted. The source of these contaminants can be natural as well as anthropogenic. The natural source of waste like remains of animals, dead plants, rotten fruits, and vegetables very rarely affects the environment in negative way. But, the waste produced from human activities or anthropogenic sources is full of harmful contaminants. Sometimes, the release of toxicants into environment can be the intentional human activity also for monetary benefits. The presence of pollutants in environment interferes with the many natural occurring processes. Industrial effluents are source of many pollutants like heavy metals, radionuclides, etc. Due to lack of municipal services dealing with waste management, inadequate ways of waste disposal are adopted, which also contribute toward accumulation of toxic contaminants. Another prominent source of pollutants is excessive use of agrochemicals (fertilizers, manures as well as pesticides) and use of untreated sewage, saline, or waste water for irrigation. Apart from this, atmosphere also contributes toward accumulation of pollutants. Gaseous pollutants from industries mix up with air leading to origination of pollution source. Acid rain and contaminated dust are examples. The various prominent sources of pollutants are explained in Fig. 8.1.

8.4 Bioremediation: Biotransformations, Biodegradation, and Biocatalysis

The contaminants present in the soil or water can undergo many fates. These toxicants can have many negative impacts on the human heath as well as environment. The bioremediation of these toxic pollutants is very essential as these contaminants pose a serious threat to mankind and ecosystem. There are many remediation technologies prevailing nowadays. Each remediation technology has its own advantages as well as drawbacks.

Bioremediation is the most promising approach for the elimination of contaminants or pollutants from natural environment like air, water, or soil. This technology of waste remediation exploits microbes with diverse functional abilities. However, the remediation technology exploiting plants (phytoremediation) is also the hot topic of talk for environmentalists. Keeping in view the sustainability and safety of environment, B3 technology is gaining interest of researchers. B3 refers to biodegradation, biotransformation, and biocatalysis. Sometimes these terms can be

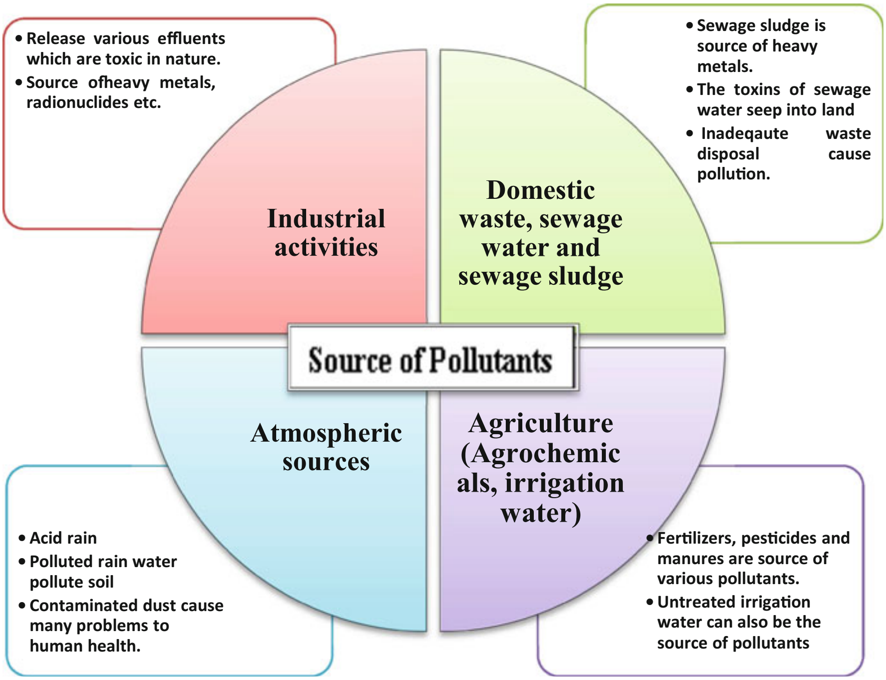


Fig. 8.1 The various causes of pollutants

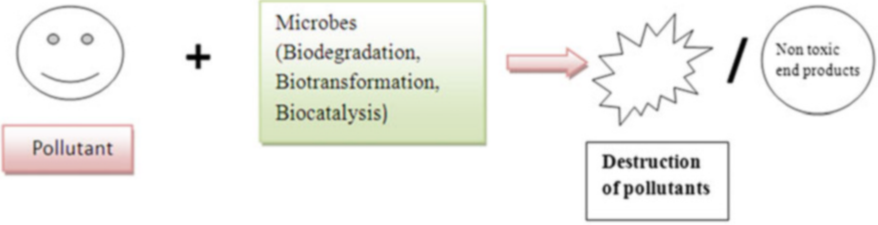


Fig. 8.2 Role of Microbes in remediation of pollutants

overlapping also. These three mechanisms work synergistically for the complete remediation of any toxicant.

Biodegradation refers to breakdown of pollutants by microbes into environmental safe end products in single step or sequence of stages. Biotransformation refers to transformation of pollutants into non-toxic form by alteration or modification in their structure. Biocatalysis refers to use of microbes or enzymes to speed up the transformation or degradation reactions (Fig. 8.2). So, biocatalysis can work synergistically with biodegradation or biotransformation to enhance the effectiveness of these processes.

8.5 Biotransformations and Microbes

Biotransformation refers to the degradation or decomposition of pollutants using microbes or any other biological method. The process of biotransformation uses the mitigation processes like natural attenuation, biostimulation, and bioaugmentation (Fig. 8.3).

In natural attenuation, the soil indigenous microflora is used and the process of decomposition or degradation is totally dependent on natural conditions. The process of biostimulation is also dependent on native microflora of soil but in this process nutrients or other substances are added which speed up the process of decomposition. Bioaugmentation process utilizes non-native microflora also, for the process of contaminant decomposition. Sometimes, genetically modified organisms, capable of degrading specific pollutant, are also used in this process. So, biotransformation process is a vital process for the cleanup of hazardous pollutants.

The process of biotransformation is also used in combination with the other traditional or conventional methods of pollutant remediation to increase the effectiveness of those processes (Vidali 2001). The various other methods of pollutant management usually involve removal of contaminants from the site and their disposal by incineration or by land filling (Speight and Lee 2000). But, with the ever increasing human population, the land area for the remediation technologies like land filling or incineration is decreasing. Moreover, the toxins from landfills seep down into the ground resulting in pollution of groundwater and soil. The gaseous pollutants produced from the process of incineration lead to pollution of air and environment. So, the traditional methods like landfilling, incineration, composting, bioslurry reactor, land farming, and biopiling do not ensure the complete cleanup of toxic pollutants. Additionally, the cost of these techniques is quite high relative to their effectiveness. The use of microbes for the management of

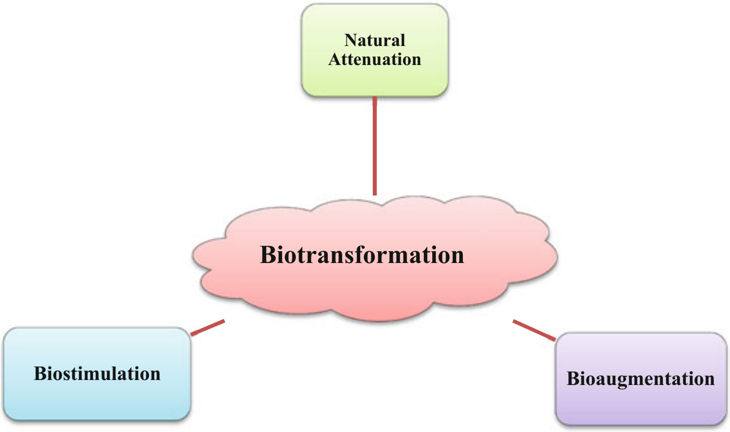


Fig. 8.3 Mitigation processes used in biotransformation

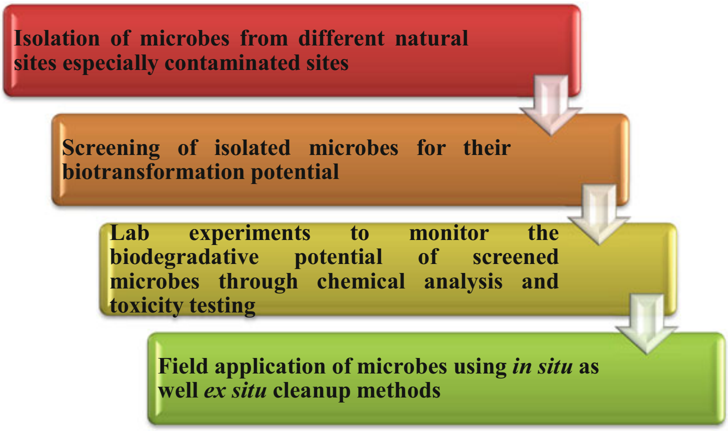


Fig. 8.4 Biotransformation using microbes: the basic procedure

contaminants has full potential. There are some basic steps employed for the use of any microbe in the biotransformation process which are described in Fig. 8.4.

Biotransformation using microbes is employed as purification process for polluted soil. Microbial biotransformation is of two types: in situ or ex situ. In situ biotransformation does not need excavation. In these, contaminants are treated in the place in which they are identified whereas ex situ biotransformation method involves excavation of polluted soil prior to treatment. In situ biotransformation has many advantages over ex situ biotransformation processes as it is not expensive and large amount of soil can be processed. However, in situ biotransformation takes more time than ex situ and is complicated to administer sometimes.

8.6 Mechanism of Biotransformation

The basic underlying principle behind the microbial transformation or biotransformation is mineralization and cometabolism. Mineralization refers to the process of converting organic substances to inorganic end products. The end products formed usually are either non-toxic or less toxic than the parent substrate. The process of mineralization is carried out by consortium microbes. The word consortium here refers to combination of two or more than two beneficial bacteria that with their biodegradative potential carry out the biotransformation process better than single microbe (Shelton and Tiedje 1984).

In the process of cometabolism, partial transformation occurs, leading to the formation of an intermediate product. This intermediate product can serve as energy or carbon source to microbes and thus can be utilized by them. However, sometimes this intermediate can be toxic to the microbial cells. The biotransformation process using microbes can be aerobic or anaerobic depending upon the type of pollutant to be degraded and the type of microbes to be employed in degradation process. In

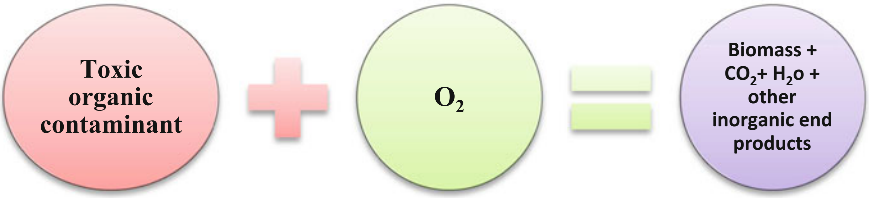


Fig. 8.5 Aerobic biotransformation mechanism

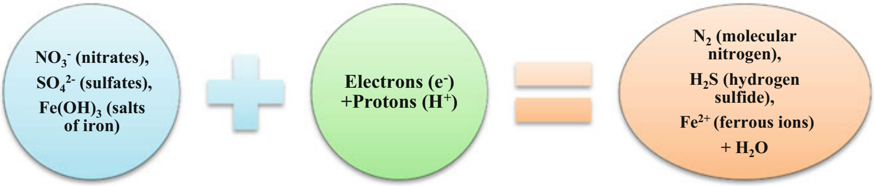


Fig. 8.6 Anaerobic biotransformation mechanism

aerobic biotransformation process, O_2 (molecular oxygen) receives electrons from organic pollutants and acts as terminal electron acceptor (Fig. 8.5). So, by addition of oxygen, oxidation of organic pollutant occurs with simultaneous reduction of oxygen to water. Some microorganisms like chemoautotrophic or lithotrophic bacteria, in order to gain energy, oxidize the inorganic contaminant (reduced) instead of using organic substrate.

Sometimes, with the activities of aerobic bacteria, the level of oxygen starts depleting. This leads to build up of anerobic conditions. In such conditions, terminal electron acceptor other than oxygen is required to carry out the process of transformation, mineralization, and cometabolism. There are many anerobic bacteria that use nitrate, sulfate, or iron salts as terminal electron acceptor as alternative to oxygen and can continue the process of biotransformation. Such transformation is called anerobic biotransformation (Fig. 8.6).

Anaerobic biotransformation is a many step process. Firstly, polymeric contaminants are broken down into monomeric by the process of hydrolysis. Then the final step is usually carried out by methanogens, denitrifying bacteria, or sulfate reducing bacteria to carry out the further decomposition to monomeric substances to alcohol, acids (soluble), hydrogen, and carbon dioxide.

8.7 Examples of Microbial Transformations

There are many remediation technologies available. But the selection of appropriate technology depends on many factors like type of pollutant, time allotted for cleanup, budget for cleanup, etc. Microbial biotransformation is employed mainly for the conversion of several toxic impurities or other wide range of contaminants like heavy metals, pesticides, pharmaceuticals, and hydrocarbons (Karigar and Rao

2011). The basic chemical reactions like isomerization, condensation, oxidation, reduction, functional groups introduction, hydrolysis, and formation of new carbon bond form the basis of microbial transformations. Microbial biotransformation has emerged as an imperative tool in bioremediation field. The characteristics of microbes like high surface to volume ratio, high expansion rate, and high rate of metabolism make them ideal choice for biotransformation of toxic pollutants. These processes are carried under sterile conditions as presence of contaminants can lead to the formation of faulty end products. Some common examples of microbial transformations are as under:

8.7.1 Transformation of Pollutants

Cleanup of polluted sites using microbes has gained momentum due to awareness regarding environment sustainability and human health issues. Microbes are used for the bioremediation of wide range of pollutants like hydrocarbons, radionuclides, polyaromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and pharmaceuticals.

Xenobiotic pollutants have been biotransformed using both aerobic and anaerobic bacteria. The examples of aerobic genera include *Bacillus*, *Escherichia*, *Pseudomonas*, *Gordonia*, *Moraxella*, *Rhodococcus*, *Micrococcus* etc., whereas the anaerobic types include *Desulfotomaculum*, *Desulfovibrio, Pelatomaculum*, *Syntrophobacter*, *Syntrophus*, and methanogens spp. (Chowdhury et al. 2008). PCB (Polychlorinated Biphenyls) has been degraded very effectively by *Pseudomonas* and *Bacillus.* The biotransformation of carcinogenic azo compounds has also been observed by the action of bacteria like *Pseudomonas*, *Acetobacter*, and *Klebsiella.* The non-chlorinated compounds like compounds like acetone, benzene, cyclohexane, styrene, dioxane, etc. can be catabolized by *Mycobacterium vaccae* (DiGioia et al. 2008). Anaerobic methanogens are also able to degrade many recalcitrant pollutants.

8.7.2 Biotransformation of Petroleum

The contamination from petrochemical industries is the topic of major concern. Accidental leakage is the principal basis of soil and water pollution by hydrocarbons. The remediation of hydrocarbon impurity from soil and water is very important as some petrochemicals are carcinogenic in nature (Das and Chandran 2010). There are several microbes which play role in the biodegradation of oil contaminants by conversion of them into non-toxic form. There are many genera of bacteria, fungi as well as yeast which have been reported to be efficient degraders of petroleum hydrocarbons. Bacterial genera, such as *Actinocorallia*, *Bacillus*, *Brevibacterium*, *Corynebacterium* sp., *Flavobacterium* sp., *Klebsiella*, *Pseudomonas fluorescens*, *P. aeruginosa*, *Rhizobium,* etc. and fungal genera such as *Amorphoteca*, *Aspergillus*, *Cephalosporium*, *Neosartorya*, *Penicillium*, *Talaromyces* have been isolated from petroleum sites. These bacterial and fungal genera were found to perform an important function in bioremediation of oil spills (Koul and Fulekar 2013).

8.7.3 Transformation of Pesticides

Pesticides are the formulations used in cultivation of agricultural crops for the control of unwanted pests. But, the presence of these pesticides in soil or environment is of great risk as these residues undergo biomagnification via food chain thus act as threat to human and animal health. Keeping this in view, many pesticides have been banned also. So, microbial biotransformations are of great interest in this field for the detoxification of pesticides.

a. The herbicide dalapon which is a chlorinated fatty acid is transformed into pyruvate by *Arthrobacter species* (Fig. 8.7). This herbicide is used as source of energy and carbon by bacteria so this conversion is the result of microbial metabolism.
b. Conversion of DDT to DDE by bacteria is example of microbial catabolism. The reaction mechanism is dehalogenation (Fig. 8.8). Such type of reactions fall under the category of cometabolism as microbes do not obtain energy from these molecules. They just modify the pollutants. However, the toxicity of modified product can be more or less than the parent product.

Apart from hydrocarbons, pesticides, etc., there are various other examples of microbial transformation like biotransformation of steroids and sterols, biotransformation of antibiotics. Such transformations have significant contribution in research and welfare of mankind.

8.8 Factors Affecting Microbial Transformation

The concentration of contaminants, their toxicity level, the biodegradation potential of microbes, the environmental conditions are among the major factors affecting the process of microbial biotransformation. The detailed explanation of various factors affecting microbial transformation is given in Fig. 8.9.

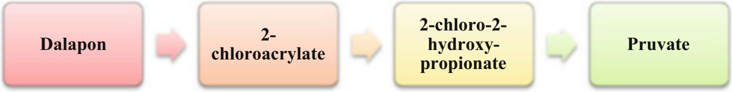
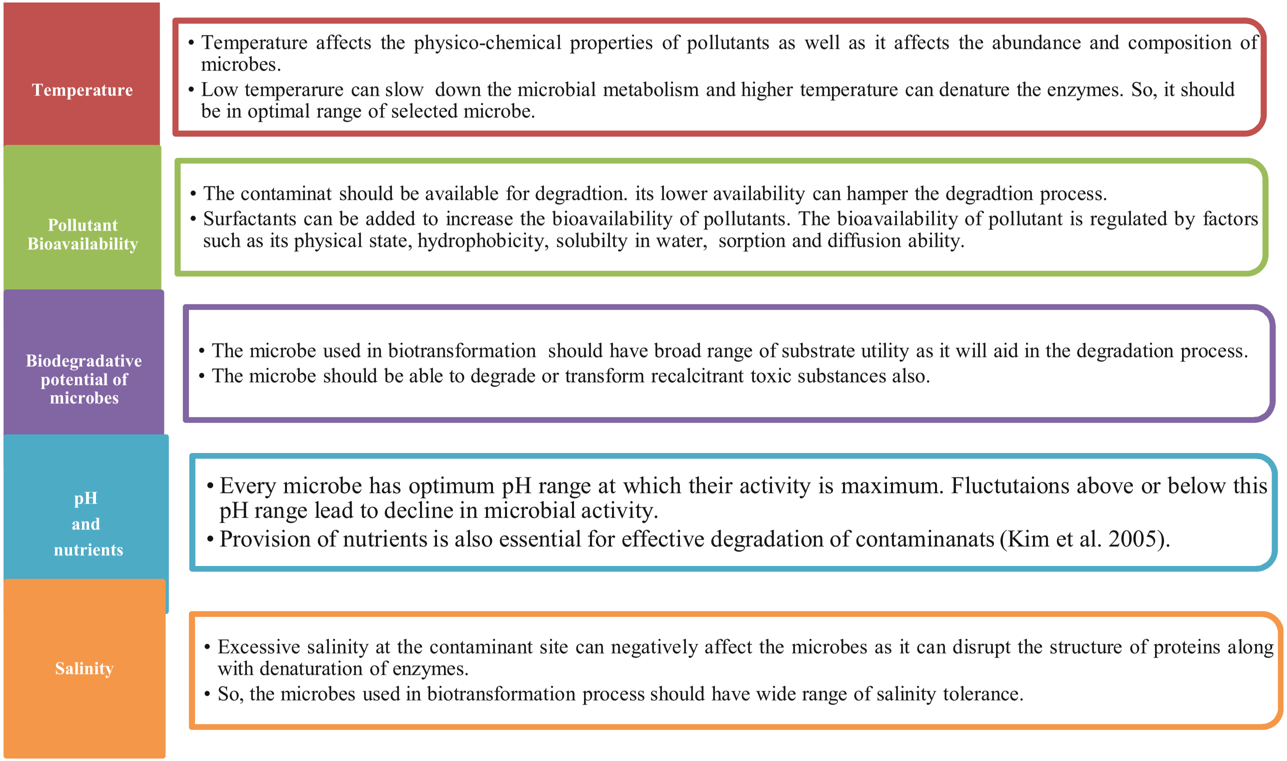


Fig. 8.7 Biotransformation of herbicide dalapon to pyruvic acid by bacteria (metabolism)

Fig. 8.8 Biotransformation of DDT pesticide to DDE by dechlorination (Cometabolism)



- Temperature affects the physico-chemical properties of pollutants as well as it affects the abundance and composition of microbes.
- Low temperarure can slow down the microbial metabolism and higher temperature can denature the enzymes. So, it should be in optimal range of selected microbe.

- The contaminat should be available for degradtion. its lower availability can hamper the degradtion process.
- Surfactants can be added to increase the bioavailability of pollutants. The bioavailability of pollutant is regulated by factors such as its physical state, hydrophobicity, solubilty in water, sorption and diffusion ability.

- The microbe used in biotransformation should have broad range of substrate utility as it will aid in the degradation process.
- The microbe should be able to degrade or transform recalcitrant toxic substances also.

- Every microbe has optimum pH range at which their activity is maximum. Fluctutaions above or below this pH range lead to decline in microbial activity.
- Provision of nutrients is also essential for effective degradation of contaminanats (Kim et al. 2005).

- Excessive salinity at the contaminant site can negatively affect the microbes as it can disrupt the structure of proteins along with denaturation of enzymes.
- So, the microbes used in biotransformation process should have wide range of salinity tolerance.

Fig. 8.9 Various factors affecting the process of microbial transformations

8.9 Future Prospects

Biotransformation of toxic contaminants using microbes is a promising remediation technology for cleanup of polluted sites. But, use of molecular approaches like genomics, proteomics, metagenomics, and other advanced molecular tools in this field can provide a good insight into the main pathways used by microbes for the degradation or transformation of toxic pollutants. The information from these studies can be major breakthroughs in bioremediation technologies as these tools can also widen the capability of organisms to accommodate to variable environmental conditions for better degradation or transformation of toxic pollutants.

8.10 Conclusion

Nowadays, biotransformation is the preferred remediation technology used for the cleanup of various contaminates sites. However, the success of this remediation technique relies on the use of adequate microbes capable of effective biodegradation. Sometimes, the prevailing environmental conditions are not optimal for biotransformation of pollutants. Therefore, biotransformation will be the effective remediation technology for reduction and elimination of harmful impurities provided that the microbes used are effective degraders and conditions are favorable for decomposition.

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9

Plant–Microbe Interactions in Bioremediation of Toxic Wastes in Tropical Environment

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Abstract

Pollution occurs through natural and anthropogenic activities. Toxic substances generated from different sources may accumulate in the soil and water bodies and potentially alter their physicochemical properties and ecosystem function. Although several environmental remediation methods have traditionally been tried with some success, bioremediation processes have been found eco-friendlier and cost-effective. Plant-assisted bioremediation, a remediation method that utilizes green plants and their associated microflora to eliminate contaminants from the soil or environment has been found commercially applicable because of its cost-effectiveness among other benefits. Phytoextraction, rhizofiltration, phytostabilization, and phytovolatilization among others are techniques commonly used to remove heavy metals and inorganic contaminants from polluted environments. Endophytes such as bacterial or fungal organisms that live within or between healthy plant tissues are known to portray either obligate or facultative association along with complex interaction with their host plant, which may be mutualistic and antagonistic in nature. Plant root exudates also contribute to plant–microbe interaction due to the fact that these exudates provide important nutrients and energy for associated soil microorganisms.

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Chemotaxis influences the movement of bacteria to plant root by the attraction of root exudates that exist between the soil and the rhizosphere. Specifically, the natural ability of most rhizospheric bacteria to tolerate environmental contaminants has lent them to phytoremediation use, especially in removing organic pollutants from food crops. Similarly, the ability of some plant species to be tolerant to specific stress in a time-dependent manner is being exploited in phytoremediation processes. For example, maintenance of high antioxidant levels that are capable of detoxifying toxic reactive oxygen species is associated with a plant's ability to tolerate environmental stress. Therefore, information on rhizospheric microorganisms and their benefits in phytoremediation processes should continually be updated, especially in tropical environments where cost is a critical factor. Furthermore, screening of plants to identify those with phytoremediation potentials, especially in tropical regions of the world that harbor rich plant biodiversity is imperative for cost-effective bioremediation of polluted environments.

Keywords

Toxic waste · Pollution · Detoxification · Phytoremediation · Rhizosphere · Endophytes

9.1 Introduction

Environmental pollution has continued to increase globally due to anthropogenic activities of man linked to urbanization, industrialization, mineral exploitation, and modern agricultural practices. Pollutants released into the environment may persist and pose threats to the biosphere. Environmental degradation issues have therefore become important concerns of governments and environmental organizations all over the world. It is now broadly accepted that polluted environments are a threat to human health, and this realization in recent times has steered global efforts at pollution control sites, in order to either mitigate the adverse health risks or to enable ecosystems recovery. Although several environmental remediation methods have traditionally been tried with some success, researchers continue to explore better and environmentally friendlier treatment methods, such as bioremediation processes.

Bioremediation is the use of microorganisms and plants in the conversion of pollutants into less harmful materials by natural biological processes (ELC 2008). As a pollution treatment option, bioremediation offers the possibility of degrading various contaminants by natural biological activities. It is therefore increasingly being employed in solid waste cleanup operations, due to its comparatively low cost and environmental impact than the more conventional clean-up technologies (Ojumu et al. 2005). Earlier reports by Blaylock et al. (1997) showed that a 50–65% reduction in remediation costs was made possible through bioremediation approaches instead of conventional methods like excavation and landfilling (Chibuike and Obiora 2014).

In bioremediation processes, naturally occurring microorganisms (bacteria and fungi) or plants use their enzymes and other metabolites to convert pollutants into less harmful compounds. Bioremediation is essentially controlled by several microbial factors and environmental factors like soil physical and nutrient characteristics (Agwu and Kalu 2012). Two basic approaches (in situ and ex situ techniques) have been applied to the bioremediation processes, depending on the nature of pollution at a site. According to Naik and Duraphe (2012), while in situ techniques are applied at the site with nominal disruption, ex situ techniques are applied to materials that have been removed from the site through excavation or pumping.

Contaminants like petroleum hydrocarbons, alcohols, solvents, industrial chemicals, pesticides, coal tars, chlorinated solvents, and poly-nuclear aromatic hydrocarbons have been shown to be biodegradable (Naik and Duraphe 2012), although some may take longer time and may require some form of augmentation (Udebuani et al. 2012). Furthermore, the success of bioremediation predicated on the appropriateness of the selected candidate organisms used in the process. For example, microorganisms isolated from the polluted site have been shown to possess inherent mechanisms that they utilize in converting pollutants into less harmful substances (Ojuederie and Babalola 2017). Similarly, microorganisms could be genetically engineered to convert pollutants to non-hazardous substances (Gupta et al. 2016). Specifically, numerous research efforts have exploited the capacity of indigenous microorganisms to sequester, precipitate, or change the oxidation status of different pollutants in the bioremediation processes (Gupta et al. 2016; Kang et al. 2016). In some cases, the application of a group of bacterial organisms may be preferred to using one strain (Ojuederie and Babalola 2017). For example, biofilm which is groups of microorganisms growing in an exudate made up of polysaccharides (Balcázar et al. 2015; Teschler et al. 2015) are being exploited for more efficient bio-sorption and bio-mineralization of metal ions based on their exopolysaccharide production associated with their processes (François et al. 2012).

The rhizosphere is the narrow area of nutrient-enriched soil adjoining the plant roots, which is influenced by the root exudates and the activities of microbes known as rhizospheric microorganisms (Venturi and Keel 2016a, b). Rhizospheric microorganisms associated with plant roots aid bioremediation through a process termed phytoremediation. Phytoremediation processes have been reported to be a particularly inexpensive, environmentally friendly, and relatively effective technique for restoring polluted sites (Jan and Parray 2016; Ojuederie and Babalola 2017). Candidate plants selected for phytoremediation processes are usually hyper-accumulators of pollutants, which may be of low biomass efficiency (Choudhary et al. 2017) or non-hyper-accumulators that exhibit high biomass yield and rapid growth (Udebuani and Ozoh 2007; Choudhary et al. 2017). For example, the sunflower plant (*Helianthus annuus*) is employed in phytoremediation processes due to its capacity to hyper-bio-accumulate heavy metals, in addition to other characteristics such as enhanced translocation of mineral elements, efficient heavy metal detoxification, good rooting system, and rapid growth rate (Muszynska and Hanus-Fajerska 2015).

Indeed, phytoextraction is increasingly being preferred over other methods used for the remediation of polluted sites because of the added beneficial effects of rhizobacteria associated with plant roots (Ojuederie and Babalola 2017). Phytoextraction has also been shown to be commercially viable (Slatter 2013). The natural ability of most rhizospheric bacteria to tolerate environmental contaminants has lent them to phytoremediation use, especially for the removal of organic pollutants in food crops. These organisms thrive near the rhizosphere of the host plant and through direct or indirect mechanisms make soil nutrients available for plant growth, synthesize plant hormones, and also safeguard the plant against harmful organisms, while performing other soil amendment functions (Ahemad and Kibret 2014; Nehra and Choudhary 2015). These rhizobacteria may include *Erwinia*, *Flavobacterium*, *Micrococcus*, *Pseudomonas*, *Serratia*, *Chromobacterium*, *Caulobacter*, *Azospirillum*, *Azotobacter*, and *Agrobacterium* genera (Bhattacharyya and Jha 2012)

Thus, several tropical plants and their associated microorganisms may possess inherent mechanisms that would make them candidates for use in the phytoremediation of polluted environments. Such candidate plants should not only be able to provide a viable habitat for its associated microbes but also should be able to improve soil's physical and nutrient qualities. The rhizospheric microorganisms in return should be able to enhance the important physiological parameters responsible for optimal plant growth. The root-associated organisms should also be able to ensure soil nutrient cycling by fixing nitrogen and by sequestering soil nutrients (Gkorezis et al. 2016). These properties and their interactions in phytoremediation processes are important for effective bioremediation. Therefore, information on rhizospheric microorganisms and their benefits in phytoremediation processes should continually be updated, especially in tropical environments where cost is a critical factor. This chapter reviews the current knowledge on plant–microbe interactions in bioremediation of toxic wastes in tropical environments.

9.2 Physicochemical, Socioeconomic, and Health Impacts of Pollution

Chemical substances existing in nature exert deleterious effects on humans and their ecosystem. The existence of these substances has far-reaching consequences on several tropical ecosystems and the services derivable from them for the benefit of mankind. An environment is polluted when there is an unfavorable change in its physical, chemical, and biological characteristics, which can greatly affect environmental health. Pollution occurs through both natural and anthropogenic activities. Intensified urban and industrial activities, modernized agricultural practices, mining, and intensive exploitation of the natural environment (Brassington et al. 2007; Ontoyin and Agyemang 2014; Mbewe et al. 2016) among others are the major anthropogenic causes of environmental pollution. The toxic substances generated from these activities can spread to remote areas, far from the source of pollution through hydrological pathways (Blas et al. 2006). Studies have shown that several toxic substances and their transformed products are persistent and bio-cumulative (Davies 1999; Adeola 2004; Theodorakis et al. 2012). Because of these qualities, they are regarded as the most dangerous group of chemicals in the natural ecosystem. For example, polycyclic aromatic hydrocarbons (PAHs), originating from crude oil may persist in the environment (Theodorakis et al. 2012). Of great concern is the soil environment which helps in sustaining ecosystem services, and whose physicochemical and biological properties may be compromised due to pollution (Pouyat et al. 2007). Since the soil serves as a general sink for many substances, toxicants emitted from different sources may accumulate in the soil and potentially alter its physicochemical properties (Hagan et al. 2012).

Soil physical characteristics include particle size distribution or soil textural class, soil structure (including micropore and macropore) constituting the total soil porosity and bulk density (in the range 1.1–1.5 g cm^{-3}). Soil physical properties are important in accessing soil productivity and potential plant root penetration in the soil (Pouyat et al. 2007; Steele et al. 2010). Soil chemical properties include pH, conductivity, and nutrient contents. Hagan et al. (2012) reported that in urban polluted soils, chemical properties showed greater changes than the physical ones. Pollutants generally reduce soil fertility, alter soil microbial distribution and abundance, and lower hydrological function (infiltration) and pH (Holman-Dodds et al. 2003; Cook and Ni 2007). Alterations in soil pH, cation exchange capacity, nutrient retention, especially storage of carbon and nitrogen, make the soil lose its ability to bind toxic substances such as heavy metals, thereby making metals more available (Farfel et al. 2005). Soil biota which contributes to ecosystem processing may also be affected. Important bacterial activities recorded in soils include decomposition of organic matter and nutrient transformation as exemplified by nitrogen fixation and denitrification (conversion of nitrate NO_3^- ion to N_2 gas). The sensitivity of soil invertebrates to chemical substances has also been reported (Reddy et al. 1996; Dureja and Rayendra 2012). Earthworms that contribute to the complex processing of the ecosystem through the decomposition of litter, cycling of nutrients, and formation of soils are susceptible to pesticides and even herbicides (Frampton et al. 2006; Dureja and Rayendra 2012).

In many tropical countries, toxic substances are indiscriminately discharged directly into the aquatic environment (rivers, lakes, streams, and ponds) from industrial activities and indirectly through runoffs from sources such automobile emissions, agrochemicals, and waste dump sites (Li et al. 2008; Zhaoyong et al. 2015). The occurrence, effects, and fate of these chemical substances in humans and aquatic organisms have been widely documented (Batayneh 2010; Zhang et al. 2011; Zhang et al. 2013). For example, high levels of these chemical substances alter the physicochemical properties of water bodies, with potential threats to the aquatic ecosystem. Some of the reported alternations include decreased pH, increased biochemical and chemical oxygen demands, increased turbidity, and reduction in light penetration in pollution, which may cause an impact in aquatic environment (Al-Taaniel et al. 2015; Zhaoyong et al. 2015). Heavy metals from industrial, agricultural, and mining processes also have some direct effect on the physicochemical properties of water, inhibiting microbial activity, and thus,

Fig. 9.1 Mangrove forest impacted by an oil spill in the Niger Delta, Nigeria

reducing nutrients supply to higher aquatic life (Davis et al. 2003; Zhaoyong et al. 2015), since the aquatic environment is diverse in nature, supporting different species of microorganisms, plants, and animals such as fish, amphibians, insects, crustaceans, snails, mussels, etc. Such negative impacts of pollution of water bodies usually start with its effects on its physical and chemical properties (Bassem 2020; Hassan 2008; Khan 2003), which are important in the functioning and maintenance of its ecological processes. Their inability to sustain ecosystem services due to pollution is, however, the driving force impacting human health.

Oil pollution in the aquatic environment, for example, may deposit thick oil films on water bodies, thereby preventing oxygen and light penetration into the water bodies. Inhibition of photosynthetic processes in primary producers such as algae, plants, cyanobacteria, etc. destroys the source of food for growth and reproduction of higher organisms. Oil pollution, therefore, leads to death and behavioral changes in animals such as birds that have physical contact with the oil through their feeding habits. Oil spillage also destroys the spawning, nursery, and feeding grounds of many aquatic organisms, for instance, the mangrove forest in Niger Delta area of Nigeria (Fig. 9.1) has devastated by crude oil pollution arising from incessant spillage (Duke 2016; Zhang et al. 2019; CEHRD 2019). Similarly, urban and agricultural runoffs have contributed to eutrophication in lakes and ponds which destroys fish and other relevant animals in the food chain.

Environmental pollution in tropical countries is caused by indiscriminate discharge of chemical substances that impact the ecosystem services of both aquatic and terrestrial habitats. The response of the terrestrial environment to such continuous pollution has been drastic because most terrestrial organisms are highly sensitive to toxic substances. Studies have shown that pollution of the terrestrial environment contributes to the direct or indirect response of soil organisms to the chemical substances, resulting in their death, decrease in soil fertility, which manifests as poor productivity of important crops. Chemical substances such as heavy metals are particularly harmful to plants (Tripathy et al. 2007; Cherian et al. 2012), thus, a major physical impacts of crude oil pollution have a devastating effect on crop farming (Nwilo and Badejo 2008; Elum et al. 2016; Osuagwu and Olaifa 2018). This is the major factor impeding agricultural productivity food security in many crude oil bearing locations in Nigeria. Ogwu et al. (2015) reported that increasing frequency oil spillage in the mangrove forest zone of Nigeria has led to losses in vegetation, with major impact being low agricultural productivity in a region that serves as a food basket of country in the recent past. Ebegbulam et al. (2013) have analyzed the effect of oil pollution on poverty and hunger in oil-producing communities of Nigeria and found a strong correlation. Agricultural land and crops in acid mined areas have also been contaminated with heavy metal (Ojeh et al. 2010). A similar report from studies carried out at Manitoba, Canada showed that a high level of trace elements prevented plant growth in the Gunnar gold mine tailing pond (Renault et al. 2007).

In many developing tropical countries, rural dwellers depend on agricultural practices to produce their staple food and fiber on a subsistence level. Therefore, any loss of farmland due to mining activities as witnessed in many of these areas is a threat to food security. Farmers and farm laborers are thrown out of jobs, leading to food insecurity, with resultant starvation and nutrition imbalance in vulnerable groups. Lack of adequate nutrition leads to stunted growth, mental retardation, and developmental disorders in children. Again, majority of rural dwellers in many tropical developing countries depend on surface water such as rivers, streams, ponds, lakes, for drinking and other domestic purposes. The freshwater ecosystems also serve the water needs of livestock and wildlife, as well as being a fishery and aquaculture resource for human livelihood. Therefore, pollution of such aquatic environments affects both human and animal well-being in many ways. Susan et al. (2001) reported the extinction of lake trout in the great lake due to contamination with chlorinated pesticides and heavy metals.

Pollutants may also accumulate in fishes (Mbewe et al. 2016; Ekpenyong and Udeme 2015) resulting in potential health problems to humans who depend on them as food. Pesticide residues have been found to accumulate in the tissues of three species of fish that are a significant part of the diet of residents of Lagos, Nigeria, and Uganda (Kasozi et al. 2005; Adeyemi et al. 2008). The pollution of fishery resources also affects the resident fishermen, who depend on fishing as both employment and source of livelihood and the mainstay of their economy. Such freshwater pollution specifically deprives fishermen of their traditional livelihood activities and their immediate families of a major source of high protein food. In most cases, children are the worst hit, because low protein intake in children and the concomitant effects such as stunting, mental and developmental retardation may be lifelong.

Health effects of pollution on humans and animals are seen in two categories, may either be an acute poisoning effect due to short exposure to relatively high dose of the toxicant and thus result in an instant or significant cause of morbidity or mortality resulting (Mansour 2012). Generally, this effect is severe and may cause the death of the organism. Ellenhorns et al. (1997) reported that 95 percent of the pesticide poisoning occurring in less developed countries is fatal. The body response to acute poisoning is usually inflammation, immunotoxicosis, myopathy, as well as reproductive effects (Ballantyne and Marrs 1992). The chronic poisoning is concerned with adverse health effects, or long-term effects, leading to chronic endpoints such as carcinogenesis, neurotoxicity, cytogenetic damage, teratogenesis, and immunological effects (Mendes 2002; Mino et al. 2002; Mansour 2012). Crude oil pollution, for example, has been shown to cause several health problems of far-reaching consequences in host communities. Studies at this location have shown that intake of water or oil contaminated food resulted in illnesses such as nausea, dizziness, neurological dysfunctions, reproductive and developmental disorders, and in extreme cases terminal illnesses such as cancer (Aguilera et al. 2010; Chang et al. 2014. Other diseases linked to exposure to toxic substances include pulmonary disease, heart failure, allergic reaction, many of these events lead to injuries or death. Organic pollutants implicated and recognized as carcinogens include polycyclic aromatic hydrocarbon (PAH), aromatic amines, benzene amino azo dyes, and vinyl chloride (Yu et al. 2011), while the inorganic substances include salts of arsenic, chromium, cadmium, nickel, lead, etc.

9.3 Phytoremediation Techniques in Removal of Toxic Waste

In phytoremediation, naturally associating plants and the microorganisms are able to sequester, detoxify, or neutralize the effects of toxic pollutants in soils, water, and air (Weyens et al. 2009; Cherian et al. 2012). Phytoremediation is an efficient, affordable, eco-friendly, aesthetically pleasing, and generally effective method of removing of toxic substances (Garbisu et al. 2002; Jing et al. 2007). The objective is usually to limit the biological availability of toxicants to other endpoints through the movement of toxicants. Higher plants are considered appropriate in this process because the contaminants are absorbed and sequestered in the roots and transported to the shoots and leaves (Reichenauer and Germida 2008). The nature and bioavailability of the contaminants, soil properties, and the type of plant amongst others are factors that can affect phytoremediation efficiency (Sreelal and Jayanthi 2017). Toxicants such as heavy metals (Jing et al. 2007; Cherian et al. 2012), petroleum hydrocarbons (Cartmill et al. 2014; Riberro et al. 2014), uranium (Malaviya and Singh 2012) can be successfully attenuated through phytoremediation processes. However, the phytoremediation is not without its own limitations. Studies have shown that phytoremediation potentials are influenced by plant growth rate, biomass generation rate, and availability of the toxicants in the root sphere (Chaney et al. 2005; Cherian et al. 2012). Major phytoremediation techniques include rhizofiltration, phytoextraction, phytostabilization, and phytovolatilization.

9.3.1 Rhizofiltration

In rhizofiltration aquatic plant roots are used to eliminate toxicants from aquatic environments. These aquatic plants are first grown and nursed in water, before being transferred into a toxicant contaminated water. Rhizofiltration can also be achieved by raising terrestrial plants in polluted water, in order to bioaccumulate the pollutants in different parts of the plant (Zhu et al. 1999; Malaviya and Singh 2012). It has been reported that rhizosphere and several microbes associated with hyper-accumulators, such as *Pseudomonas fluorescens* G10 (Sheng et al. 2008), *Pseudomonas putida* (Farwell et al. 2007, 2006), *Bacillus* sp. (Sheng and Xia 2006), *Enterobacter* sp., and *Pseudomonas* sp. (Mastretta et al. 2009) also participate in the remediation of heavy metals.

9.3.2 Phytoextraction

Plants can also extract some soil toxicants (heavy metals and organic content) by concentrating them in their biomass (Ali et al. 2013), so that the toxicants are eliminated when the biomass is harvested and discarded elsewhere. The toxicants are taken up from the soil and are transformed into another product or are accumulated in the tissue area of the plant and biomass (Table 9.1). Phytoextraction occurs in plants characterized by rapid growth and optimal biomass yield, which encourages substantial removal of contaminants from the soil. The biomass when harvested could be incinerated to completely eliminate the contaminants. The phytoextraction technique depends essentially on bioaccumulation factor or bioconcentration factor: $C_{\text{plant}}/C_{\text{soil}}$, which is the ratio of the concentration of toxicants in harvested plants to the concentration of the toxicant in the soil. Studies have described over 400 hyper-accumulators made up of annual and perennial shrubs and used in phytoextraction (Li et al. 2009a; Bissonnette et al. 2010). Uranium transfer factor (UTFs) for shoots range from 0.0002 to 0.34 kg^{-1}, while that of the roots range from 0.007 to 8.1 (Malaviya and Singh 2012). Molecular techniques have revealed that root UTFs could be raised to the range of

Table 9.1 Some tropical plant with hyper-accumulation capabilities

S/N	Plants	Source
1	*Solanum lycopersicum*	Hediji et al. (2015)
2	*Brassica napus*	Wu et al. (2015)
3	*Daucus carota*	Carvallo et al. (2015)
4	*Solanum aethiopicum*	Nabulo et al. (2012)
5	*Oryza sativa*	Khalid et al. (2017)
6	*Brassica juncea*	Khalid et al. (2017)
7	*Zea mays*	Avci and Deveci (2013)
8	*Allium cepa*	Chiroma et al. (2014)
9	*Spinacia oleracea*	Khan et al. (2013)
10	*Lactuca sativa*	Perveen et al. (2012)

76.69–123.52 (Eapen et al. 2003). Plants such as *Alyssum bertolonii*, *Pteris vittata*, and *Thlaspi caerulescens* have been used in the phytoextraction of contaminants from soil (Vander Ent et al. 2013).

9.3.3 Phytostabilization

Plant roots control the availability and mobility of toxicants, by preventing their movements to other receptors (Berti and Cunningham 2000; Cherian et al. 2012). They use biological amendments to immobilize toxic elements to prevent further spread or their entrance into the food chain. The aim is to prevent migration or mobilization of such contaminants, thus limiting their diffusion into the soil and other environmental components (Ali et al. 2013). This will stop the spread of such toxic elements toward underground waters or through runoffs, wind, and the food chain. Phytostabilizers are able to tolerate stress from soil conditions and must be able to grow rapidly, have a dense rooting system, and be able to self-propagate (Cherian et al. 2012). The biological amendment could be done by the use of fungi for the removal of such toxicants. Rufyikiri et al. (2004) highlighted the effectiveness of the soil fungus, *Arbuscular mycorrhizal* (AM), as the most widely distributed root symbiosis that forms an association with terrestrial flowering plants. Other studies (Rufyikiri et al. 2002; Chen et al. 2005; Roos and Jakobsen 2008) have also reported the effectiveness of *Arbuscular mycorrhiza* in the phytostabilization of uranium accumulation in various plants. Plants that act in phytostabilization processes are usually trace element extruders that exhibit sufficient root to shoot transfer coefficient (Kidd et al. 2009).

9.3.4 Phytovolatilization

Certain green plants can accumulate toxic substances in their tissues and then subsequently convert them into less toxic compounds, which they release into the atmosphere. The technique through which the toxicant is naturally released into the atmosphere is usually by harvesting the part of the plant involved and disposing of it, especially through incineration and the like. Through this method, heavy metals such as mercury, selenium, and arsenic-containing compounds have been removed from contaminated sites (Banuelos and Lin 2010; Lin et al. 2000). Some of the plants used in the phytovolatilization process are *Nicotiana tabacum* and *Brassica napus* (Ali et al. 2013). The method has also been applied to the removal of organic contaminants such as petroleum hydrocarbons (Ali et al. 2012) from polluted soils. Phytovolatilization therefore is a viable approach to the removal of toxic substances that may be harmful to the biota.

9.4 Uptake and Transportation of Toxic Substances in Plants

Terrestrial plants may be exposed to toxicants in two major ways: exposure of leaves to atmospheric pollutants and uptake or absorption of pollutants through plant roots growing in the contaminated site (Udebuani and Ozoh 2007; Uzu et al. 2010). The uptake and transportation mechanisms of heavy metals such as cadmium, mercury, lead and organic substances such as pesticides and petroleum hydrocarbons in candidate plants have been researched. The essential micronutrients such as iron, molybdenum, and manganese are important to plants for normal growth and functioning, while trace elements (Zn, Ni, Cu, Cr, Pb, Cd, Hg, etc.) are not important in plant biological functions (Schutzendubel and Polle 2002), although at high concentrations they may become toxic (Gamalero et al. 2009). The absorption of pollutants through the roots primarily depends on the availability of the toxicants in their ionic form. For example, Arsenic (As) is absorbed by plants mostly as As (III) or As(V) into the plant cell (Neidhardt et al. 2015), where As(V) is subsequently reduced to As(III) by the enzyme arsenic reductase (Ghosh et al. 2015). Similarly, Cd is passively absorbed in the form of Cd^{2+} (Cherian et al. 2012). The xylem and phloem are the tissues in both roots and shoots involved in the distribution of the toxic element to other parts of the plant (Mirza et al. 2014).

In rice (*Oryza sativa*), the accumulation of methylated arsenic species through the roots using the aquaporin nodulin-26-like intrinsic proteins (NIP2) has been observed (Li et al. 2009a). The methylated organic arsenic is generally less absorbable than inorganic form (Chandrakar et al. 2016). Raab et al. (2005) reported that the movement of methylated As in the xylem tissue is fastest from root to shoot. Several complex transport mechanisms have been implicated in the movement of arsenic from the soil into the plant xylem (Mitani-Ueno et al. 2011), with the Lsi1 and Lsi2 transporters being prominently involved in arsenic inclusion and exclusion movements, respectively (Khalid et al. 2017). Nodulin-26-like intrinsic proteins (NIP) transporters are equally part of the arsenic transport mechanism.

Lead absorption at plant roots is mostly achieved through Ca^{2+}-permeable routes and usually bound to compounds located on the rhizoderm cell surface Experiments conducted with *Funaria hygrometrica* have shown that lead can enter roots inactively and travel translocating water streams. Again, Pb absorption in plant roots depends on the concentration available at root tips; however, it should be noted that lead concentrations are usually high at the root tips. Low pH increases the solubility of lead in soil solution. Thus, lead absorption is essentially a non-selective energy-dependent process that sustains the appropriate lead concentrations in rhizoderm cells (Pourrut et al. 2008).

Cadmium (Cd) uptake and transport mechanism, by plants, depend on its concentration and bioavailability in soil, modulated by pH, organic matter, redox potentials, and concentration of other elements (Jingguang et al. 2019). Benavidez et al. (2005) reported that zinc and cadmium co-accumulate in aerial parts of *Arabidopsis halleri*, suggesting that their uptake is genetically correlated and that both metals are similarly transported and regulated. Studies carried out with rice have specifically highlighted similar uptake mechanisms for Cd, Mn, Zn, and Fe

(Nakanishi et al. 2006; Sasaki et al. 2012). Cadmium accumulates in the shoot after absorption from the soil, and this can be determined by xylem-mediated Cd translocation from the roots (Uraguchi and Fujiwara et al. 2012). The transporters playing this role include OsHMA2 and OsHMA3 (Satoh-Nagasawa et al. 2013). Transporter OsHMA2 translocates Cd through the roots to the shoots, while regulating its circulation via the phloem to other tissues. The level of OsHMA2 is however significantly low (Yamaji et al. 2013), while the contribution of OsHMA3 indicates functional deficiency resulting from high root to shoot cadmium translocation (Miyadate et al. 2011).

Toxicants like heavy metals and polyaromatic hydrocarbon are known to react with substances already in the soil to form new complexes, thereby ensuring that only a fraction of the toxicants are made available to plants. Toxicants absorbed by plants often enter the food chain. Although they may play significant roles in plant development, their presence constitutes a serious threat to higher animals. Absorption of heavy metals usually occurs through the Ca^{2+} permeable routes. Metals uptake by plants is however mediated by its form, soil physicochemical characteristics, speciation, and the amount of mycorrhizal transpiration (Cherian et al. 2012).

Caspian strips located in the endodermis of the root cells exhibit a blocking effect that ensures that some of the metal toxicants accumulate in root cells after uptake (Pourrut et al. 2011). Excessive accumulation of such toxic substances may however impair essential structural, functional, and chemical activities in the plant. The adverse toxic effects arising from metal accumulation in plants, especially on the leaves integrity, seed germination, and overall plant health have been documented (Perfus-Barbeoch et al. 2002; Rahman et al. 2005). For example, Tomulescu et al. (2004) and Islam et al. (2007) reported the inhibitory effects of lead on seed germination even at low concentrations, while other researchers (Islam et al. 2007; Sengar et al. 2009) specifically reported the inhibitory effects of lead on *Hordeum vulgare*, *Elsholtzia argyi*, *Spartina alterniflora*, *Pinus halepensis*, *Oryza sativa*, and *Z. mays* seeds germination. These inhibitory effects have been attributed to the disruption of the enzymes, protease and amylase, in particular by lead (Sengar et al. 2009). Pb accumulation also results in low biomass production linked adverse effects on leaf structure and functions (Islam et al. 2007, 2008; Piotrowska et al. 2009; Gupta et al. 2009; Singh et al. 2010). Zinc can form complexes with histidine in the root cells and organic acids in the shoot cells, which are ultimately accumulated in the plant cell vacuoles (McGrath and Zhao 2003; Cherian et al. 2012). This explains the physiology of zinc hyper-tolerance usually observed in plants. Again, metals can cause oxidative injury to plants by activating chemical processes that produce reactive oxygen species (ROS) or oxygen-free radical species. Flora (2009) reported that ROS disrupts essential chemical balance in cells, gene and protein structures, and membrane integrity in plant cells, thereby causing cell death.

9.5 Detoxification of Toxic Substances in Plant Species

Plants have well-developed defense mechanisms such as chelation, compartmentalization, biotransformation, and cellular repair that ensure tolerance of the negative effect of toxic metals or metalloids. These mechanisms include chelation, compartmentalization, biotransformation, and cellular repair. Under stress conditions, the defense systems mounted by plants become hyperactive in order to control the ROS facilitating cellular injury more efficiently (Armendariz et al. 2016). In addition, certain plants can block induced toxicity by producing and accumulating of osmolytes, which may include glycine, betaine, proline, and mannitol. Accumulation of osmolytes has specifically been shown to be an essential characteristic needed for plants survival during stress (Ghulam et al. 2019).

Mechanism of detoxification of toxic substances by plants includes the following: Phytochelatins (PC) formation, which occurs through binding of toxicants (heavy metal) to the cysteinyl sulfhydryl group and carboxyl groups binding site to form stable complexes. Such complex formation culminates in the degeneration of protein or enzyme structures, resulting in their inactivation (Dwivedi et al. 2012). Phytochelatins at toxic levels have been known to display high affinity for heavy metals (Shukla et al. 2013). They are also involved in the defense against metal-related stresses and excess heat, salt, UV-B, and herbicide induced stress, thereby serving as biomarkers of stress in plants exposed to such stressors (Saba et al. 2013). Cd^{2+} ions were reported to stimulate four to sixfold more PCs synthesis than Cu^{2+} and Zn^{2+} in cell cultures of *Rauwolfia serpentina* and *Picea rubens Sarg*, respectively, indicating that it is the most effective stimulator of PCs synthesis in plant cells (Thangavel et al. 2007).

Arsenic (As(III)) has a strong attraction to peptide groups such as the sulfhydryl found in PCs and GSH (Zhao et al. 2009). The As(III) binding site produced due to this strong affinity has been found to be more stable in acidic than basic environments (Raab et al. 2007; Zhao et al. 2009). Generally, the arsenic tolerance observed in non-As-hyper-accumulator plants occurs through this As(III) and PC complex formation (Kumar et al. 2015). Phytochelatin can also combine with anti-oxidative enzymes, to form a synergistic defensive system in some plants, and under heavy metal stress conditions can help to inhibit intoxication in such plants. Studies with *Brassica chinensis* have shown that cadmium detoxification was achieved through increased enzymatic biosynthesis of PCs and amplified anti-oxidative system activity in the plant.

Metallothioneins (MTs), ligands found in plants, help to nullify heavy metal toxicity via cellular confiscation, homeostasis of various metal ions, and metal passage modification (Guo et al. 2013). These ligands are acknowledged active mediators of a number of cellular events, such as ROS scavenging and redox levels maintenance (Macovei et al. 2010), plasma membrane repairs, cell multiplication, and growth and restoration of impaired DNA (Grennan 2011). Apart from toxic heavy metals, other factors such as water stress, poor nutrients availability, disease, and aging among others have been shown to induce metallothionein production. The types 1, 2, 3, and 4 MTs in roots, shoots, leaves/fruits, and seeds, respectively, are the MTs identified in plants. These MT types have also been subdivided further into isoforms (Guo et al. 2013). The MT types include heavy metals, forming metal chelators. There is evidence, however, that these plant MTs exhibit distinct treatment characteristics for different metal types, while their functionality, metal-binding, affinity capacity, and tissue localization also vary within a plant species. Furthermore, MT types have shown dissimilar and sometimes corresponding functions during homeostasis and heavy metal decontamination (Du et al. 2012).

Proline is a major osmoprotectant, known to accumulate in plants in response to different stress conditions (Begum et al. 2016). Rejeb et al. (2014) reported that proline as an osmolyte exhibits a stabilizing effect on the plant cell wall while aiding the maintenance of the minimal hydration level required in cells and cell membranes (Rejeb et al. 2014). Again, proline has been implicated in the protection of plants against damages mediated by ROS (Ozturk et al. 2010), especially by acting as a singlet oxygen quencher and OH forager. Through these functions proline therefore aids in the stabilization of protein, DNA, and cell membrane structures (Chandrakar et al. 2016). As a proteinogenic five-carbon α-amino acid, proline has also been shown to function as temporary carbon and nitrogen source for developing embryos. Elevated proline level is equally known to activate a non-enzymatic reaction to a variety of tensions caused by biotic and abiotic stressors in plants (Szabados and Savour 2010). In summary, proline plays an important role in combating the roles of adaptation, recovery, and signaling in plants (Fidalgo et al. 2013).

Proline uses different mechanisms to enhance resistance to metal toxicity in plants. Clemens (2006) reports that accumulation of proline in plants is not actually induced by heavy metal stress but due to water balance disorder that occurs because of excess metal. Again, proline scavenges for ROS mostly by neutralizing hydroxyl radicals and reducing singlet oxygen associated with metal stress. According to Mourato et al. (2012) proline also enhances the antioxidant activities, guards, and conserves redox homeostasis, in addition to other functions like choline reconstruction and intracellular pH control (Rastgoo et al. 2011). Indeed, proline initiation into heavy metal stress depends on the concentration gradient, type of metal, and specific organ. Interestingly, a corresponding increase in endogenous proline concentration, linked to exogenous proline application has been reported to aid better mental stress response in plants (Shahid et al. 2014).

9.6 The Response of Plants to Stress from Toxic Substances

Stress in plants caused by external factors affects their growth, development, and productivity (Verma et al. 2013). Stress activates a different response in plants such as the alteration in gene expression and cellular metabolism, as well as alterations in plant growth and yield among others. Under stress, plants are usually able to mirror any sudden change in environmental conditions. Thus, plant species that are stress-tolerant on exposure to a particular stress are able to initiate physiological adaptations to the stress condition in a time-dependent manner. The sessile nature of plants, when exposed to various environmental stressors, often induces oxidative and genotoxic stress resulting in various forms of lesion formation in the DNA double helix structure (Dutta et al. 2018). Plant stress has been divided into abiotic and biotic stress. Abiotic stress is caused by environmental factors, which have been categorized into physical (drought, flood, high soil salinity, etc.) and chemical (poor nutrients, high UV light, etc.) factors, while biotic stress is caused by biological factors (diseases, insects, etc.) affecting the plants (Verma et al. 2013). However, plants can recover from an injury caused by mild stress, while severe stress induces plant loss through flowering, seed formation, and induced senescence prevention. Most wild plant species are known to survive different forms of stress (Sewelam et al. 2014).

9.6.1 Plant Stress Response Induced by Environmental Pollutant

9.6.1.1 Reactive Oxygen Species Signaling

Reactive oxygen species (ROS) are formed due to unavoidable escape of electrons during electron transport in different cellular compartments or different metabolic pathways (Blokhina and Fagerstedt, 2010). Environmental stress induced ROS poses serious threats to cells and usually results in cell damage and death (Mishra et al. 2011). ROS though having destructive activity are known as secondary messengers in several of cellular functions that include stress tolerance (Yan et al. 2007). Plants are able to detect ROS signal and translate them into applicable cellular response through certain redox-sensitive proteins and other metabolic activities, including gene expression (Sharma et al. 2012). Excess ROS is eliminated through specific antioxidant activities comprising enzymatic and non-enzymatic antioxidants (Sharma 2012). Maintenance of high antioxidants capable of detoxifying toxic ROS is, therefore, connected to an increase in the tolerance of plant to environmental stress (He et al. 2012).

9.6.1.2 Abscisic Acid Signaling

Abscisic acid (ABA) is one of the stress induced signaling primary hormones (Cramer 2011) that moderates the abiotic stress. Biotic stress on the other hand is specifically facilitated by the antagonism amongst the other stress hormones such as acid JA/ET (Liu and Schnoor 2008). However, ABA has been shown to accumulate after certain infections (Ton et al. 2009), with resultant overriding of other defense reactions (De Torres-Zabala et al. 2007). ABA has been shown to initiate SnRK2s production, which phosphorylates the plasma membrane enzyme, NADPH oxidase RbohF to generate O_2^-, and subsequently forms hydrogen peroxide. The hydrogen peroxide in turn serves as a signaling chemical that regulates different types of ABA responses, like stomatal closure (Sirichandra et al. 2009).

9.6.1.3 Osmolytic Signaling

The large families of mitogen-activated protein kinase (MAP) pathway components in plants can combine in different ways to form MAP kinase modules, such as MAP3K, MAP2K, and MAPK (de Zelicourt et al. 2016). Activation og these

MAPKs has been described in plants during both biotic and abiotic stress (de Zelicourt et al. 2016), especially biotic stresses like osmotic and temperature stress that mediate the generation of various lipid signals (Hou et al. 2016). These lipid signal molecules have however been shown to bind to other signaling proteins, with resultant modulation of their activities and that of membrane associations.

9.6.1.4 Systemic Signaling

Pathogen infections trigger systemic responses in plants, although abiotic stressors also elicit systemic responses both at their point of application and in tissues distal. Such abiotic stressors are capable of initiating systemic acquired acclimation (SAA) in plants, involving long-distance signals (Choi et al. 2014). Stress triggered by such long-distance signals is known to move at substantial speed (>1000μm/s) in plants and can cause transcriptional reactions in distal tissues (Choi et al. 2014). Enzymes like NADPH oxidase, derived from plasma membrane, are particularly needed for ROS signal propagation, while the calcium signals rely on certain vacuolar ion channels (Choi et al. 2014). It is therefore postulated that the generation of ROS triggers the calcium signal which subsequently through other complex reactions also generates a self-propagating mutual activation circuit that links ROS and calcium signals (Dubiella et al. 2013). Similarly, H_2O_2 generated by NADPH oxidase also plays a role in the activation of plasma membrane calcium channel (Grondin et al. 2015), with the aid of certain receptor-like kinases (Hua et al. 2012).

9.7 Plant–Microbe Interactions in Attenuation of Toxic Substances

9.7.1 Plant–Microbial Interactions in Remediation of Polluted Aquatic and Terrestrial Ecosystems

Plant–microbe interactions are of great relevance in agronomy, not only in bio-fertilization as seen in various rhizobia-plant root relationships, but also in detoxification of contaminants. In bio-fertilization, a substance which contains living microbes is smeared on the plant material, or the soil, so that the microbes take over the immediate environment (rhizosphere) or the interior of the plant. Biofertilizers exert their effects by promoting the growth and development associated crops by enhancing the generation of primary nutrients for the host. Such biofertilizers include *Rhizobium*, *Azotobacter*, *Azospirillum*, phosphate-solubilizing bacteria, mycorrhiza, and blue-green algae (BGA). Generally, biofertilizers are classified as mycorrhizae, organic fertilizers, algal biofertilizers, symbiotic and non-symbiotic nitrogen fixers, and phosphate-solubilizing bacteria. Sometimes, bacteria are used as the major component of the product and have been referred to as bacterial fertilizer.

Soil microbes produce siderophores and protons when micronutrients such as iron are deficient in soils. Bacteria implicated in this process include *Psychrobacter* species etc, hence their application on iron-deficient and nickel-contaminated soils cultivated with sunflower (*Helianthus annuus*) as this association enhances iron solubilization and uptake. Studies have shown that bacteria, such as *Janthinobacterium* species, *Arthrobacter* species, Leifsonia species, and *Polaromonas* species increase the speed of the mineral nutrients dissolution and deployment in soils (Uroz et al. 2009). Through this mechanism, biofertilizers trap atmospheric nitrogen to the soil where it is transformed to plant usable forms. Again, some biofertilizers able to make phosphates more available for plant use. Biofertilizers are therefore critical to the supply of nutrients by nitrogen fixation, stimulation of crop growth through the production of growth-stimulating compounds, and solubilization of phosphorus to make it more available to the crop. Bacteria are known to possess several traits that are beneficial or otherwise in the plant–microbe interactions, which has been categorized into symbiosis, antibiotic production, competence, conjugation, motility, sporulation, biofilm, and virulence.

9.7.2 Plant–Microbe Interaction by Mutualism

Microbes are in symbiotic relations with plant roots and this associative cooperation is vital in the root zone of the soil system. Some bacteria and arbuscular mycorrhizal fungi are used as bio-inoculants which positively influence metabolic activities of associated plants and membrane permeability of their root cells. These organisms enhance the formation, growth, and development of hyper-accumulators in polluted soils. Multi-beneficial effects of plant–microbe mutualistic interactions include phytostimulation, phytoavailability of nitrogen, calcium, phosphorus, potassium and iron, stress bioalleviation, biomodification of root biomass, and utilization of some as biopesticides (Song et al. 2004). Phytoavailability is the accessibility of toxic metals to plants for their uptake (Song et al. 2004). An example is the uptake of trace elements by the perennial ryegrass, *Lotium perenne* (Antonangelo and Zhang 2019). Gomez-Bernal et al. (2017) reported *B. rapens* and *T. domingnensis* as important plant species that can take up heavy metals and store them in various tissues. Phytoavailability makes nutrient elements in the soil available for plant growth and development in times of stress. In this way, plants have interacted with bacteria to achieve fixing and mobilizing nutrient elements such as nitrogen, phosphorus, and other mineral elements for plant development (Hardoin et al. 2008).

Under varying climatic conditions, fungi like arbuscular mycorrhizal have been shown to develop a symbiotic association with plant roots, especially vascular plant species. In such symbiotic association, these mycorrhizal fungi benefit through photosynthetic activities of the plants, while in return they help to enhance mineral utilization by the plants (Upadhyaya et al. 2010). This type of plant-fungi association has also been shown to aid better plant pollution tolerance. Rahmati and Khara (2011) in their study of chromium (Cr) stressed maize plants treated with the arbuscular mycorrhizal fungus, *Glomus intraradices*, suggested that such plant-fungi association can also produce early stress warning signals that help the plant initiate protective mechanisms early enough. Abdelmoneim et al. (2014) reported that no such benefit was observed with Cu and Cd stressed maize plants inoculated with two species of mycorrhizal fungi (*Glomus mosseae* and *Acaulospora laevis*). These contradictory results may be due to differences in the type of metal stressors applied or maize variety used in the studies.

9.7.3 Plant–Microbe Interaction in Decontamination of Soils

Plant roots and soil microbes have long-standing relationships in the rhizosphere. Secretions or exudates and soil biota are therefore important components of the rhizosphere ecosystem as they perform important roles in transforming soil materials leading to the bioavailability of metals and nutrients. Root exudates, for example, supply soil microbiota abundant energy and nutrients while in return they stimulate the release of exudates from roots of plants. Some plants and their obligate or facultative microorganisms struggle for existence, and in their relationship, they coexist for mutualistic or beneficial purposes. Plant exudates promote phytoremediation by stimulating activities of soil microorganisms in the root zone (Sessitsch et al. 2013) and release of organic acid-metal complexes that acidify soils and speed up the mobility of nutrients and metallic ions. Plant root exudates are also capable of forming intracellular binding materials like amino acids, organic acids, and phytochelatins. Solanki and Dhankhar (2011) reported that phytochelatins and certain metal-binding peptides can be produced through several available chemical options like enzymatic reactions or even from tripeptide glutathione. It has been reported that the phytotoxic effects of metal ions can be through the effects of metal-binding peptides, thus, allowing for metal uptake and other physiologic processes within the plant. Hyper-accumulators exude various compounds that stimulate bacterial growth, solubilize mineral nutrients like phosphorus, iron, and zinc, and detoxify some metals such as arsenic, cadmium, and lead (Li et al. 2009b).

Hyper-accumulators are able to eliminate metal toxins through chelation at the plant root zone. Their ability to release exudates from the roots, also hence their high tolerance of elevated concentrations of contaminants. According to Magdziak et al. (2011), this prevents metal ions from entering the cell symplast. In agronomy, some crops are known to undergo root exudation of citric, oxalic, malic, and succinic acids when stressed by heavy metals and other contaminants thereby minimizing their proneness to phytotoxicity. Soil microbiota can withstand high concentrations of pollutant metals. Ma et al. (2015) reported that soil microbes evolve resistance strategies against soil contaminants. Soil microorganisms enhance phytoremediation by plant biomass by increasing phytoextraction or by reducing the available metals in the soil (phytostabilization), as well as enabling metal transport into the roots (bioaccumulation) and subsequently to the shoot (Rajkuma et al. 2012). Some microbes are used in cleaning contaminated soils or in reducing the level of contamination in soils through the biological degradation and transformation of toxicants into non-toxic substances.

Some plant roots release flavonoids, which play significant roles in plant-microbe collaborations in the soil system. Included in such interactions are legume-rhizobia symbiosis as well as mycorrhiza formation. The flavonoids play key roles in the growth of hypha, its diversity, and root establishment in arbuscular mycorrhizal formation–plant interaction, as well as in spore formation. In addition to this, flavonoids act as chemo-attractants and inducers of the nodulation genes implicated in the production of lipochitin–oligosaccharide, and also promote the growth of host-specific rhizobia. There are other flavonoids related compounds like isoflavonoids and flavones, which are identified as inducers of rhizobial nodulation gene expression (Juan et al. 2007). In a mycorrhizal association, certain fungi symbiotically relate to the roots of some vascular plants. All these are necessary in the activities of soil biota and in the chemical reactions taking place in the soil sphere. Because of their capacities in recycling recalcitrant polymers like lignin and hazardous toxicants, and use in bioremediation, application of mycorrhizal formation in improving soil quality is often known as mycorrhizo remediation.

9.7.4 Plant–Microbe Interaction by Phytostabilization and Phytoextraction

Some microbes like *Funneliformis mosseae* have been linked with phytostabilization of toxic metals (Hassan et al. 2013), through metal mobilization or immobilization processes (Ma et al. 2011). Arbuscular mycorrhizal fungi establishment by *Rhizophagus irregularis* has been shown to aid phytoextraction of cadmium (Hassan et al. 2013). Again, organic acids enhance the heavy metal immobilization via the formation of stable metal complexes in soil milieu. However, rhizospheric bacterial interactions with plant roots can be beneficial, neutral, or harmful. Plant growth-promoting rhizobacteria (PGPR) produce a mixture of complex volatile substances that is different from other bacteria species (Groenhagen et al. 2013). These volatile substances can encourage plant growth (Penuelas et al. 2014), stimulate suppression of disease (Yi et al. 2013), and antagonize phytopathogens, insects, or nematodes. In addition, rhizospheric bacteria also ensure soil nutrients availability for optimal plant growth, while phytohormones elaborated also provide protection against important pathogens in addition to remediation of contaminated soils (Paul and Lade 2014).

PGPR are found in the surroundings of the rhizosphere where they boost performance by different mechanisms (Bhattacharyya and Jha 2012). Through a direct mechanism that includes solubilization of phosphate, and production of siderophore, among other processes, it enhances the plants' ability to withstand biotic stress. PGPR through an indirect mechanism can also act as a biocontrol agent that allows the decontamination of heavy metals and pesticides (Glick 2010). *Pseudomonas aeruginosa*, a growth-promoting rhizobacteria has been shown to tolerate heavy metals like cadmium and is used as bioremediation against Cd induced stress (Huang et al. 2016). Reports have established that rhizospheric bacteria not only mitigate damage arising from metal toxicity (Etesami and Maheshwari 2018), but also through several mechanisms help to reduce the access of plants to metallic pollutants (Etesami 2018).

9.8 Plant–Microbe Interaction in Biodegradation Processes

Microbes are excellent agents of biodegradation. They are able to break down many foreign and natural chemical substances found in animal and human wastes. Human and animal waste are bio-wastes made up of remains from food and feed digestion as well as the microorganisms resident in them. Bio-wastes also include agricultural residues, like wood, paper wastes, leaves, grass clippings, and several food processing wastes among many others. Bio-wastes are biodegradable and have recently been used to produce biodegradable plastics and packaging materials. The biodegradation process involves essentially the breakdown of these materials by microorganisms in nature, certain bacteria, and fungi. The metabolites released into the rhizosphere in situ by microbes are also biodegradable, thus, they do not constitute much danger when compared with inorganic compounds. The use of plant growth-promoting microorganisms in biodegradation processes, therefore, ensures biosafety, in addition to remediation of contaminated soils. This they do by immobilizing or mobilizing or transforming heavy metals in soil, thereby reducing metal toxicity. Scholars (Huang et al. 2016) reported reductions in metal-induced toxicity, alteration in soil reaction, thereby minimizing metal availability (Rajkuma et al. 2012).

Some bacteria are able to alleviate the effects of metal toxicity, while metal immobilizing or mobilizing bacteria reduce metal availability, while others known as solubilizing bacteria help to plant growth bacteria by solubilizing metallic elements like phosphate and potassium. Certain bacterial organisms with properties such as siderophores, biosurfactants, indole-3-acetic acid, organic acid, and nitrogen-fixing have also been found to play beneficial roles in their associations with plants. The effective microorganisms (EMs), on the other hand, are those organisms that have been shown to improve soil quality, and therefore crop production under different agro-ecological settings when applied to the soil as inoculants (Yamada and Xu 2000). Because soil physical properties play important roles in crop production and water efficiency, EMs are useful in conditioning important soil physical properties. Invariably, plants are inherently able to selectively promote the establishment of the root microbes in their surrounding soil, and this has been linked to the properties of rhizosphere soil and the nature of root exudates.

9.8.1 Plant–Endophytes Interaction

Endophytes are bacterial and fungal organisms living in normal plant tissues without being harmful to the host (Dhanya and Padmavanthy 2014). Endophytes are microbes that have an either obligate or facultative association or complex interaction with their host plant. Their relationship may be either mutualistic or antagonistic (Dhanya and Padmavanthy 2014). The obligate relationship shows the two living organisms relying on each other. Endophytes depend on plants for their metabolic activities and survival as the plants secrete substances used in this capacity, and the plant depends on the endophytes for nutrient element supply (Andreote and Durrer

2014). Plants are able to restrict the growth of endophytes, through the synthesis of several growth-promoting substances which also help to improve plant survival in the environment. These endophytes also assist in protecting the plant from bacterial and viral infections, colonization of plants by rhizobium-host, thereby improving the capacity of such plants to withstand stress condition (Hashem et al. 2016). The symbiotic association of the plant species and endophytes provides protection to organisms which in turn produce metabolites that enhance nutrient absorption, growth, and biomass production. Essentially, therefore, endophytes are useful to plants through nutrients and bioactive compounds supply, protection against biotic and abiotic stresses, and detoxification of pollutants (Brader et al. 2014).

Thus, the several beneficial properties of endophytic bacteria have been exploited in promoting the growth of important crops (Mitter et al. 2013). Importantly, endophytes have been employed in bioremediation of polluted soils because of their capacity to support plant life and development in such soils (Glick 2010). They are particularly able to aid their associated plants in breaking down organic pollutants already taken up by the plants (Bittsánszky et al. 2011; Van et al. 2011). During this process of phytoremediation of organic pollutants, endophytes secrete various enzymes for the mineralization of these pollutants. Endophytic bacteria are widespread in nature and have been isolated from plant species, including crops, aromatic and medicinal plants (Sharma et al. 2012). Examples of endophytes isolated from plant tissues include *Acetobacter*, *Anthrobater*, *Bacillus*, *Burkholderia*, *Enterobacter*, *Herbaspillum*, and *Pseudomonas* (McGuinness and Dowling 2009). Endophytic bacteria used in degrading pollutant can be isolated from plants internal tissues grown on soils contaminated with organic pollutants (Germaine et al. 2009), degradation of aromatic hydrocarbon (e.g., toluene, xylene, ethylbenzene, and benzene) as well as from different parts of poplar tree (Taghavi et al. 2011), oak tree, and common ash for the degradation of volatile organic pollutants (Kang et al. 2012).

9.9 Conclusion

This study has uncovered plants with phytoremediation, phytoavailability, phytostimulation, and biomodification qualities. Natural plants exist, which help in mobilizing, absorbing, accumulating, and detoxification of toxic substances, from activities of man, thereby sustaining our ecosystem. Many of these plants with phytoremediation qualities are yet to be covered and the fact that many of the plants are going into extinction because of the devastating effect of climate change. Identification of these plants will help boost the phytoremediation technique, which is an aesthetically accepted environmentally friendly method with the potentials of cleaning our polluted environment. In addition, microorganisms inhabiting the tissues of plants have been discovered as an important complementary tool in mitigating and total removal of toxic substances in the environment. This approach has helped to establish environmental quality standards that sustain the anthropogenic release of toxicants in impacted areas.

The presence or use of plant–microbe association in enhancing phytoremediation highlighted two important microbes; endophytes and rhizosphytes as important species in removing toxic substances. Endophytic species generally promote plant yield, nutrient uptake, and totally detoxify and render toxic substances in the environment harmless. In this mutual relationship, plant root provides root exudate which attracts chemoattractant bacteria that increases ion solubility thereby increasing the activities of microbes associated with plant root. Rhizospheric bacteria are also implicated in the bioaccumulation of toxic substances in the tissues of the shoot and roots of plants. And more still the toxic elements can be sequestered in the vacuoles of the plant cell. Plant–microbe interaction is an important method that appears with prominence in achieving sustainable clean-up at pollution sites without further damage to the ecosystem.

However, knowledge of the general mechanism involved in toxicant's accumulation, translocation, and detoxification is important in developing efficient and sustainable phytoremediation techniques. Many plants capable of secreting chelating substances that attract microbes utilizing them exist in nature. Knowledge of these chemical secreting plants is limited, therefore, screening of plants to identify those with this potential, especially in tropical regions of the world that harbor rich plant biodiversity is needed for cost-effective bioremediation of polluted environments.

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Advanced Bioremediation Strategies for Mitigation of Chromium and Organics Pollution in Tannery

10

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Abstract

Recent past has witnessed to increase in environmental pollution because of rapid urbanization and industrialization. Various organic and inorganic toxicants are present in tannery effluents such as metals and other xenobiotic compounds which cause imbalance to the ecosystem having carcinogenic effects threaten plants, human, and animals' health. Chromium is one of the major pollutants discharged from tanneries, is highly toxic, mutagenic, and carcinogenic in nature. There are several remedial measures for the removal of such toxicants. Physicochemical approaches remove the pollutants but they are not cost-effective and eco-friendly. Microorganisms based treatment of toxic chemicals either in liquid or solid system is one of the most economic, effective, environment friendly, robust, and sustainable remediation strategy. Several microbes of different physicochemical orientation and plants may selectively be employed for such remedial measure of any type of toxic chemicals of industrial effluent. This chapter discusses the recent advances and challenges in bioremediation methods of tannery wastewater.

Keywords

Bioremediation · Chromium · Heavy metals · Tannery · Pollution

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10.1 Introduction

In the past few years, industrialization and modernization produced many problems in the form of hazardous pollutants in the environment. Industrial processes insert various types of hydrocarbons, heavy metals, chlorinated phenols, biocides, and dyes to the environment (Garg and Tripathi 2011; Nicolopoulou-Stamati et al. 2016; Tripathi et al. 2019). These pollutants cause pollution in water, soil, and air resulting in harmful effects on environment and human health (Zhang et al. 2020). Chromium has contaminated all types of water resources (Szulczewski et al. 1997). There are several other industries such as chemical, iron, and steel producing bulk of chromium pollution (Chirwa and Wang 2000, 2005; Garg et al. 2012). The excessive use of hexavalent chromium (Cr^{6+}) in industries has caused substantial environmental pollution (Sultan and Hasnain 2007). Such waste is discharged into the ecosystem through leakage and inappropriate remediation methods (Palmer and Wittbrodt 1991). Chromium is listed as a priority pollutant by United States Environmental Protection Agency with discharge limit of 0.05 mg L^{-1} (U.S. EPA 1979). While the permissible limit for Cr^{6+} is 0.1 mg L^{-1} in India (Bhide et al. 1996). Chromium exists from -2 to +6 oxidation states (Avudainayagam et al. 2003); however, the most common oxidation states of Cr are +6 and + 3 (Garg et al. 2012). Cr^{6+} is toxic, carcinogenic, mutagenic, and teratogenic (Garg et al. 2013; Tripathi et al. 2011a, b, 2019). It is important to remove such toxicants or at least transform them to nontoxic form before they release into the environment. Our ecosystem is damaging due to discharge of improperly treated large quantities of heavy metals and organics containing toxic waste. Due to their bioaccumulation, persistence, and resistance to bioremediation, metal pollution has become hazardous to all living forms of our environment. To tackle the challenges due to Cr^{6+} pollution, a concerted effort should be undertaken involving both surveillance of its use and improvements in remediation processes (Garg et al. 2012).

Another major toxicant is pentachlorophenol, also discharged from tannery effluent which is highly toxic and recalcitrant (Srivastava and Thakur 2007; Thakur et al. 2001; Tripathi et al. 2014a, b). Due to its toxicity, US EPA listed PCP in the list of priority pollutants. According to the ISI, the standard limit for phenolics is 0.002 mg L^{-1} in surface waters (Tripathi and Garg 2013). Phenolic compounds are accumulated in biological food chains causing toxic effects (Garg et al. 2013). Thus, remediation of such pollutants from effluent is necessary. There are many strategies that have been used for preventing harmful effect of such pollutants up to certain level. Physical and chemical methods are being used to remediate these pollutants but due to some limitations such as cost and non-ecofriendly nature, it has not been applied successfully. Despite this, microbiological methods or bioremediation are currently applied to decrease the toxicity of pollutants from soil, water, and environment.

Bioremediation is the application of live forms of organisms, particularly microbes, to remove pollutants and transform them into innocuous forms in the environment (Garg et al. 2012). Microbe based remediation has been developed to degrade toxicants through various biosynthetic pathways. A number of bacteria, fungi, algae, actinomycetes, etc. are being used for bioremediation. This process is facilitated by two ways, in situ (on site) and ex situ (away from site). Microbial systems are being introduced to the contaminated site to enhance the remediation process known as bioaugmentation (Vidali 2001) which are mechanized by bioreduction, biosorption, and bioaccumulation (Rehman et al. 2007). Bioreduction is another approach of bioremediation in which the toxic Cr^{6+} is reduced to Cr^{3+} using microbial enzyme chromate reductase (Tripathi and Garg 2014a, b). The main benefits of bioremediation over traditional methods include cost effective, less amounts of secondary pollutants, good efficiency, and regeneration of biomass for further use (Garg et al. 2013). This chapter discusses different advanced methods of bioremediation, and their mechanisms using potential microorganisms in the treatment of hexavalent chromium and organic pollutants from the tannery wastewater.

10.2 Physicochemical Characteristics of Tannery Wastewater

Tannery wastewater causes serious problems to ecosystem because of various toxic components. Such toxicants came in the environment through discharge from industries affecting almost all living systems. Some researchers discussed common characteristics of the organic pollutants (Yadav et al. 2016). There are several parameters like biological oxygen demand (BOD), chemical oxygen demand (COD), total dissolved solid (TDS), residual chlorine, sulphide, nitrate, phenol, total chromium along with other heavy metals, oil and grease were found above than the standard permissible levels of tannery wastewater (Table 10.1). Heavy metals cause serious toxicological concerns to human health (Davis et al. 2000; Yadav et al. 2017).

Both BOD and COD values indicate the level of organic pollution in wastewater (Tripathi et al. 2011a). Tiwari et al. (2012) used a bacterium, *Pediococcus acidilactici* B-25 strain for the removal of color, COD, and BOD of distillery wastewater. There are many inorganics such as Cr^{6+} along with other heavy metals which are not easily removed from the polluted sites and persist in the environment. Thus, it is very important to treat properly such toxicants from tannery effluent before discharge into the environment.

10.3 Chromium and Organics Pollution

Chromium and organics pollution may be due to several weathering of rocks, discharge of improperly treated industrial effluent such as tannery waste and leaching of soils (Oliveira 2012). However, contamination from oil spills, leakages, domestic, and industrial wastes contributes to organics pollution in the environment (Fig. 10.1). Cr^{6+}contamination in the environment adversely affects the soil microbial communities (Yadav et al. 2016).

It causes several health problems to living systems (Chandra et al. 2011; Turick et al. 1996). These contaminants are entering and increasing in our ecosystem

Table 10.1 General properties of the treated tannery wastewater (Source: Tripathi et al. 2011a)

Physicochemical parameter/heavy metal	Permissible limit[a]	Obtained value
pH	5.5–9.0	7.3 ± 0.15[b]
Temperature	<35 °C	34 ± 0.27
Total solid (mg L^{-1}) Total suspended solid (mg L^{-1}) Total dissolved solid (mg L^{-1})	– 600 2100	3468 ± 1.89 1102.25 ± 0.22 2366.62 ± 1.65
Total alkalinity (mg L^{-1})	–	340 ± 3.05
Total acidity (mg L^{-1})	–	201.33 ± 1.08
Residual chlorine (mg L^{-1})	1	5.17 ± 0.18
Hardness (mg L^{-1})	–	780.45 ± 1.02
Sulfide (mg L^{-1})	2.0–5.0	9.43 ± 0.20
Oil and grease (mg L^{-1})	10.0	19.86 ± 0.67
B.O.D. (mg L^{-1})	30.0	104.90 ± 0.25
C.O.D. (mg L^{-1})	250.0	490.93 ± 1.27
Total nitrogen (mg L^{-1})	100.0	30.64 ± 0.69
Nitrate (mg L^{-1})	10.0	15.09 ± 0.05
Phenol (mg L^{-1})	1–5.0	11.93 ± 0.17
Cr^{6+} (mg L^{-1}) Total-Cr (mg L^{-1})	0.1 2.0	1.26 ± 0.05 8.89 ± 0.74
Pb^{2+} (mg L^{-1})	0.1	0.47
Cu^{2+} (mg L^{-1})	3.0	0.006
As^{3+} (mg L^{-1})	0.2	0.39
Ni^{2+} (mg L^{-1})	3.0	0.72
Zn^{2+} (mg L^{-1})	5.0	0.36
Cd^{2+} (mg L^{-1})	2.0	0.002

[a] Permissible limits prescribed by United States Environment Protection Agency (USEPA) and Ministry of Environment and Forest (MOEF)

[b] Mean value ± SD

because of rapid industrialization and urbanization. There must be strict rules to overcome from pollution. Xenobiotics are synthesized chemicals that persist in the ecosystem for longer period at higher concentrations. They are recalcitrant compounds such as pentachlorophenol and synthetic dyes discharged from various industrial discharges (Garg et al. 2012; Garg and Tripathi 2011; Tripathi et al. 2019).

10.4 Toxicity of Chromium

Chromium of hexavalent nature is more toxic, mutagenic, and carcinogenic in aquatic systems (Losi et al. 1994; Lovely and Coates 1997; Pal et al. 2005; Ray and Ray 2009), whereas Cr^{3+}is innocuous form of chromium. The increased bioconcentration of metals and their toxicity to all the live forms show the urgent call for the treatment of these toxicants from the polluted soil and water. The metals are generally accumulated in living systems through the food (Perpetuo et al. 2011).

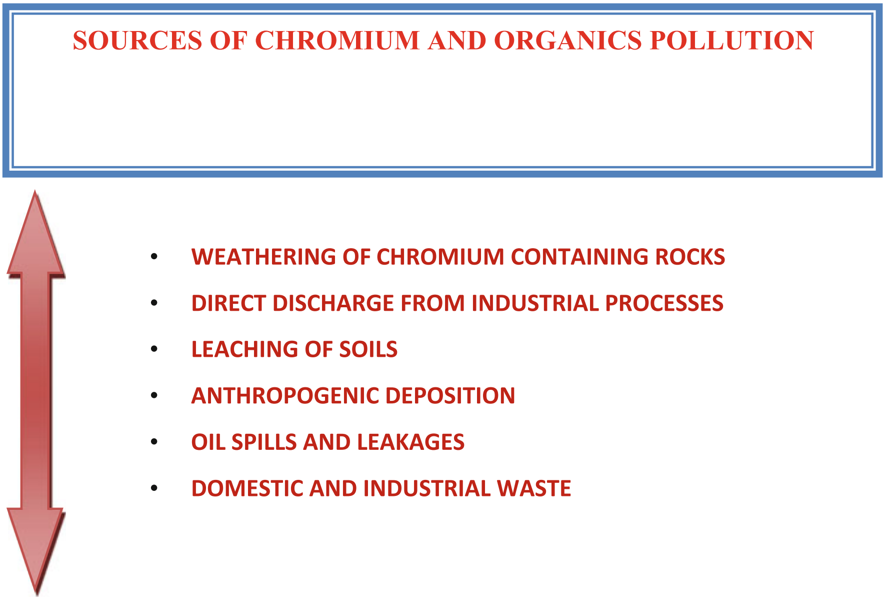

Fig. 10.1 Different sources of chromium and organics contamination in the environment

Heavy metal like Cr inhibits photosynthesis, growth and causes chlorosis in plants by hindering iron metabolism (Purakayastha and Chhonkar 2010; Upadhyay et al. 2017). Chromium affects various tissues in human and animals that include dermal, lung, liver, kidney, red blood cells, and spleen (Holmes et al. 2008). Kumar et al. (2013) reported adverse effects of heavy metals to human health. There are number of diseases such as respiratory and nephrotic ailments found in the workers of tannery industry (Maria et al. 1999).

10.5 Bioremediation

Bioremediation is one of the most important approaches for pollution mitigation. It offers the possibility of using indigenous or exogenous microbes to detoxify or degrade various toxicants that are hazardous to ecosystem. Bioremediation occurs aerobically or anaerobically. It removes pollutants which are detrimental to the environment by the application of phyto- and microbial remediation (Kumar et al. 2017). A number of bioremediation processes such as bioaugmentation, biostimulation, bioreduction, biosorption, bioaccumulation, immobilization, and phytoremediation are being used for Cr^{6+} remediation and organic pollutants.

Figure 10.2 shows the different strategies for Cr^{6+} and organic pollutants remediation from contaminated sites. These methods include physical, chemical, and biological along with modern approaches for treating contaminated sites. In general, bioremediation process can be performed by ex/in situ. In situ bioremediation

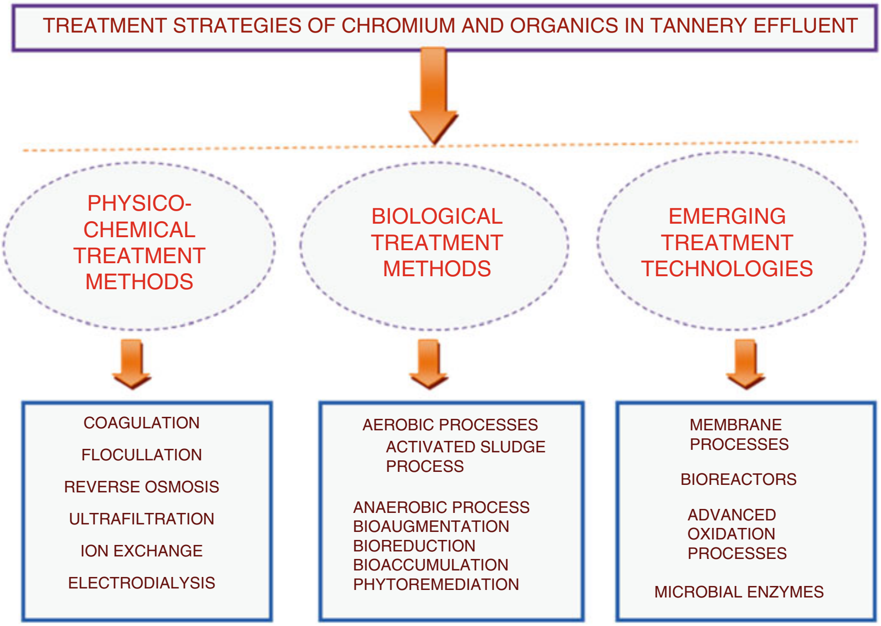

Fig. 10.2 Different methods for remediation of hexavalent chromium and organics from polluted sites

(bioventing, biosparging, phytoremediation) involves the treatment of contaminant on site of its origin. However, in ex situ bioremediation (composting, land fills, biopiles), treatment of pollutants occurs away from the contaminated origin sites that involve transportation.

Thus, in situ bioremediation is better option for treatment due to its cost effectiveness and feasibility.

It has been showed in many studies that microbes can interact with heavy metals ions (Cr^{6+}) for their removal (Garg et al. 2018; Ishibashi et al. 1990; Shen and Wang 1995; Upadhyay et al. 2017; Tripathi et al. 2018; Tripathi and Garg 2014a, b). The reduction of Cr^{6+} to $Cr^{3+}$is used to detoxify Cr^{6+} from polluted sites. Genetic engineering of microbial cells may change their characteristics in such a way that may help to bioremediation.

There are some important factors such as the use of low cost waste biomass, its immobilization and regeneration for opting bioremediation as a strategy for the removal of toxicants from industrial effluent (Quintelas et al. 2006; Garg et al. 2012; Tripathi et al. 2019). Also, there are various physicochemical and nutritional parameters that may affect the bioremediation of tannery waste (Fig. 10.3) which control the treatment process in the ecosystems that are polluted with Cr^{6+} and organic pollutants.

Different bioremediation approaches for mitigation of Cr^{6+} and organic pollutants are discussed below.

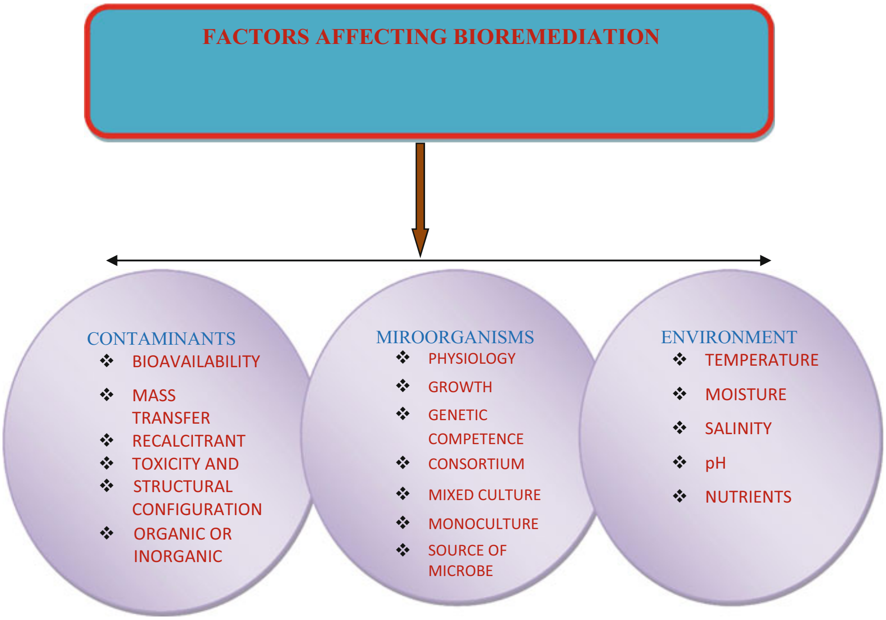

Fig. 10.3 Factors affecting bioremediation of Cr^{6+} and organic pollutants in tannery effluent

10.5.1 Mechanism of Cr^{6+}Removal by Microorganisms

Several microbes have been used with their applicability in Cr^{6+}bioremediation (Garg et al. 2013; Tripathi et al. 2011a, b, 2014a, b; Tripathi and Garg 2010, 2013). There are some important methods applied in heavy metal bioremediation by decreasing the solubility of metals by altering the pH, redox reaction, and adsorption from the contaminated sites. In redox reactions, heavy metals are transformed into the less toxic form that is less mobile and stable. The major bioremediation mechanisms of Cr^{6+} are biosorption, bioaccumulation, bioreduction, bioaugmentation, phytoremediation, and enzymatic transformation (Fig. 10.2). The efficiency of these techniques depends on several parameters that include the type and nature of organism used, the existing environmental factors, nutrients availability, and the concentration of pollutant present in that environment (Fig. 10.3).

10.5.1.1 Biosorption

It is an independent passive metabolic process in which physicochemical interaction occurs between metal species and the cellular components of microbial species (Shumate and Strandberg 1985). The biosorption process comprises different kinds of mechanisms that include physical adherence, ion exchange, and surface complexation, which differs based on the type of microorganisms used and method of processing (Srivastava and Dwivedi 2015). There are different biosorbent materials such as bacteria, yeast, algae, and fungi, which carry out the biosorption process through several mechanisms, including ion exchange, redox processes, electrostatic interactions, surface complexation, and precipitation (Beiyuan et al. 2017). Different functional groups such as carboxyl, imidazole, sulfhydryl, amino, phosphates, etc. are present on biosorbent which interact with metal species (Garg et al. 2012). The selection of biosorbent material requires certain criteria that must be followed, including low cost and reusable biosorbent, rapid movement of metals, and effective separation from the solution (Kumar et al. 2016).

Microorganisms, due to their widespread presence, play significant role in transforming toxic heavy metals into nontoxic forms. Microbes act as effective biosorbents due to their small size for removal of such toxicants. The bacterial cell wall is the main barrier which save microbes from toxic heavy metals. The cell wall carries a natural negative charge and has various functional groups that are involved in the metal binding and also regulate their movement across the membrane. These bacteria contain carboxyl and phosphate groups present in their cell wall that acts as the main binding site for metal cations (Fomina and Gadd 2014; Ayangbenro and Babalola 2017). The type of interaction involves ion exchange, chemical, and physical processes (Garg et al. 2012). The cell wall of microbes consists of proteins, lipids, and polysaccharides (Dixit et al. 2015).

Various microbial groups such as bacteria, fungi, algae, actinomycetes, etc. are applied for biosorption of toxic hexavalent chromium by many researchers. Biosorption is carried out by dead and live cells (Srinath et al. 2002; Tripathi et al. 2011b). Several researchers used microorganisms for removal of Cr^{6+} (Garg et al. 2013; Park et al. 2005; Srinath et al. 2002; Tripathi et al. 2011b). The pH specificity also plays an important role in biosorption (Volesky 1990).

Generally, industrial effluents are characterized by coexistence of many types of toxic cationic and anionic species (Garg et al. 2012). Industrial effluents generally contain numerous cations and anions of metals/non-metals, the latter of which may impart assistance in binding of the concerned heavy metals. Thus, it is important to study the influence of toxicants mixtures on the growth of microbes when studying bioremediation strategies.

10.5.1.2 Bioaccumulation

It is energy-dependent, i.e., it uses the metabolic energy of bacteria to transport heavy metals by several processes like adsorption, intracellular accumulation, and bioprecipitation mechanisms. These mechanisms are reported to be related with the transport of heavy metals. Several researchers study the bioaccumulation of Cr^{6+} by different types of microorganisms (Congeevaram et al. 2007; Srivastava and Thakur 2007; Tripathi et al. 2011b). Parameswari et al. (2009) observed the efficacy of *Azotobacter chroococcum*, *Bacillus* sp., and *Pseudomonas fluorescens* for Cr^{6+} removal. However, biosorption, as a passive process, has several advantages over bioaccumulation. In biosorption, the simple physical method of recovery of heavy metal is achieved without breaking the biosorbents structural integrity, while bioaccumulation is a passive as well as active process in which cells get disrupted during the process.

10.5.1.3 Biostimulation

Nutritional amendment also enhances the process of bioremediation. Biostimulation process facilitates the growth of native microbes of the polluted site by providing nutrients, oxygen, surfactants, and pH alteration substances which are responsible to increase the bioremediation process (Li and Li 2011). Garg et al. (2018) studied the effect of nutrient addition on Cr^{6+} removal by adding carbon and nitrogen sources in diluted tannery effluent. They observed better removal efficiency than nutrients unaided effluent.

10.5.1.4 Bioaugmentation

In this approach, exogenous microbes are added to the population of native microbes in order to increase the capability of already existing microbes to remove the pollutants. The microbes that have naturally occurring catabolic genes or that are genetically modified can be used in this process. This process is affordable, efficient, and quick, making its way among remediation experts. Garg et al. (2016) reported better Cr^{6+} ability in *Pseudomonas* sp. augmented diluted effluent medium than unaugmented medium.

10.5.1.5 Bioreduction

The oxidation state of toxic metals is affected by the activities of microorganisms for the reduction of Cr^{6+} to Cr^{3+} (Asatiani et al. 2004; Farag and Zaki 2010; Ilias et al. 2011; Liu et al. 2008; Tripathi et al. 2011a). Bacteria that grow in high Cr^{6+} containing natural environment develop chromium resistance indicate that they have ability to reduce Cr^{6+}, thereby may be isolated such resistant strain directly from ecosystem (Liu et al. 2008). Tripathi and Garg (2014a, b) reported 74.5% reduction by indigenous bacterial isolate *B. cereus* at initial 200 mg Cr^{6+} L^{-1} within 48 h incubation in minimal salt medium. However, Garg et al. (2018) found that *P. putida* strain has the ability to survive and reduce chromate in tannery effluents. The isolate survived in the native diluted tannery effluent and reduced Cr^{6+}. However, supplementation with carbon and nitrogen sources enhanced the bioremediation of Cr^{6+} in native diluted effluent. The microbial mechanisms for Cr^{6+} reduction is a detoxification mechanism that occurs intracellularly with the help of enzyme chromate reductase (Tripathi and Garg 2014a, b).

10.5.1.6 Immobilization and Elution of Chromium

The cell biomass used for biosorption as well as bioaccumulation is loaded with metals, and desorption of the loaded metal separate metal from adsorbent for reuse in industry, and the regenrated biomass is suitable for next round(s) of biosorption which make cost effective bioremediation process (Garg et al. 2012). Agar, polyacrylamide, and alginate matrices have been used in several immobilization studies (Tripathi and Garg 2013). The elution of bound chromium from cell biomass depends on its ionic state. It is normally found that when chromium is bound in hexavalent state, its simple elution by acidic solutions is based on reduction to trivalent state, which is then subsequently released into the eluent fraction (Garg et al. 2012). Some researchers reported sulfuric acid (1.0 M) and found to be the most efficient eluent (Srinath et al. 2003). Benazir et al. (2010) studied the chromium bioremediation efficiency in the consortium of *B. subtilis, P. aeruginosa,* and *S. cerevisiae* in immobilized and nonimmobilized cells. Tripathi and Garg (2013) also used immobilized cells of *B. cereus* with alginate for Cr^{6+} removal. Similarly, Garg et al. (2018) also used *Pseudomonas putida* for bioremediation of Cr^{6+} in raw diluted tannery effluent. Immobilized cells may be better option for bioremediation than free cells because free cells are more exposed to the toxicity of pollutants which may cause lesser bioremediation by them.

10.6 Methods for Removal of Organic Pollutants from Tannery Wastewater

10.6.1 Chemical Methods

10.6.1.1 Coagulation and Flocculation

The tannery wastewater contains different types of organic pollutants, solid matters, and toxic metal ions which impose serious threat to the environment when disposed off without treatment (Table 10.1). Some of the important organic pollutants present in wastewater are benzene, naphthalene sulfonates, and syntans (Lofrano et al. 2013). Syntans are synthetic tannins added to soften the leather (Lofrano et al. 2008). Syntans have complex structure composed of naphthalene-, phenol-, formaldehyde-acrylic resins and melamine (De Nicola et al. 2007; Lofrano et al. 2007; Munz et al. 2009). Besides, tannery wastewater contains the considerable amount of chromium, which is above the permissible limit of 0.1 mg L^{-1}. The different types of inorganic coagulants have been applied for the coagulation and removal of organic pollutants, total solids, and toxic metal ions from tannery wastewater before proceeding for biological treatment (Lofrano et al. 2013). Different coagulants act differently in terms of reduction in organic load (COD), BOD, total dissolved solid, suspended solids, and toxic metal ions such as chromium (Ates et al. 1997; Kabdasli et al. 1999; Song et al. 2004; Lofrano et al. 2006). Coagulants are effective at specific pH that depends on the properties of wastewater (TE) as well nature and concentration of coagulants (Song et al. 2004). Using $FeSO_4$, $FeCl_3$, and alum, more than 99% of chromium and 40–70% of COD was removed from the wastewater of leather tanning (Kabdasli et al. 1999). In another study, only 30–37% of total COD and 74–99% of chromium were removed when 800 mg $L^{-1}$of alum was used as coagulants (Song et al. 2004). Nevertheless, chemical treatment methods have been effective in limited application due to generation of TE at very large scale that requires huge quantity of chemicals increasing the pollution which limits the application of chemical treatment method.

10.6.2 Biological Treatment

Biological treatment method involves activities of mixed microbial communities to remove organic pollutants from TE. It is a friendly and less-expensive alternative to chemical treatment. However, high concentration of tannins, toxic metal ions, and persistence organic compounds hampers the microbial activities (Lofrano et al. 2013). Biological treatment processes have been categorized into aerobic or anaerobic process. This has been further sub-divided into activate sludge, anaerobic stirred tank reactors, or attached biofilm process.

10.6.2.1 Aerobic Processes

During aerobic treatment, tannery wastewater is mixed with aerobic microorganisms in the presence of oxygen. Soluble, suspended, and colloidal organic pollutants that contribute to BOD are metabolized by microorganisms leading to production of carbon dioxide and decrease in the level of BOD. Production of excess microbial biomass during the process of biodegradation is a major drawback of aerobic process. Besides higher concentration of tannins, toxic metal ions and persistence organic compounds inhibit the biological treatment process (Lofrano 2013). In a study, growth of heterotrophic bacteria was significantly inhibited in the presence of 10 mg L^{-1} Cr (VI) (Stasinakis et al. 2002). A conventional sequencing batch reactor (SBR) has specialized architecture to support various group of microorganisms for effective biological treatment processes (Farabegoli et al. 2004; Ganesh et al. 2006). The most commonly used aerobic biological treatment processes are conventional activated sludge processes and trickle filters.

Activated Sludge Processes (ASP)

The ASP was described first in the year 1914 by Arnold and Locker. In ASP, wastewater that has undergone primary treatment is treated with the flocculated suspension of mixed microbial population within aerated and agitated reactor. It is a two-step process, biological treatment, and secondary settlement. The biological treatment is carried in aerated tanks containing flocculated suspension of diverse microorganisms. In the aerated tank, microorganisms grow and clump together to form a stable flocs, activated sludge. The different types of microorganisms that are involved in ASP include nitrifying, denitrifying, carbon oxidizers, fungi, protozoans, and algae. The species of *Acinetobacter* and *Zoogloea ramigera* are important microorganisms that play a key role in formation of flocs by production of polysaccharide gels. The microflora of activated sludge must be capable of producing all enzymes that can potentially degrade soluble as well insoluble pollutants. After flocs formation, effluent is passed into a secondary settlement tanks where flocculated microorganisms settle down to form a secondary sludge. Most often, after removal of secondary sludge, supernatant is disposed, but sometime tertiary treatment is required to remove the inorganic nutrients.

Trickle Filters

In aerobic trickle filter technique, microbial biofilm is formed on an inert support material placed within a bioreactor. Effluent is continuously sprayed over the microbial biofilm and percolates down the filter bed. While passing through the bed, organic matter is degraded by the microorganisms in the biofilm. As process continues, microorganisms grow and thickness of biofilm increases penetrating downward. At a point, when threshold thickness is achieved, concentration of oxygen drops at the surface of the biofilm and decrease in the biomass called sloughing occurs. Within filter, microbial population varies, a diverse range of microorganisms are present at top including bacteria, fungi, algae, and protozoan. Within filter, carbon oxidizing microorganisms dominate, while nitrifiers are predominant group present at the bottom of the bed. For efficient operation, larger the surface area of inert material, greater would be the concentration of biomass and thus, faster rate of degradation. Secondly, large void volume is required for efficient oxygenation and to prevent the clogging while passage of water through the filter bed. Trickle filter operates under two modes, low rate and high rate filter. Low rate filter consists of stone or other denser medium that have low surface area but high density, while high rate filter uses plastic material having large void volume and high surface area.

10.6.2.2 Anaerobic Biological Treatment

Anaerobic treatment processes of sludge and heavily polluted wastewater involve the activity of facultative and obligate anaerobic microorganisms that degrade organic pollutants in the absence of oxygen. Anaerobic degradation of organic pollutants is accompanied with the production of CO_2, biomass, and energy in the form of methane. The three different groups of microorganisms are involved in this process. The fermentative or hydrolytic bacteria secrete extracellular enzymes that degrade complex polymers (polysaccharide, proteins, and lipid) to generate CO_2, H_2, methanol, and volatile fatty acids (VFAs), viz. acetic, butyric, and propionic acid. The acetogenic bacteria metabolize the end product of fermentative bacteria into acetic acid, CO_2, and H_2. The methanogenic bacteria are the terminal member in the process of anaerobic degradation. The acetotrophs are group of methanogens that causes the breakdown of acetic acid into methane and CO_2, while hydrogenotroph mediates CO_2 reduction coupled to oxidation of H_2 to generate methane. The anaerobic treatment processes are mainly carried out in simple mixed sludge reactor, upflow anaerobic sludge blanket reactors, anaerobic filters (AFs) that consist of upflow and down-flow AFs, and anaerobic baffled reactor (Lofrano 2013; Lefebvre et al. 2006; El-Sheikh et al. 2011; Zupancic and Jemec 2010).

10.6.3 Advanced Treatment Technologies

10.6.3.1 Membrane Technologies

The use of membrane technologies for treating tannery effluent is a cost-effective treatment system of chromium contaminated water. Previous studies have demonstrated that ultrafiltration and nano-filtration can be efficiently used in tanning industry for the recovery of chromium and reducing pollutant load (Ashraf et al. 1997; Cassano et al. 2001). Moreover, refractory organic compounds (sulfate and chloride) have been removed by reverse osmosis with a plane membrane (De Gisi et al. 2009). In addition, membrane bioreactor (MBR) has emerged as an alternative to activated sludge process (ASP), as no additional settling tank is required for wastewater treatment. However, the main limitation of membrane technology is clogging of membrane (Lofrano et al. 2013).

10.6.3.2 Oxidation Processes (OPs)

In recent past, role of different oxidation processes (OPs) in treatment of tannery wastewater has been well documented. Treatment method that involves OPs uses strong oxidants (H_2O_2, O_3,) and/or catalysts (TiO_2, Fe, Mn) (Schrank et al. 2004). The basic principles of oxidation processes the production of hydroxyl radicals (a powerful oxidants) that causes rapid but unselective oxidation of broad range of organic compounds leading to the reduction in the COD level. Some examples of OPs include Fenton oxidation, photooxidation, ozone oxidation, and photocatalysis (Lofrano et al. 2013). The selection of optimum OPs wastewater treatment requires proper assessment. The heavily polluted wastewaters are pre-treated before the application of OPs (Schrank et al. 2004).

10.6.3.3 Bioreactor System in Bioremediation

The vessel system which is generally known as fermenter or bioreactor provides a controlled and desired levels either physicochemical or nutritional parameters or both for the growth of a microorganism alone or in combinations at optimum level. Tannery effluent is a serious environmental problem. Khan et al. (2020) also studied the bioremediation of chromium using pilot scale sand bed bioreactor.

The development of bioreactor technology can change any process parameters economical. Bioreactor technology may depend upon the microorganisms and nature of the effluent. Bioreactor design is one of the important components in bioprocess engineering (Gaur et al. 2017). In spite of such development, still there is lack of efficient bioreactor system for effective treatment. Bioreactor system for treatment of tannery effluent through specific architecture and design specially Degrimond, Sulzer, and Aquatech has been successfully used for the treatment of such waste from industries. But these technologies must be updated on the ground of efficient recycling of active/alive microbial biomass transfer, proper treatment/recycling of heavy metals along with use of microbial consortium in a specialized vessel system within large bioreactors where entirely different environment is created for effective degradation of aromatic hydrocarbon or other xenobiotic compounds. To achieve the above parameters, any bioreactor system is optimized on the basis of these parameters either fed batch or continuous system. Most of the bioreactor for such work is designed for continuous bioremediation process including the following parameters:

1. Substrate utilization rate, where variety of substrates have been used from simple to complex requires different amount of enzymes, biomass, and retention period. These factors must be optimized in the labs and may be designed in the same bioreactor in multiple vessel systems having specialized microbial consortium, which specially degrade xenobiotic compounds, further this vessel effluent should be passed to the vessel where simple organic compounds easily utilized leading to some other organic compounds that will further degraded as long retention period will facilitate higher degradation.
2. Another parameter is biomass production and its recycling outlets with in a vessel where biomass is recycled in the initial vessel to achieve active biomass using gravity based recycling outlet as live cells are heavier, but microbial flocculation of dead or live nature must be evaluated prior to develop design/architecture.
3. This component is important but difficult to maintain, i.e., microbial metabolites mainly in the form of enzymes which act on xenobiotic/simple organic matter decomposition for effective bioremediation. These parameters generally affected by the variation of substrate concentration which generally vary in bulk treatments. For this, the temperature tolerant, aero-tolerant, acid, and alkali-tolerant with high and low substrate concentration tolerant may be isolated and used in such bioreactors. Gaur and Tiwari (2015) isolated such strains from natural ecosystem and used for the production of amylases and cellulases for effective degradation of lignocellulosics and starchy materials at very high substrate concentration as these parameters are very essential. Nature is a rich reservoir of microorganisms, therefore any desired microbial system are available, only isolation and optimization can solve this goal efficiently.
4. The ultimate effects can be minimized by designing and architecture of an effective bioreactor system. For example, most of the industrial effluent contains heavy metals that must be separated from the water bodies otherwise contaminate ground water, pond, river water, soil. It affects crops as well as human and animal health. The heavy metals are not metabolized by microbial system. Most of the microorganisms can only change its oxidation state or accumulate on the cell surface/membrane only up to some extent and further release after the death of microorganisms and their viable cells again accumulate, therefore cannot be efficiently removed from the system. Therefore, phytoremediation for heavy metal removal from aquatic system is the effective measure for the treatment because it absorbs high flux of almost all types of metals from the effluent. Various plants of aquatic origin have been grown in polluted sites and after removal of the plants from the contaminated sites, thereafter burned in furnace to get the ashes of metals for extraction. Thus, this approach must be designed in such a way the bioreactor treated effluents should be passed through such ponds attached in series by removal of weeds continuously. This is only way of effective removal of toxic heavy metals from industrial effluent especially from tanneries. The role of bioreactor in bioremediation requires upgradation in their design in which multivessel system designed in such a way that original microbial biomass should be maintained for longer period monitored by specific device and reloading of fresh culture without restricting the process. Thus, a variety of

specific consortia are required for the treatment of intermediates of the xenobiotic compounds efficiently within 48–72 h; therefore, size of the bioreactor, retention period of the effluent along with the requirement of oxygen or without oxygen can be created depending on the nature of microbial communities required for bioremediation. The main problems associated to this are blockage of pores, pipe, lives and hydrolic load which must be evaluated accordingly.

10.7 Future Prospects and Challenges in Bioremediation

Industrialization and urbanization are the social need of every country, but its proper management is equally essential and need of the hour. Industrial effluent of distillery, tannery, pulp and paper industries is highly toxic due to presence of color compounds and complex organic compounds along with heavy metals. It has been proved that bioremediation is the ultimate alternative over the physical and chemical approaches because of the cost effective as well as ecofriendly means. The management of biosystem for efficient treatment requires certain technology and management of microbial system. The microbial application strategies with combinations of microbes at different stages is the most essential part of this area. Xenobiotic compounds are also treated by co-metabolism in which some specific group converts the complex form to simple form without utilizing the original compound for carbon and energy source. The converted compound is metabolized by another group of microorganisms. Therefore, the selection of such microorganisms which can co-exist without any negative interaction with them and ability to utilize different carbon and nitrogen sources via different metabolic pathways is necessary. Such combinations are long lasting and effective for bulk treatment at industrial scale. Another important aspect is the use of thermotolerant/thermophilic microorganisms at large scale treatment of effluent in bioreactor as temperature increases from 5° to 10° C. Furthermore, the selection of microbial combination in different stages in bioreactor is another important aspect which is totally based on the organic and inorganic load of the effluent and the microbial nature. In this process, proteolytic, lipolytic along with chemolithotrophic groups are being used in combinations, because at this level, the chemoorganotrophs utilize all proteins, lipids, and fats, as keratinophilic microbial combination will liquefy the hair from follicles and short hairs present in the effluent. In this stage, large closed jacket of non-reactive metals is required in order to reduce the putrefaction odors as well as other gaseous compositions. This stage may also release several pathogenic microorganisms especially for bacteria and some surface growing fungi which may cause aeroallergenic diseases. This stage has high nutritional effluent which generates bulk of microbial groups, therefore, close jacket treatment using airlift or hydrodynamic fermenter models may be recommended. At this stage, 24–48 h retention period cuts the BOD and COD by 75 to 80% along with other easily available carbohydrate, proteins, lipids, and other minerals. A huge microbial biomass and some of xenobiotic compounds along with the inorganic components especially heavy metals like chromium, arsenic, or other may be down streamed along with open pond system for remediation. The microbes which have capability to produce peroxidases, phenoxidases, laccases, mono-, dioxygenases will be used to eliminate tannin, oils, paint compounds. Further, heavy metals may be extracted through phytoremediation within 5–10 days in small oxidation ponds attached in series of 4–5 numbers depending on the capacity of industry. The bioremediation with proper management under the supervision of microbiologist is always essential because fermentaion kinetics norms at various stages in bioreactor is very essential. Microbial system is much diversified, therefore, regular isolation and characterization of microorganisms is required to find a better strain of the diversified level, as microbial diversity is abundant and newer strains always reform through recombination process in the natural ecosystem through transformation, conjugation, and transduction especially in bacteria.

Since the microbial handling especially the cultivation without contamination and monitoring its population and application of various combinations of consortia requires strict monitoring and everyday observation under microscope regarding the existence of consortia as well as their norms set by processing and downstreamed products required for the treatment process. There are some major challenges in bioremediation such as understanding the nature of chemical compound means simple or complexity in structure, selection of potential microbial strain, and the management of environmental conditions. Further, the bioremediation requires update in the area of bioreactor design and architecture alongwith multivessel, and multi-steps bioremediation with specific group of microorganisms depending on the nature of effluents in bulk treatment. Most of the industries release bulk liquid waste which contains high organic and inorganic loads. The organic load can be best treated by using various groups of microorganisms especially those which have high capability to degrade xenobiotic compounds. Further the heavy metals of the effluent should also be remediated using different microbial system. The remedial measure is not only based on the capability of the microorganisms but also based on the design and protocol for specific effluents treatment. Such challenges require space, microbial quality, microbial differentiation, aerobic and anaerobic situations for effective remediation. The microorganisms having capability of producing degradative enzymes, etc., mono and/or dioxygenases, laccases, peroxidases by different microbial groups may be used in consortium of aerobic to anaerobic as well as mesophilic to thermophilic origin in large bioreactors.

10.8 Conclusion

Bioremediation based treatment of xenobiotic compounds either in liquid or a solid system is one of the most economic, eco-friendly, and safe method. The most diversified microbial groups in consortium have been suggested for an efficient bioremediation process. The bulk quantities of industrial solid and liquid wastes are being treated with naturally occurring microorganisms. The microbes which degrade xenobiotic compounds are limited in soil and water ecosystem, therefore, must be deliberately introduced during the treatment process. The initial population follows the co-metabolism process, through which the intermediate compounds again initiate another group of microbial process which further ultimately reduce the time limit as well as productivity of the remediation process, the deliberate introduction of some specific microbial inoculum in the ratio of 2–5% having population 50×10^6 cfu of each group depending on the nature of xenobiotic compound is suggested. In this approach, the chemical nature of xenobiotic compounds and metabolic pathways alongwith their intermediate are to be known for effective bioremediation process. Further this remedial measure requires appropriate bioreactor technology in multivessel continuous fermentation having different concentration gradients can be facilitated through airlift and hydrodynamic architecture of bioreactor. The gases released from such process are CO_2, SO_2, NO_2, and CH_4 which can be utilized for the use to reduce the air pollution. Such approach will be safe for soil, water, and air for sustainable environment. The efficient microbial groups, especially bacteria are the dominating flora of such process as they are fast multiplying and able to grow at wide range of temperature and from aerobic, facultative to anaerobic conditions, while fungi are slow growing as well as mostly aerobic but some anaerobic fungi have also been identified but very limited. The quick multiplication in all the conditions, bacteria is the dominating and potential microorganisms. The downstream processing is also not required in such process; therefore, bacteria are more appropriate than any existing microbes. The tannery effluent generally has more color compounds of aromatic hydrocarbons origin which requires higher population of specific bacteria which produce certain enzymes like mono-dioxygenases, laccases as well as peroxidase essentially required for beta keto adipic, mandelate or meta cleavage pathways where catechol and other intermediates of aromatic hydrocarbons are degraded to super compounds like muconic acid, muconolactone to pyruvate. Leading to complete degradation of xenobiotics.

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Current Approaches in Bioremediation of Toxic Contaminants by Application of Microbial Cells; Biosurfactants and Bioemulsifiers of Microbial Origin

11

Amrita Kharangate-Lad and Nezlyn Cressida D'Souza

Abstract

The increase in global human population has resulted in swift and extensive urbanization and industrialization. These anthropogenic activities along with natural phenomena result in the release of toxic compounds in the environment. These toxic compounds are recalcitrant in nature and accumulate in the environment, contaminating the soil and aquatic ecosystems. They pose a risk to human health and ecosystem through the contamination of drinking water, ingestion through the food chain and reduction in water and food quality. Microorganisms such as bacteria, fungi, yeast and algae possess various mechanisms that metabolize and detoxify these toxic pollutants. In this chapter, we emphasize the use of these microorganisms for bioremediation of toxic pollutants like heavy metals such as Cd, Hg, Pb, Zn, Cu and others; polyaromatic hydrocarbons and petroleum-based hydrocarbons; plastic polymers and recalcitrant dyes and agro-based compounds. Apart from naturally occurring microorganisms, genetically engineered microorganisms have been designed to degrade these recalcitrant toxic compounds. Bioremediation using both these natural and genetically engineered microbes is an economic and eco-friendly alternative to conventional physicochemical technologies.

Keywords

Biosurfactants · Bioemulsifiers · Hydrocarbons · Microbes · Toxic pollutants

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11.1 Introduction

Environmental pollution from toxic metals, organic pollutants and other hazardous materials has affected the natural ecosystem and human health. Anthropogenic activities like industrialization, mismanagement of toxic waste and natural activities like hurricanes, storms and volcanic eruptions are responsible for the discharge of toxic pollutants into the environment. Due to the expense and inefficiency of chemical methods, bioremediation using nanoparticles, microorganisms or their components is an eco-friendly and economical alternative for reclaiming the environments that are contaminated with toxic pollutants.

Bioremediation is detoxification of toxic xenobiotic compounds using living organisms including plants (phytoremediation) and microorganisms such as algae, bacteria and fungi (microbial remediation). The toxic compounds usually include pesticides, plastics, polyaromatic hydrocarbons (PAHs), heavy metals and toxic metal contaminants discharged in soil and aquatic environments due to anthropogenic activities (Das and Dash 2014). Due to the interaction between air, water and land, the toxic pollutants move in the environment and are transported beyond geographical boundaries by air and water currents (Fig. 11.1).

11.2 Microbial Cells in Bioremediation of Toxic Pollutants

Microorganisms are extensively studied for their role in bioremediation of toxic pollutants. The indigenous bacteria from contaminated sites are stimulated by providing optimum conditions of growth such as pH and nutrients such as phosphorous and sulphur by addition of compost and biochar (Ojuederie and Babalola 2017). This stimulates the microorganisms and makes the environment more favourable for bioremediation enabling the microbes to metabolize the toxic pollutants more efficiently (Das and Dash 2014). The efficacy of biodegradation of the toxic pollutants during bioremediation therefore depends on the nutrient availability, oxygen, temperature and pH of the surrounding environment. These factors influence the chemistry of the pollutant such as viscosity and volatility thereby affecting the bioavailability of the toxic pollutant to the microorganisms.

11.3 Factors Affecting Bioremediation

The factors that govern the efficiency of the microbial bioremediation are of two types: abiotic and biotic factors. The abiotic factors include environmental influences such as soil type, oxygen content, temperature, pH, presence of electron acceptors, nutrients and metal ions.

The metabolic abilities of the microorganisms and the physicochemical properties of the pollutant are the major properties that determine the fate of the target pollutant. Environmental factors like soil structure and site characteristics, pH, temperature, moisture, redox potential, oxygen content and availability of nutrients affect the

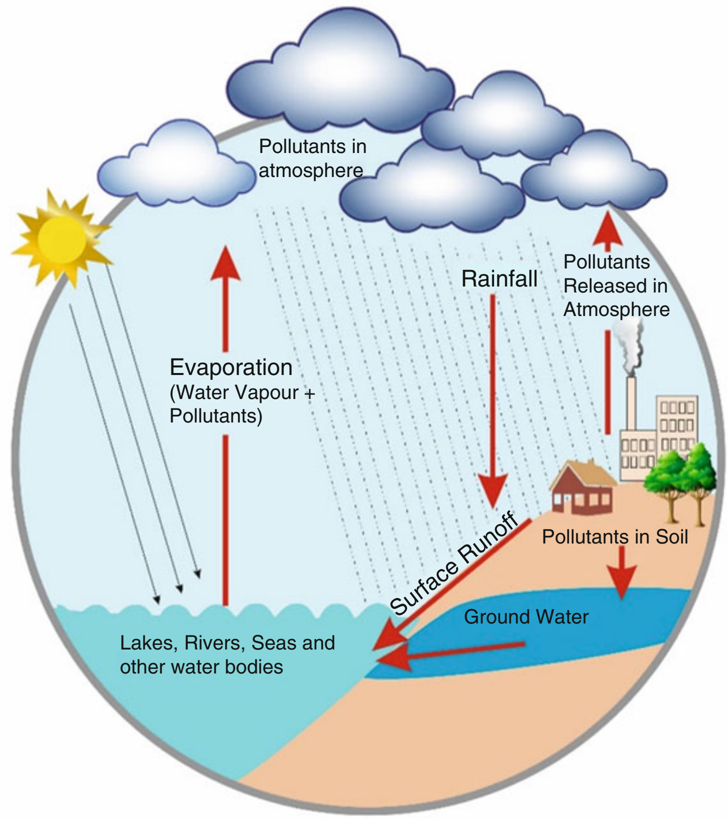


Fig. 11.1 Movement of toxic pollutants in the three spheres of the environment: lithosphere, hydrosphere and atmosphere

growth and interaction of the microorganisms with the pollutant (Fig. 11.2). Whereas the physicochemical properties such as the structure and toxicity of the pollutant govern the bioavailability of the compound to the microorganisms.

11.3.1 Availability of Nutrients

Essential nutrients, mainly nitrogen and phosphorus play a crucial role in microbial growth, reproduction and degradation of the toxic pollutant. Supplementing microorganisms with these essential nutrients has been reported to significantly impact the metabolic activity and increase the degradative capacity of microorganisms in the cold environments since biodegradation in cold environment is limited due to lack of nutrient availability. Similar improvement in degradation of hydrocarbons was reported on addition of nutrients (Abatenh et al. 2017).

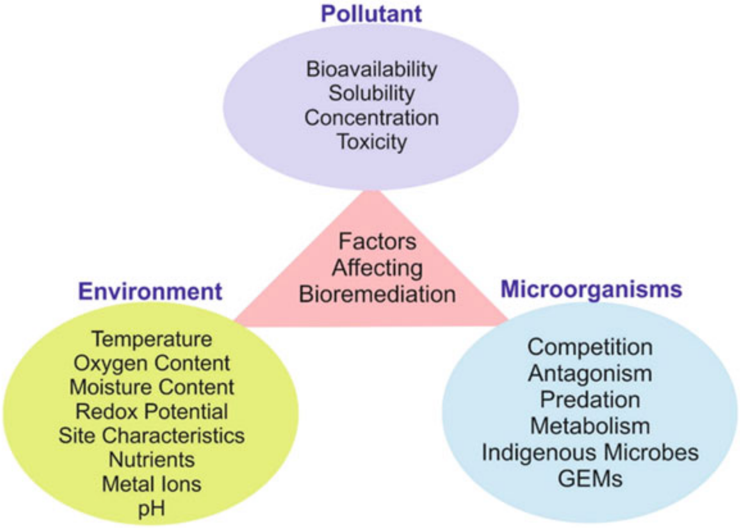


Fig. 11.2 Factors affecting microbial bioremediation

11.3.2 Temperature

Temperature is the most vital factor that determines the survival of the microorganism as well as the bioavailability of the pollutant. In colder regions of the Arctic, it becomes difficult to employ microorganisms for a cleanup as the sub-zero temperature freezes the microbial transport channels and the cytoplasm rendering the microbe metabolically inactive (Abatenh et al. 2017). All enzymes have an optimum temperature below and above which the rate of conversion for the pollutant will not be as effective as at optimum temperature. The metabolic activity of a microorganism increases with the increase in temperature. At a specific temperature the metabolic activity reaches a maximum which is known as the optimum temperature. The metabolic activity of microorganisms is slow at temperatures below and above the optimum temperature. Thus, temperature either increases or decreases the rate of bioremediation as it directly influences physiological activities of the microbes.

11.3.3 Oxygen Content

Oxygen requirement of microorganisms differs depending upon the nature of the microorganisms and widely affects their ability to degrade complex compounds. Biological degradation of various complex compounds has been carried out by both aerobic and anaerobic microorganisms (Abatenh et al. 2017). However, presence of oxygen is significant for the degradation of hydrocarbons by the enzymes oxygenases.

11.3.4 Moisture Content

Availability of water is an important factor as most microorganisms have ion transfer mechanisms at the cell surface level. The uptake of these ions depends upon their solubility in water. Moisture around the cells renders the pollutant more accessible for biosorption by microbial cells (Abatenh et al. 2017). Moisture influences the osmotic pressure, pH and the kind and amount of solubility of nutrients and pollutant; therefore, it directly influences the rate of degradation of the pollutant.

11.3.5 pH of Soil

The pH of the surrounding environment affects the growth and survival of the microorganism as it has no means of adjusting its inherent pH to that of surroundings. The pH also affects the structure and characteristics of the pollutant and thus its bioavailability to the microorganisms. A pH of 6.5–8.5 is optimal for biodegradation in most terrestrial and aquatic ecosystems (Abatenh et al. 2017).

11.3.6 Site Characterization

A detailed study of the site of contamination is needed to decide the best bioremedial strategies when employing microorganisms. It is necessary to study the extent of contamination in the vertical and horizontal zones of the site in addition to the abiotic parameters of the site (Abatenh et al. 2017). This helps determine the techniques to be used for sampling and analysis.

11.3.7 Metal Ions

Metals ions form an integral part of the biochemical components of the microorganisms. They are necessary in small amounts either in biosynthesis of new cell components or for carrying out metabolic activities. Limitation of these essential metal ions is known to have adverse effects on the rate of biodegradation of a compound. Microorganisms therefore have evolved strategies such as production of siderophores and metallothionein proteins to acquire these metal ions from the environment (Davis et al. 2003).

The microorganisms degrading the pollutant often face competition (from other microorganisms for carbon and energy sources), antagonistic interactions (from bacteriocins) and predation (from bacteriophages and protozoa). These negative interactions result in a decrease in production of enzymes by the microorganisms as well as it reduces the population of effective microbes responsible for degradation of the pollutants. These affect the degradative capacity of the microorganisms towards the toxic pollutant (Abatenh et al. 2017). Furthermore, the microorganism needs to maintain its ability to degrade the pollutant without undergoing changes at a gene level (mutations) that may cause it to lose its affinity to the target pollutant.

11.4 Types of Microbial Bioremediation

Bioremediation techniques can be carried out by either in-situ or ex-situ approach. The in-situ treatment involves treating of the contaminated area without excavation of the contaminated site. In-situ treatment uses processes like biostimulation, bioattenuation, bioaugmentation, bioventing and biosparging. In-situ treatments are usually more desirable as it involves less cost and prevents disturbance of the environment. However, it faces limitations due to its inability to penetrate desired depth. Therefore, to make it more desirable diffusion of oxygen is allowed by means of external pipes and pump systems.

Ex-situ involves excavation of the soil from contaminated area. It mainly involves two major processes: the solid phase and slurry phase systems. The solid phase systems involve approaches such as biopiles, landfarming and composting (Fig. 11.3). The slurry phase system uses the bioreactor technique (Abatenh et al. 2017; Kumar et al. 2018a).

11.4.1 Biostimulation

Biostimulation involves the injection of nutrients at the site of contamination in order to stimulate the indigenous and naturally occurring microbial population. This involves the use of minerals, fertilizers, compost and growth supplements and providing environmental conditions such as pH, temperature and oxygen for

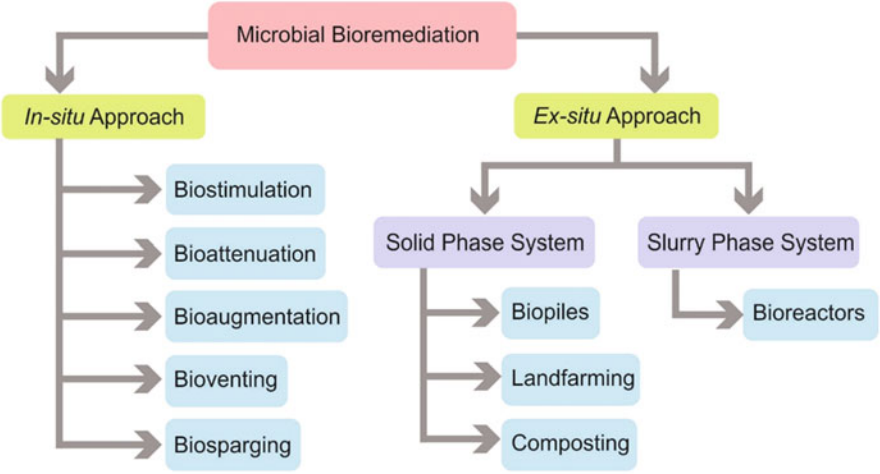


Fig. 11.3 Approaches in microbial bioremediation

optimum functioning of metabolic processes. The presence of small amounts of the pollutant can also trigger enzyme operons required in bioremediation (Abatenh et al. 2017). These nutrients provide the basic elements such as carbon, nitrogen and phosphorous that are needed for cell biomass and energy to produce enzymes that degrade the pollutant (Kumar et al. 2018a).

11.4.2 Bioattenuation

Bioattenuation or natural attenuation is the eradication of pollutant from the surrounding environment. Biologically it involves aerobic and anaerobic biodegradation; plant, animal or microbial uptake. Physical processes (advection, dispersion, dilution, diffusion, volatilization, sorption/desorption) result in clean up of the pollutant, and chemical mechanisms (complexation and ion exchange) result in abiotic transformation. Bioattenuation relies on nature to clean up the environmental pollutant. Microorganisms metabolize the pollutant as a source of carbon and energy converting them into water and harmless gases. Soil particles interact with the pollutant binding to it strongly and keeping them from entering the groundwater. The movement of pollutant through soil and into groundwater results in dilution of the pollutant. Volatile pollutants can evaporate from soil on exposure to sunlight and air (Abatenh et al. 2017). If bioattenuation has not completely cleared the pollutant, then bioremediation using biostimulation or bioaugmentation can be considered (Kumar et al. 2018a).

11.4.3 Bioaugmentation

Microorganisms that have a capacity to degrade the target pollutant are added to augment the biodegradative capacity of the natural and indigenous microbial populations at the contaminated site. GEMS or genetically engineered microorganisms are microbes that are collected from site of bioremediation and genetically modified to increase the efficiency of degradation. This technique has been specifically proven successful for chlorinated ethenes, such as tetrachloroethylene and trichloroethylene and ensures complete removal of these contaminants from the contaminated sites or their conversion to non-toxic forms (Abatenh et al. 2017; Kumar et al. 2018a).

11.4.4 Bioventing

Vents or wells in the soil are engineered to carry oxygen and nutrients to the soil to stimulate the growth of either the natural microorganisms or the introduced microorganisms. It can only be used for compounds that undergo aerobic degradation such as fuel residuals, volatile compounds and petroleum hydrocarbons (Abatenh et al. 2017; Sutar and Kumar 2012).

11.4.5 Biosparging

Biosparging refers to injecting air under pressure to increase the level of oxygen in groundwater for stimulating the indigenous population of microbes to degrade the contaminants. Biosparging enhances the interaction in the saturation zone and therefore increases the contact between soil and groundwater (Abatenh et al. 2017).

11.4.6 Biopiles

Soils contaminated with the pollutants are piled to form mounds and air is supplied to the biopile system by means of pumps. This enhances the microbial activity through microbial respiration resulting in efficient degradation of pollutants. This is a commonly used technique for aerobic degradation of petroleum pollutants (Abatenh et al. 2017; Sutar and Kumar 2012).

11.4.7 Landfarming

In landfarming, the contaminated soil is excavated, spread over an area and periodically tilled until pollutants are degraded. Tilling stimulates indigenous microorganisms and facilitates aerobic degradation of contaminants. This technique has limitations as it is effective upto10–35 cm of soil (Sutar and Kumar 2012). Efficient cleaning ability and low maintenance and monitoring costs make it a feasible option for bioremediation.

11.4.8 Composting

In this technique contaminated soil is mixed with known proportions of organic compost, manure or agricultural waste. These organic materials allow and support microbial population that degrades the contaminants (Kumar et al. 2018a; Sutar and Kumar 2012). The elevated temperature generated during composting is characteristic of this process.

11.4.9 Bioreactor

It involves the use of slurry reactors or aqueous reactors. The contaminated soil, sediment or sludge or contaminated water is introduced in the reactor (Kumar et al. 2018a; Sutar and Kumar 2012). A slurry bioreactor mixes the contaminants with water and gas to facilitate biodegradation by the indigenous microorganisms. The disadvantages include excavation and pre-treatment of the contaminated soil or water before being introduced into the bioreactor which is economically expensive.

11.5 Mechanisms of Interaction Between Microbial Cells and the Metal Pollutant

Heavy metals such as mercury, cadmium, nickel, cobalt, chromium, arsenic, lead have found their way into the environment due to natural and anthropogenic activities. For potential application of microbial cells in bioremediation, the microbial cells should not be inhibited by the toxic pollutant and should possess either one or more of the metal pollutant processing mechanisms (Kumar et al. 2016b). These mechanisms include uptake of the metal by means of metallothionein or metal sequestering proteins or by acquisition and interaction with the toxic pollutants by means of extracellular polymers (extracellular polymeric substances (EPS), biofilms, capsules, slime or sheath), biosorption into the cell membrane, intracellular assimilation, mobilization and immobilization, bioaccumulation, complexing and precipitation of the metal, efflux, reflux and release of the detoxified or transformed metal pollutant (Fig. 11.4). On uptake, the metal pollutant may be processed in mechanisms either dependent on the metabolic pathway of the organism or independently by using the metal pollutant processing mechanisms (Das and Dash 2014).

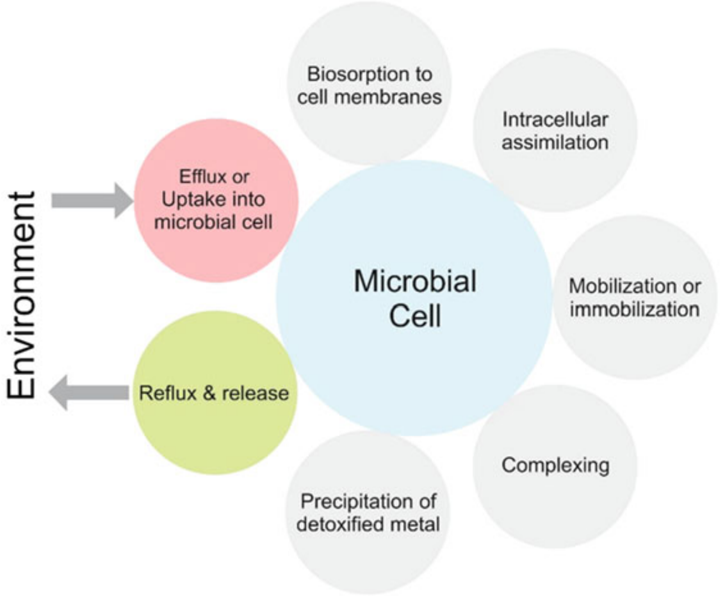


Fig. 11.4 Mechanisms possessed by microorganisms for dealing with metals and metal pollutants in the environment

11.6 Bioremediation of Toxic and Heavy Metals by Microorganisms

Bioremediation of heavy metals has been reported using bacteria, fungi and algae (Table 11.1). Microbial cells are negatively charged owing to the presence of negatively charged groups like hydroxyl groups, phosphate groups, carbonyl groups, sulphate groups and uronic acid of carboxyl groups on the surface of the bacterial cell wall. These bind to the heavy metal ions resulting in biosorption. *Enterobacter cloacae* has been reported to chelate cadmium, copper and cobalt. *Rhodobium marinum* NW16, *Rhodobacter sphaeroides* KMS24, purple non-sulphur bacteria have exhibited potential to remove zinc, copper, cadmium and lead from contaminated environment by bioaccumulation and precipitation (Panwichian et al. 2011). Research studies show that *Desulfovibrio desulfuricans,* a *s*ulphate-reducing bacterium can convert sulphate to hydrogen sulphate. This hydrogen sulphate reacts with heavy metals such as Zn and Cd and transforms them into insoluble forms of these metal sulphides (Chibuike and Obiora 2014).

Reports on viable and dead cells of *Mucor rouxii* demonstrated their ability to absorb cadmium, lead, zinc and nickel. It also established that the viable cells were more effective at low pH and optimum biosorption was achieved by the dead biomass and live cells above a pH of 4.0 (Yan and Viraraghavan 2003). Yeast *Saccharomyces cerevisiae* is used in bioremediation of contaminated wastewaters and is reported to remove toxic metals by biosorption. Detoxifying mechanisms like mobilization, immobilization and transformation by using metal-binding peptides called phytochelatins have been studied and reported in yeasts like *Schizosaccharomyces pombe* and *Candida* sp. (Bahafid et al. 2017; Wifak et al. 2017). Some strains of yeast such as *Hansenula polymorpha, Saccharomyces cerevisiae, Pichia guilliermondii, Rhodotorula pilimanae, Rhodotorula mucilage* and *Yarrowia lipolytica* have exhibited conversion of Chromium (VI) to Chromium (III) (Chatterjee et al. 2012; Ksheminska et al. 2008).

The large biomass of algae allows them a greater biosorption capacity in comparison to both bacteria and fungi (Mustapha and Halimoon 2015). Burdin (1985) reported ability of the algae to bioaccumulate heavy metals such as aluminium, cadmium, chromium, cobalt, copper, gold, lead, manganese, nickel, silver, tin and zinc. Many marine algae such as *Durvillaea potatorum, Ecklonia radiata* and *Laminaria japonica* have been reported to exhibit a higher biosorption capacity for heavy metals in comparison with zeolites or activated carbon sorbents (Kumar et al. 2013). Brown marine algae was studied to be effective in bioremediation of Cd, Ni and Pb due to presence of carboxyl, sulphonate, amino and sulphydryl groups on its surface (Davis et al. 2003). *Euglena gracilis*, a single celled alga has been reported for the bioaccumulation of Zn and *Chlorella vulgaris* and *Scenedesmus acutus* have been studied for bioaccumulation of Zn, Cr and Cd (Travieso et al. 1999). Biosorption of cadmium ions by *Spirulina platensis* has been demonstrated by using its dry biomass (Al-Homaidan et al. 2015). Marine algae have also shown to react differently to cadmium: *Tetraselmis suecica* exhibited affinity for cadmium, *Gracilaria fisheri* accumulated cadmium (II) and copper (II) while *Dunaliella salina*

Table 11.1 Microorganisms used in bioremediation of toxic metals at contaminated sites

Toxic Metal degrading microorganisms		
Microorganism	Pollutant	Reference
Bacteria		
Acidithiobacillus ferrooxidans	Cu	Rehan and Alsohim 2019
Alcaligenes sp.	Pb	Acosta-Rodríguez et al. 2018
Bacillus cereus strain XMCr-6 *Bacillus cereus*	Cr (VI)	Kanmani et al. 2012; Dong et al. 2013; Coelho et al. 2015
Bacillus megaterium	Ni	Acosta-Rodríguez et al. 2018; Igiri et al. 2018
Bacillus pumilus	Cd, Pb	Fulke et al. 2020
Bacillus subtilis	Cr (VI)	Balamurugan et al. 2014
Bacillus subtilis, Bacillus cereus	Cobalt, cadmium, zinc	Abdelatey et al. 2011
Bordetella sp.	Cadmium	Abou-Shanab et al. 2003
Desulfovibrio desulfuricans	Cr (VI), Cu, Ni	Igiri et al. 2018
Enterobacter cloacae B2-DHA	Cr (VI)	Rahman et al. 2015
Enterobacter cloacae	Cu, Cd, Co	Iyer et al. 2005
Frankia	Cu	Rehan and Alsohim 2019
Kocuria flava	Cu	Coelho et al. 2015
Pseudomonas aeruginosa	Organic and inorganic Hg	De et al. 2008; Das and Dash 2014
Pseudomonas putida	Cr (VI)	Balamurugan et al. 2014
Pseudomonas sp..	Phenols and aromatic compounds	Selvaratnam et al. 1997
Pseudomonas sp.	Co, Cd, Zn	Abou-Shanab et al. 2003
Pseudomonas veronii	Cd, Zn, Cu	Vullo et al. 2008; Coelho et al. 2015
Rhodobium marinum NW16, *Rhodobacter sphaeroides* KMS24	Cd, Cu, Pb, Zn	Panwichian et al. 2011
Sporosarcina ginsengisoli	As (III)	Achal et al. 2012; Coelho et al. 2015
Staphylococcus aureus	Chromate	Aguilar-Barajas et al. 2008
Vibrio harveyi	Cd, Pb	Mire et al. 2004; Abd-Elnaby et al. 2011
Fungi		
Aspergillus fumigatus	Pb	Kumar Ramasamy et al. 2011
Aspergillus niger	Zn, Hg, Co, Pb, Cd, Cu, Ni	Acosta-Rodríguez et al. 2018
Aspergillus versicolor	Ni, Cu	Coelho et al. 2015; Tastan et al. 2010
Aspergillus versicolor	Ni, Cu	Tastan et al. 2010; Coelho et al. 2015
Coprinopsis atramentaria	Cd, Pb	Igiri et al. 2018
Gloeophyllum sepiarium	Cr (VI)	Achal et al. 2011
Mucor rouxii	Pb, Cd, Ni, Zn	Yan and Viraraghavan 2003

(continued)

Table 11.1 (continued)

Toxic Metal degrading microorganisms		
Microorganism	Pollutant	Reference
Penicillium chrysogenum	Cr (VI)	De et al. 2008
Penicillium sp.	Pb	Igiri et al. 2018
Pleurotus ostreatus HAAS	Pb, Cd, Cr	Acosta-Rodríguez et al. 2018
Rhizopus oryzae (MPRO)	Cr (VI)	De et al. 2008; Sukumar 2010
Rhizopus stolonifer	Pb, Cd, Cu, Zn	Acosta-Rodríguez et al. 2018
Yeast		
Candida sp.	Ni, Zn, Pb, Cd, Cu, Co, Hg, Ag, As	De et al. 2008; Acosta-Rodríguez et al. 2017; Igiri et al. 2018
Saccharomyces cerevisiae	Pb, Cd	Farhan and Khadom 2015; Bahafid et al. 2017
Schizosaccharomyces pombe	Cu	Bahafid et al. 2017
Algae		
Chlorella vulgaris	Zn, Cd, Cu, Pb, Tributylin (TBT)	Travieso et al. 1999; De et al. 2008
Euglena gracilis	Zn	Travieso et al. 1999
Hydrodictyon, Oedogonium and *Rhizoclonium* sp.	As	Coelho et al. 2015; Srivastava and Dwivedi 2015
Rhodotorula mucilaginosa	Hg, Cu, Pb	Acosta-Rodríguez et al. 2018
Scenedesmus acutus	Cd, Zn, Cr	Travieso et al. 1999
Spirogyra sp. and *Cladophora* sp.	Pb (II), Cu (II)	Lee and Chang 2011; Coelho et al. 2015
Spirogyra sp. and *Spirulina* sp.	Cr Cu, Fe, Mn, Zn	Mane and Bhosle 2012; Coelho et al. 2015
Spirulina platensis	Cd	Al-Homaidan et al. 2015
Bacterial consortium		
Acinetobacter sp. and *Arthrobacter* sp.	Cr	De et al. 2008
Viridibacillus arenosi B-21, *Sporosarcina soli* B-22, *Enterobacter cloacae* KJ-46 and *E. cloacae* KJ-47	Lead, cadmium, copper	Kang et al. 2016

exhibited tolerance to cadmium. *Chlamydomonas* produces phytochelatins which sequester many metals and they have potential application in bioremediation of heavy metals (Kumar et al. 2013).

Pseudomonas sp. have been reported to degrade a wide range of toxic compounds including compounds of cobalt, zinc, cadmium; organic and inorganic mercury; phenols and other aromatic compounds and tributyltin in the aquatic environments. At low concentration of heavy metals, *Vibrio harveyi* which is a common bacterium of the saline environment exhibited bioaccumulation of cadmium (Abd-Elnaby et al. 2011) and precipitation of divalent lead into lead phosphate (Mire et al. 2004; Rehan and Alsohim 2019). Bacteria such as *Citrobacter freundii* avoid toxicity of metals by converting divalent lead to lead phosphate. Other bacteria such as *Acidithiobacillus* *ferrooxidans* and *Frankia* detoxify copper by precipitating the metal by forming metal phosphate complexes (Rehan and Alsohim 2019).

The ability of bacteria to produce EPS is an important feature in metal sequestration and therefore in bioremediation. Exopolysaccharides produced by bacteria protect it against environmental stresses such as salinity, heavy metal toxicity, desiccation, presence of antibiotics, etc. Bacterial EPS such as alginate from *Pseudomonas aeruginosa* and *Azotobacter vinelandii*, sphingans from *Sphingomonas paucimobilis*, hyaluronan from *Pseudomonas aeruginosa*, *Pasteurella multocida* and attenuated strains of *Streptococci*, xanthan from *Xanthomonas campestris*, galactopol from *Pseudomonas oleovorans* and fucopol from *Enterobacter* A47 are some of the heteropolysaccharides that have potential applications in metal sequestration and reduction of metal from contaminated sites (Gupta and Diwan 2016). The bacteria, *Rhodobium marinum* NW16, *Rhodobacter sphaeroides* KMS24 were found to be more efficient in the removal of heavy metals from contaminated shrimp ponds when incubated for production of EPS (Panwichian et al. 2011).

Bioremediation of heavy metals is more efficient when a consortium of bacterial strains is used in comparison with a single strain. Kang et al. (2016) reported that a bacterial consortium containing *Viridibacillus arenosi* B-21, *Sporosarcina soli* B-22, *Enterobacter cloacae* KJ-46 and *E. cloacae* KJ-47 were more effective in bioremediation of soil contaminated with Pb, Cd and Cu due to the synergistic effect of bacterial consortium. The bacterial consortium showed greater resistance to the heavy metals in comparison to using a single strain. Bioremediation studies using consortium of marine bacteria exhibited efficient removal of mercury in the bioreactor (De et al. 2008). Therefore, a consortium of microbial isolates is metabolically more effective in biosorption of metals and therefore more potent in field applications (Table 11.1).

11.7 Microbial Mechanism of Degradation of Hydrocarbon Pollutants

Hydrocarbon pollutants are mainly of two types: polycyclic aromatic hydrocarbons and petroleum-based hydrocarbons (crude oil-based hydrocarbon). Polycyclic aromatic hydrocarbons are unsaturated hydrocarbons that contain two or more aromatic rings. These are generated by incomplete combustion of organic material such as wood, petroleum, coal, natural gas. Crude oil-based hydrocarbons or petroleum hydrocarbons usually include the *n*-alkanes and cyclohexanes which are saturated hydrocarbons (Kumar et al. 2018b). These are found to contaminate the soil and water due to spillages from oil tankers, shipping activities, storm water and industrial discharge. The degradation pathway employed by microorganisms for the degradation of these hydrocarbons and most of the organic pollutants involves the oxidation of the pollutant by cell oxygenases and peroxidases (Das and Dash 2014). The resulting catechol in case of PAHs and primary alcohols in case of crude oil-based hydrocarbons undergo degradation by the peripheral pathways of the cell forming intermediates that enter the central intermediary pathway like the Tricarboxylic acid

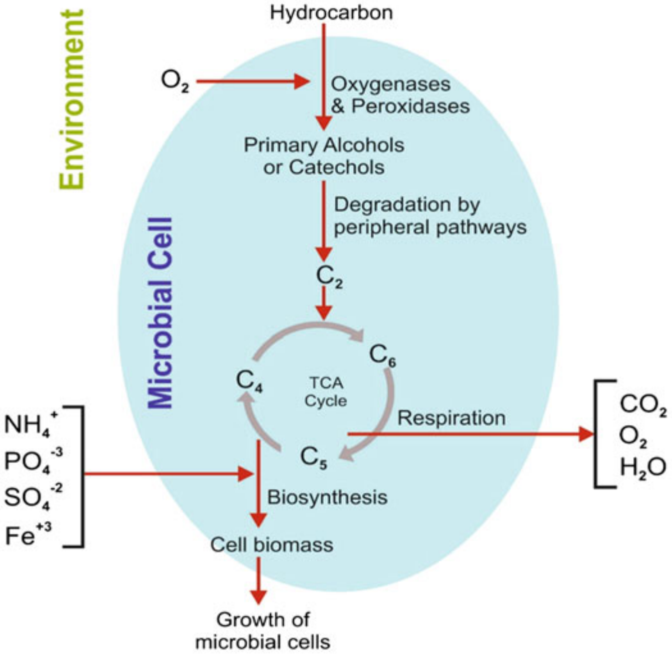


Fig. 11.5 Biodegradation of hydrocarbon compounds by microorganisms

pathway (TCA) (Fig. 11.5). The central precursor molecules of the TCA cycle (acetyl-CoA, succinate, pyruvate) then enter the biosynthesis pathway for sugar synthesis by gluconeogenesis and by formation of cell biomass.

In the biodegradation of hydrocarbons, the genera *Pseudomonas* is found to be the most prominent member that is capable of degrading wide number of polyaromatic hydrocarbons and petroleum hydrocarbons. *Pseudomonas stutzeri* was found to be a very dominant organism in the petroleum pipelines which had an ability to utilize aromatic hydrocarbons such as toluene, phenol, xylene and naphthalene.

11.7.1 Bioremediation of Polyaromatic Hydrocarbons by Microorganisms

Polyaromatic hydrocarbons are of environmental concern owing to their persistence in nature and their toxigenic, mutagenic and carcinogenic properties. PAHs include recalcitrant compounds such as naphthalene, benzopyrene, phenanthrene, anthracene, etc. Many bacteria, fungi and algae have been studied for their ability to metabolize and degrade these PAHs (Bhatia et al. 2018). Table 11.2 shows the list of bacterial, fungal and algal microorganisms that have the potential to degrade polyaromatic hydrocarbons. The bioremediation potential of the microorganisms

Table 11.2 Microorganisms used in bioremediation of polyaromatic hydrocarbons (PAHs)

Polyaromatic hydrocarbon degrading microorganisms		
Microorganism	Polyaromatic hydrocarbon (PAH)	Reference
Bacteria		
Achromobacter xylosoxidans DN002	Mono and poly aromatic hydrocarbons	Xu et al. 2018
Cycloclasticus sp.	Naphthalene, Phenanthrene, pyrene	Ghosal et al. 2016; Bhatia et al. 2018
Lutibacterium anuloederans	Phenanthrene	Chung and King 2001; Das and Dash 2014
Mycobacterium sp.	Naphthalene, Phenanthrene	Ghosal et al. 2016; Bhatia et al. 2018
Neptunomonas naphthovorans	Naphthalene	Hedlund et al. 1999; Das and Dash 2014
Pseudomonas sp.	Naphthalene, Phenanthrene	Ghosal et al. 2016; Bhatia et al. 2018
Sphingomonas paucimobilis EPA505	Phenanthrene	Das and Dash 2014; Ghosal et al. 2016
Fungi		
Aspergillu*s terreus*	Pyrene, Benzopyrene, Phenanthrene	Capotorti et al. 2004; Capotorti et al. 2005; Cerniglia and Sutherland 2010
Cunninghamella elegans	Naphthalene, anthracene, phenanthrene	Cerniglia and Sutherland 2010
Fusarium sp.	Benzopyrene	Cerniglia and Sutherland 2010
Ganoderma lucidum	Phenanthrene, pyrene	Agrawal et al. 2018
Irpex lacteus	Pyrene	Cajthaml et al. 2008
Phanerochaete chrysosporium	Fluorene	Cerniglia and Sutherland 2010
Phanerochaete sordida	Creosote	Cerniglia and Sutherland 2010
Pleurotus ostreatus	Creosote, pyrene, anthracene, fluorene, and dibenzothiophene	Bezalel et al. 1996; Bogan et al. 1999; Cerniglia and Sutherland 2010
Scopulariopsis brevicaulis	Phenanthrene, benzopyrene	Mao and Guan 2016
Trametes versicolor	Anthracene, benzopyrene	Cerniglia and Sutherland 2010
Algae		
Chlamydomonas sp.	Lindane, naphthalene, phenol	Ardal 2014
Chlorella sp.	Lindane, chlordimeform	Ardal 2014
Dunaliella sp.	Naphthalene	Ardal 2014
Elkatothrix viridis	Anthracene	El-Sheekh et al. 2012
Lyngbya lagerlerimi	Phenol	El-Sheekh et al. 2012
Nitzschia sp. and *Skeletonema costatum*	Phenanthrene and fluoranthene	Hong et al. 2008
Nostoc linckia	Naphthalene	El-Sheekh et al. 2012

(continued)

Table 11.2 (continued)

Microorganism	Polyaromatic hydrocarbon (PAH)	Reference
Polyaromatic hydrocarbon degrading microorganisms		
Scenedesmus obliquus	Phenanthrene, naphthalene, Sulphonic acid	Safonova et al. 2005
Selenastrum capricornutum	Benzo[a]pyrene	Ardal 2014
Volvox aureus	2-methythie 3-phenyl quinazlin-4- 3H	El-Sheekh et al. 2012
Microbial consortium		
Burkholderia cepacia GS3C, *Pandoraea pnomenusa* GP3B *Pseudomonas* GP3A *Sphingomonas* GY2B,	Phenanthrene and Methylphenanthrenes	Gupta et al. 2015
Bacillus pumilus *Staphylococcus warneri*	Phenanthrene, Pyrene and Benzo[a]anthracene	Moscoso et al. 2012
Serratia marcescens L-11, *Streptomyces rochei* PAH-13 *Phanerochaete chrysosporium* VV-18	Fluorene, anthracene, phenanthrene and pyrene	Sharma et al. 2016
Rhodococcus sp. ASDC1 *Bacillus* sp. ASDC2 *Burkholderia* sp. ASDC3	Chrysene	Vaidya et al. 2018
Aeromonas hydrophila *Bacillus megaterium* *Raoultella ornithinolytica*, *Serratia marcescens*	Acenaphthene, fluorene	Alegbeleye et al. 2017
Aphanocapsa sp., *Chlorella minutissimma*, *Citrobacter* sp. SB9, *Pseudomonas aeruginosa* SA3, *Bacillus subtilis* SA7	PAH in crude oil effluents	Godsgift and Fagade 2016

may be DNA based or plasmid based. *Cycloclasticus* sp. are the most common and widely studied bacteria that have the potential to degrade multiple PAH compounds (Wang et al. 2018). Marine bacteria such as *Cycloclasticus spirillensus, Lutibacterium anuloederans and Neptunomonas naphthovorans* have been studied for their ability to degrade PAHs in the marine environment (Das and Dash 2014). Bacteria such as *Mycobacterium* sp., *Moraxella* sp., *Burkholderia cepacia, Pseudomonas fluorescens, Pseudomonas putida, Pseudomonas paucimobilis, Bacillus cereus, Rhodococcus* sp., *Streptomyces* sp., *Achromobacter denitrificans, Brevundimonas vesicularis, Comamonas testosteroni, Vibrio* sp., *Sphingomonas, Brevibacterium, Arthrobacter, Nocardioides* have exhibited their ability to degrade naphthalene and phenanthrene (Ghosal et al. 2016). *Sphingomonas paucimobilis* EPA505 has also shown an ability to grow on fluoranthene utilizing it as the sole carbon source (Das and Dash 2014). Research studies have shown other bacteria such as *Sphingobacterium, Alteromonas, Streptomyces* and fungi *Irpex lacteus, Aspergillus fumigatus* can be used either individually or as a consortium with other PAH degrading microorganisms for bioremediation of PAH-contaminated environments (Bhatia et al. 2018). The degradation of the polyaromatic hydrocarbon, like in case of other substrates also depends upon the pH of the environment. The degradation of *Burkholderia cocovenenans* increases from 40% to 80% when the pH is changed from 5.5 to neutral (Mahjoubi et al. 2017).

The fungi *Pleurotus ostreatus, Phanerochaete chrysosporium, Phanerochaete laevis* HHB-1625*, Rigidoporus lignosus, Aspergillus terreus, Cunninghamella elegans, Fusarium* sp.*, Trametes versicolor, Phanerochaete sordida* have been studied for their ability to degrade various polyaromatic compounds (Bogan et al. 1996; Cerniglia 1982; Cerniglia and Sutherland 2010). Though degradation of PAHs by bacteria and fungi has been widely studied, much less is known about the degradation of these compounds by algae. *Scenedesmus obliquus*, a green alga has been reported to degrade phenanthrene by biotransformation (Safonova et al. 2005). *Nostoc linckia, Elkatothrix viridis* and *Volvox aureus* degraded naphthalene, anthracene and 2-methythie 3-phenyl quinazlin-4-3H, respectively. *Nitzschia* sp. and *Skeletonema costatum* biodegrade phenanthrene and fluoranthene by bioaccumulation of these compounds inside the cells (Hong et al. 2008). The algae *Prototheca zopfi* has also been reported to degrade polyaromatic hydrocarbons extensively.

Degradation of PAH has been found to be more effective on application of consortium of microorganisms to PAH-contaminated soils. Microbial communities from the rhizosphere have been reported to degrade PAHs in contaminated soils by synergistic action between the microorganisms (Bisht et al. 2015). Investigations using a consortium of *Staphylococcus warneri* and *Bacillus pumilus* in the degradation of Phenanthrene, Pyrene and Benzo[a]anthracene were found to yield results with the removal of about 80–90% of the aromatic compound in 3 days in a bioreactor (Moscoso et al. 2012). Bacterial consortium *Serratia marcescens* L-11, *Streptomyces rochei* PAH-13 and *Phanerochaete chrysosporium* VV-18 were found to be 85–100% effective against soil contaminated with fluorene, anthracene, phenanthrene and pyrene within a period of 30 days when the soil was amended with compost (Sharma et al. 2016). A bacterial algal consortium with *Chlorella minutissimma* and *Aphanocapsa* sp. as the algal counterparts and *Citrobacter* sp. SB9, *Pseudomonas aeruginosa* SA3, *Bacillus subtilis* SA7 as the bacterial inoculants was studied for its efficiency in degradation of PAHs from crude oil effluents. A combination of *Chlorella minutissimma* and the bacterial inoculants was found to be the most effective in comparison with all the algal and bacterial inoculants used together or when *Aphanocapsa* sp. was used along with the bacterial inoculants. Therefore, the success and efficiency of the consortium depends on the synergistic action between the inoculants (Godsgift and Fagade 2016).

11.7.2 Bioremediation of Crude Oil-Based Hydrocarbons by Microorganisms

Crude oil-based hydrocarbons pose a major threat to humans as well as to the terrestrial and marine ecosystems. Bioremediation approaches for the removal of these crude oil-based hydrocarbons have received much attention largely due to their efficacy in detoxifying the contaminants effectively. The interaction and biodegradation of hydrocarbon substrates depend essentially on the adhesion mechanisms of the bacterial cell that include the outer membrane proteins and lipids, fimbriae, pili and extracellular polymers and capsules. It has been reported that in *Acinetobacter* sp. RAG-1 (Table 11.3), the utilization of Alkane is dependent upon the presence of fimbriae. However, it is not just the bacteria with hydrophobic cell surface that degrade the pollutants. Bacteria with hydrophilic cell surface have also been demonstrated to metabolize hydrocarbon pollutants owing to modifications in their outer membranes. These hydrophilic hydrocarbon degrading bacteria possess more potential in degrading the hydrocarbon as it involves direct assimilation and action on the hydrocarbon substrate in comparison with the hydrophobic bacteria. This is due to the high cell surface hydrophobicity which promotes cell aggregation and biofilm formation (Prakash et al. 2014).

Bioremediation of hydrocarbon involves two approaches: Bioaugmentation and biostimulation. Bioaugmentation involves introduction of highly efficient hydrocarbon degrading bacteria to degrade the hydrocarbon (Mahjoubi et al. 2017), whereas biostimulation is the stimulation of the indigenous bacteria by modifying the environmental conditions. Though biodegradation of the hydrocarbons has been studied in bacteria yeast and fungi, bacteria are the major class of microorganisms involved in biodegradation of hydrocarbons. Hydrocarbon biodegradation by various marine strains that has been studied includes bacteria belonging to the genera *Acinetobacter, Achromobacter, Alcanivorax, Alkanindiges, Alteromonas, Arthrobacter, Burkholderia, Dietzia, Enterobacter, Kocuria, Micrococcus, Marinococcus, Methylobacterium, Marinobacter, Mycobacterium, Pseudomonas, Pandoraea, Nocardia, Planococcus, Rhodococcus, Staphylococcus, Streptococcus, Streptobacillus, Sphingomonas* and *Vibrio* (Tremblay et al. 2017). A wide number of pseudomanads are capable of degrading a wide variety of petroleum-based hydrocarbons (Varjani and Upasani 2012; Wu et al. 2018; Muriel-Millán et al. 2019).

Bioremediation of oil spills by novel bacterial isolates, capable of degrading crude oil has been reported which can utilize these hydrocarbons as a source of carbon and energy. *Vibrio* and *Acinetobacter* sp. reported by Kharangate-Lad and Bhosle (2014) were capable of growing on crude oil and produced EPS which were capable of bioemulsifying hydrocarbons. Surface sediment bacteria, *Halomonas* sp. MS1 isolated from the Kish Island in the Persian Gulf showed a significant ability to utilize crude oil as the sole source of carbon and energy and making it a potentially important bacteria in bioremediation of crude oil contaminated sites (Sadeghi et al. 2016). Interestingly bacteria such as A*lkanindiges* sp. which are rare in non-polluted sediments show a dominance in these sediments when polluted with diesel. Similarly, bacteria belonging to the obligate hydrocarbonoclastic (OHCB) group such as *Alcanivorax, Marinobacter, Thallassolituus, Cycloclasticus, Oleispira* were undetectable or few in number before pollution. However, they were found to be abundant and dominating the site after pollution with petroleum oil. These rare-to-dominant phenomenon of hydrocarbon degrading bacteria play a crucial role in the biotransformation and bioremediation of the crude oil hydrocarbons. Though bacteria utilizing wide range of crude oil components like *Dietzia* sp. and *Achromobacter xylosoxidans* DN002 have been reported, no bacteria can degrade the entire spectrum of petroleum hydrocarbons (Xu et al. 2018). Therefore, efficient removal of crude oil requires combined action of multiple bacteria degrading various hydrocarbons.

Commercial consortiums have been developed for bioremediation of hydrocarbons with bacteria such as *Agreia, Marinobacter, Pseudoalteromonas, Pseudomonas, Psychrobacter* and *Shewanella*. This consortium has been reported to efficiently degrade crude oil and its components. Bacterial consortium developed using *Ochrobactrum* sp., *Stenotrophomonas maltophilia* and *Pseudomonas aeruginosa* could effectively degrade 3% of crude oil by 83%. Significantly, when exogenous *Bacillus subtilis* was applied with indigenous bacterial consortium, it effectively accelerated the degradation of crude oil (Xu et al. 2018). A bioaugmentation field study, on the treatment of diesel oil-contaminated soil demonstrated that with exogenous consortium containing *Aeromonas hydrophila, Alcaligenes xylosoxidans, Gordonia* sp., *Pseudomonas fluorescens, Pseudomonas putida, Rhodococcus equi, Stenotrophomonas maltophilia* and *Xanthomonas* sp. a high biodegradation efficiency of 89% was observed in 365 days. Other bacterial consortiums that effectively degrade hydrocarbon pollutants have been mentioned in Table 11.3. Bacterial-fungal consortiums have found to be very efficient in the degradation of both PAH and petroleum-based hydrocarbons (Tang et al. 2012).

Fungi such as *Amorphoteca, Graphium, Neosartorya, Talaromyces* and yeast like *Candida, Yarrowia* and *Pichia* have been isolated from petroleum contaminated soils and that exhibit hydrocarbon degradation. Other genera such as *Aspergillus, Cephalosporium, Penicillium, Rhizopus, Paecilomyces, Pleurotus, Alternaria, Mucor, Talaromyces, Gliocladium, Fusarium* and *Cladosporium* have also been reported to have potential to degrade crude oil hydrocarbons. The yeast species isolated from contaminated water, *Candida lipolytica, Geotrichum* sp., *Torulopsis, Rhodotorula mucilaginosa* and *Trichosporon mucoides* were also seen to degrade petroleum compounds (Das and Chandran 2011).

Algae such as *Prototheca zopfi* has been studied for its ability to utilize crude oil and mixed hydrocarbon substrates. It also was reported to extensively degrade *n*-alkanes and isoalkanes (Das and Chandran 2011).

11.8 Bioremediation of Plastic Polymers by Microorganisms

With growth in industrialization and population, synthetic plastic pollution poses a major problem to the environment. Among the global plastic usage, 80% are petrochemical plastics that include polyethylene (PE), polypropylene (PP),

Table 11.3 Microorganisms used in bioremediation of crude oil-based hydrocarbons

Crude oil and crude oil component degrading bacteria		
Microorganism	Pollutant	Reference
Bacteria		
Achromobacter xylosoxidans DN002	Mono and polyaromatic hydrocarbons	Xu et al. 2018
Alcanivorax sp.	*n*-alkanes	Xu et al. 2018
Brevibacillus laterosporus	Diesel	Amina and Chibani 2016
Dietzia sp.	*n*-alkanes (C6–C40)	Xu et al. 2018
Halomonas sp. MS1	Crude oil	Sadeghi et al. 2016
Pseudomonas aeruginosa	*n*-alkanes	Wu et al. 2018; Muriel-Millán et al. 2019
Fungi		
Aspergillus sp.	Petroleum hydrocarbon	Al-Nasrawi 2012; Al-Hawash et al. 2018b
Beauveria bassiana		Al-Nasrawi 2012
Cochliobolus lunatus	Crude oil	Al-Nasrawi 2012
Cunninghamella echinulate *Cunninghamella elegans*	Crude oil	Rudd et al. 1996
Fusarium solani	Crude oil	Al-Nasrawi 2012
Meyerozyma guilliermondii	Gasoline	Sangale et al. 2019
Mortierella sp.		Sangale et al. 2019
Penicillium sp. *Penicillium documbens*	Crude oil	Al-Nasrawi 2012; Govarthanan et al. 2017; Al-Hawash et al. 2018a
Scolecobasidium obovatum	Crude oil	Mahmoud and Bagy 2018
Yeast		
Candida lipolytica *Candida glabrata* *Candida krusei*	*n*-alkanes	Das and Chandran 2011; Burghal et al. 2016
Geotrichum sp.	Crude oil	Das and Chandran 2011
Rhodotorula mucilaginosa	Crude oil	Das and Chandran 2011
Trichosporon mucoides	Crude oil	Das and Chandran 2011
Saccharomyces cerevisiae	Crude oil	Burghal et al. 2016
Polysporus sp. S133	Crude oil	Burghal et al. 2016
Algae		
Prototheca zopfi	*n*-alkanes and isoalkanes	Das and Chandran 2011
Fucus vesiculosus	Petroleum waste	Aditi et al. 2015
Consortium		
Burkholderia cepacia GS3C, *Pandoraea pnomenusa* GP3B *Pseudomonas* GP3A *Sphingomonas* GY2B	Alkanes, alkylcycloalkanes, alkylbenzenes	Tang et al. 2012

(continued)

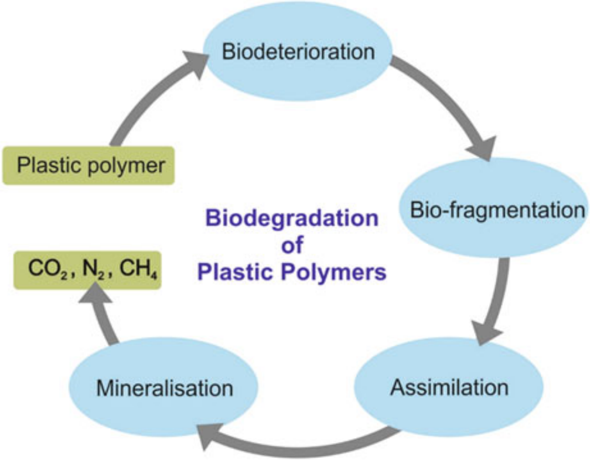
Table 11.3 (continued)

Crude oil and crude oil component degrading bacteria		
Microorganism	Pollutant	Reference
Ochrobactrum sp., *Pseudomonas aeruginosa* *Stenotrophomonas maltophilia*	Crude oil	Xu et al. 2018
Brachybacterium sp., *Cytophaga* sp., *Sphingomonas* sp., *Pseudomonas* sp.	Oil spills	Angelim et al. 2013
Micrococcus sp., *Bacillus* sp., *Corynebacterium* sp., *Flavobacterium* sp., *Pseudomonas* sp.	*n*-alkane	Rahman et al. 2003
Alteromonas putrefaciens, *Klebsiella pneumoniae, Pseudomonas fragi* *Moraxella saccharolytica*,	Diesel hydrocarbon	Sharma and Rehman 2009
Acinetobacter faecalis, *Staphylococcus* sp. *Neisseria elongate*	Crude petroleum oil	Mukred et al. 2008
Brachybacterium sp., *Cytophaga* sp., *Pseudomonas* sp. *Sphingomonas* sp.,	Oil spills	Angelim et al. 2013
Aeromonas hydrophila, *Alcaligenes xylosoxidans*, *Gordonia* sp. *Pseudomonas fluorescens*, *Pseudomonas putida*, *Rhodococcus equi*, *Stenotrophomonas maltophilia*, *Xanthomonas* sp.	Diesel	Xu et al. 2018

polystyrene (PS), polyethylene terephthalate (PET) and polyvinyl chloride (PVC) which pollute the soil and water environment.

Biodegradation of plastic polymers by microorganisms proceeds via four important steps, biodeterioration, biofragmentation, assimilation and mineralization (Fig. 11.6). Biodeterioration involves initial colonization by microorganisms by adhesion thereby affecting the physical, chemical and mechanical properties of the plastic. Abiotic factors play a synergistic role in initializing the degradation. Microorganisms colonize and produce biofilm or EPS that invade the polymeric pores resulting in grooves and cracks. Therefore, weakening the polymeric structure of the plastic and physically deteriorating the polymer. The release of corrosive compounds during metabolism such as sulphuric acid (*Thiobacillus* sp.), nitrous acid (*Nitrosomonas* sp.) or nitric acid (*Nitrobacter* sp.) by chemolithotrophic bacteria and production of organic acids such as citric, fumaric, oxalic, gluconic, glutaric, oxaloacetic and glyoxalic acids affects the microplastic matrix resulting in chemical deterioration of the polymer. In biofragmentation the polymeric plastic is cleaved

Fig. 11.6 The different steps in biodegradation of plastic polymers by microorganisms



into oligomers, dimers or monomers by the action exo-enzymes or free radicals produced by the microorganisms. Bacteria that degrade plastics usually contain the enzyme oxygenases that catalyses the addition of an oxygen molecule to the polymeric chain converting it to a less recalcitrant molecule such as an alcohol or peroxyl group. Assimilation involves the absorption of molecules across the cell cytoplasm for metabolic process to form cell biomass or cell structures. Mineralization is the complete degradation of the absorbed molecules into oxidized metabolites such as carbon dioxide, nitrogen, methane and water vapour (Dussud et al. 2018).

In studies involving biodegradation of plastic polymers, *Pseudomonas* and *Clostridium* are the most dominant bacteria that can metabolize plastics like polyethene, PVC, PHB (Table 11.4) (Ghosh et al. 2013). Studies on *Rhodococcus* sp. demonstrate the ability to degrade plastic by 8% of its dry weight in 30 days (Urbanek et al. 2018). Other bacteria known to degrade plastic polymers are *Acidovorax* sp., *Alcaligenes* sp., *Brevibacillus borstelensis, Comamonas acidovorans, Diplococcus* sp., *Moraxella* sp., *Pseudomonas* sp., *Streptococcus* sp., *Staphylococcus* sp. and *Micrococcus* sp., *Thermomonospora fusca, Schlegelella thermodepolymerans* and *Amycolatopsis* sp. (Ghosh et al. 2013; Kathiresan 2003). Bacteria degrading plastic polymers such as *Alcanivorax, Shewanella, Moritella, Psychrobacter*, *Pseudomonas* and *Tenacibaculum* that exhibited biodegradation ability against polyester PCL have been reported from the deep-sea sediments. The highest biodegradation capacity for PCL was observed in *Pseudomonas* and *Rhodococcus* (Urbanek et al. 2018).

Bacteria such as *Phormidium, Pseudophormidium, Bacteroides, Lewinella, Proteobacteria, Arcobacter and Colwellia* sp. isolated from the surface of PET bottles and microplastic polymers have been identified for their ability to degrade these polymers. Analysis of enzymatic profiles of most plastic degrading microorganisms suggests that the presence of the enzyme lipase plays a crucial role in the ability of these microorganisms to degrade plastic polymers as it catalyses

Table 11.4 Microorganisms used in bioremediation of plastic polymers

Plastic polymer degrading microorganisms		
Microorganism	Pollutant	Reference
Bacteria		
Alcanivorax	Monofilament fibres of PCL, PHB/V, PBS	Sekiguchi et al. 2011
Arcobacter sp., Colwellia sp.	LDPE	Urbanek et al. 2018
Bacillus brevis	Polycaprolactone	Urbanek et al. 2018
Ideonella sakaiensis	PET	Urbanek et al. 2018
Moritella sp.	PCL	Sekiguchi et al. 2011
Ochrobactrum sp.	PVC	Ghosh et al. 2013
Phormidium, Lewinella	PET	Urbanek et al. 2018
Proteobacteria, Bacteroides	Microplastics	Urbanek et al. 2018
Pseudomonas sp.	PCL, commercially available bag based on potato and corn starch monofilament fibres of PCL, PHB/V, PBS	Sekiguchi et al. 2011
Psychrobacter sp.	PCL	Sekiguchi et al. 2011
Rhodococcus sp.	PCL, commercially available bag based on potato and corn starch	Sekiguchi et al. 2011
Rivularia	PP, PE	Urbanek et al. 2018
Shewanella sp.	PCL	Sekiguchi et al. 2011
Stanieria, Pseudophormidium	PET	Urbanek et al. 2018
Streptomyces sp.	PHB, poly(3-hydoxybutyarate-co-3-hydroxyvalerate), and starch or polyester	Ghosh et al. 2013
Tenacibaculum sp.	Monofilament fibres of PCL, PHB/V, PBS	Urbanek et al. 2018
Zalerion maritimum	PE	Urbanek et al. 2018
Fungi		
Aspergillus versicolor, Aspergillus sp. *Aspergillus sydowii*	LDPE PVC	Urbanek et al. 2018; Sangale et al. 2019
Clonostachys rosea, Trichoderma sp.	PCL, commercially available bag based on potato and corn starch	Urbanek et al. 2018
Ochrobactrum anthropi strain L1-W	di-2-ethylhexyl phthalate	Nshimiyimana et al. 2020
Pleurotus ostreatus	PE	Rodrigues da luz et al. 2019
Myceliophthora sp.	Polyethylene	Ibrahim 2013
Penicillium chrysogenum	Polythene	Sangale et al. 2019
Trichoderma viride	LDPE	Munir et al. 2018

(continued)

Table 11.4 (continued)

Plastic polymer degrading microorganisms		
Microorganism	Pollutant	Reference
Pestalotiopsis microspora	Polyurethane	Russell et al. 2011
Yeast		
Candida rugosa	Polyurethane	Russell et al. 2011
Pseudozyma sp.	Poly-butylene succinate or poly-butylene succinate-co-adipate	Kitamoto et al. 2011
Algae		
Anabaena spiroides	Polyethylene	Kumar et al. 2017
Scenedesmus dimorphus	Polyethylene	Kumar et al. 2017
Navicula pupula	Polyethylene	Kumar et al. 2017
Consortium		
Vibrio alginolyticus, Vibrio parahaemolyticus	PVA-LLDPE	Urbanek et al. 2018

the hydrolysis of ester bonds. Microbial lipases can efficiently hydrolyse polyesters of PCL. Therefore, lipase producing strains *Agreia, Cryobacterium*, *Polaromonas, Micrococcus, Subtercola, Leifsonia* and *Flavobacterium* from the marine environment have potential to degrade plastic polymers. Other microbial enzymes like cutinases, ureases, depolymerases (PHA-depolymerases, PHB-depolymerases PLA depolymerases, PCL depolymerases), esterases, proteinases (proteinase K against PLA) and dehydratases produced by microorganisms also aid in degradation of plastic polymers. Recent studies on the bacterium *Ideonella sakaiensis* have shown the presence of a novel enzyme PETase (Urbanek et al. 2018).

Fungi, *Clonostachys rosea* and *Trichoderma* sp. have been reported to degrade plastic polymers. *Aspergillus versicolor* and other *Aspergillus* sp. actively degrade LDPE plastic polymers. Saprophytic fungi capable of degrading polyurethane, *Agaricus bisporus*, *Marasmius oreades*, *Cladosporium cladosporioides, Xepiculopsis graminea* and *Penicillium griseofulvum* were isolated from floating plastic litter from the shorelines of Lake Zurich, Switzerland (Brunner et al. 2018). *Alternaria* sp., *Aspergillus niger, Geomyces pannorum, Nectria* sp., *Phoma* sp., *Paraphoma* sp., *Penicillium* sp., *Plectosphaerella* sp. and *Neonectria* sp. are fungi that utilized polyurethane as the sole source of carbon. Yeast *Candida rugosa* has been reported to have polyurethane degrading enzymes and *Pseudozyma* sp. exhibits ability to degrade poly-butylene succinate or poly-butylene succinate-co-adipate films (Kitamoto et al. 2011).

The microalgae *Anabaena spiroides* (blue-green alga), *Scenedesmus dimorphus* (Green microalga) and *Navicula pupula* (Diatom) are being considered as the novel solutions for degradation of polyethylene (Kumar et al. 2017). Microalgae promote efficient biodegradation of plastic polymers by using its enzymes and toxins (Bhuyar et al. 2018).

Microbial consortium using microorganisms with enzymatic profiles necessary for degradation of LDPE and polyethylene has been obtained from culture collection and tested for their potential application in degradation of these plastic polymers (Skariyachan et al. 2016). A consortium of marine bacteria *Vibrio alginolyticus* and *Vibrio parahaemolyticus* when incubated with polyethylene for 15 days showed disintegration of the polymer in the form of grooves and cracks. Studies on bacterial consortium are focused on biodegradation of plastic polymers using indigenous microbial population and biostimulation, by incorporating microbial strains that produce specific plastic degrading enzymes. Research on bacterial consortium also suggests that tailored consortia can thrive in the plastic mixtures and participate in their biodegradation (Syranidou et al. 2019).

11.9 Bioremediation of Recalcitrant Agro-Chemicals by Microorganisms

The rise in the global population has increased the demand for food supplies and therefore involves incessant use of fertilizers, pesticides, fungicides, insecticides and herbicides in farming. Pesticides and herbicides are chemicals that are used to control insects and unwanted weeds, respectively. It is necessary to use these in moderate amounts, only as required in order to control the pests and weeds. However unrestricted use of these pesticides has led to their accumulation in the soil as well as in the water bodies resulting in problems due to biomagnification. Landfilling and pyrolysis of these xenobiotic compounds lead to formation of toxic intermediates. Therefore, bioremediation of these compounds using microorganisms is a promising technique for the removal of these compounds from the soil and marine environment.

The bacteria involved in degradation of pesticides include *Alteromonas undina*, *Alteromonas haloplanktis, Bacillus diminuta, Flavobacterium* sp., *Arthrobacter* sp., *Azotobacter* sp., *Burkholderia* sp., *Pseudomonas* sp., *Raoultella* sp., and *Bacillus sphaericus*. These have been reported to degrade herbicidal and fungicidal compounds (Table 11.5) (Uqab et al. 2016). The biodegradation of these xenobiotic compounds involves complete oxidation of the compound to carbon dioxide and water with the release of energy for the microbes. Bacterial strains of *Pseudomonas fluorescens* and *Bacillus polymyxa* from the Kyrgyzstan pesticide dumping sites exhibited high rate of degradation of aldrin. These dumping sites also showed an abundance of bacteria belonging to the genera *Pseudomonas, Bacillus* and *Micrococcus*. Reports on biodegradation of endosulfan highlight the degradative abilities of *Klebsiella* sp., *Acinetobacter* sp., *Alcaligenes* sp., *Flavobacterium* sp. and *Bacillus* sp. in degradation of this compound. The microbial action on endolsulfan results in the production of intermediates (endosulfan diol, endosulfan ether, and endosulfan lactone) of lesser toxicity than the original compound. Bioremediation of pesticide and related compounds by using microorganisms is preferred due to the production of less toxic intermediates. However, in soils where the innate microbial population is unable to degrade these compounds, addition of external microflora

Table 11.5 Microorganisms used in bioremediation of recalcitrant agro-chemicals

Recalcitrant agro-chemical degrading microorganisms		
Microorganism	Pollutant	Reference
Bacteria		
Acidomonas sp.	Allethrin	Paingankar et al. 2005
Aminobacter sp. MSH1	2,6-dichlorobenzamide (BAM)	Ellegaard-Jensen et al. 2017
Bacillus amyloliquefaciens IN937a *Bacillus pumilus* SE34	Propamocarb and Propamocarb hydrochloride	Ardal 2014
Bacillus polymyxa	Aldrin	Uqab et al. 2016
Bacillus thuringiensis	Melathion	Javaid et al. 2016
Micrococcus	Aldrin	Uqab et al. 2016
Mycobacterium chlorophenolicum	PCB	
Ochrobactrum anthropi NC-1	Phenmedipham	Pujar et al. 2019
Ochrobactrum anthropi Strain SH14	Azoxystrobin	Feng et al. 2020
Pseudomonas sp.	Organophosphates, neonicotinoids, endosulfan, atrazine	Uqab et al. 2016; Doolotkeldieva et al. 2018
Rhizobium meliloti	Chlorinated phosphates	Javaid et al. 2016
Sphingobium japonicum	Hexachlorocyclohexane	Javaid et al. 2016
Stenotrophomonas maltophilia	Endosulfan, DDT	Javaid et al. 2016
Shewanella sp.	Methyl parathion	Javaid et al. 2016
Fungi		
Aspergillus sp.	Endosulfan, organophosphates	Frazar 2000
Fusarium proliferatum CF2	Allethrin	Bhatt et al. 2020
Mortierella sp. LEJ701	Diuron	
Mortierella sp. LEJ701, *Aminobacter* sp. MSH1	2,6-dichlorobenzamide (BAM)	Ellegaard-Jensen et al. 2017
Phanerochaete	Aldrin, DDT, etc.	Uqab et al. 2016
Pleurotus ostreatus	Aldrin, DDT, etc.	Uqab et al. 2016
Pleurotus sp.	Endosulfan, chlorothalonil paraquat	Camacho-Morales and Sánchez 2016
Variovorax sp. SRS16 *Arthrobacter globiformis* D47 *Mortierella* sp. LEJ702	Diuron	Ellegaard-Jensen et al. 2017
Algae		
Chlorella sp..	Mirex, chlordimeform	Ardal 2014
Chlamydomonas sp.	Toxaphene, methoxychlor	Ardal 2014
Chlorococcum sp.	Mirex	Ardal 2014
Cylindrotheca sp.	DDT	Ardal 2014
Dunaliella sp.	Mirex	Ardal 2014
Euglena gracilis	DDT, parathion	Ardal 2014
Scenedesmus obliquus	DDT, parathion	Ardal 2014

(continued)

Table 11.5 (continued)

Recalcitrant agro-chemical degrading microorganisms		
Microorganism	Pollutant	Reference
Selenastrum capricornutum	Benzene, toluene, chlorobenzene, 1,2-dichlorobenzene, nitrobenzene Naphthalene, 2,6-dinitrotoluene, phenanthrene, di-*n*-butylphthalate, Pyrene	Ardal 2014
Consortiums		
Bacillus sp. *and Chryseobacterium joostei*	Lindane, methyl parathion, and carbofuran	Javaid et al. 2016
Pseudomonas putida (NII 1117), Klebsiella sp., *(NII 1118), Pseudomonas stutzeri (NII 1119), Pseudomonas aeruginosa (NII 1120)*	Chlorpyrifos	Sasikala et al. 2012

capable of degrading these compounds has been recommended. The biodegradation depends on enzymatic abilities of the microbes as well as the factors such as pH, temperature, nutrients, oxygen, etc. *Pseudomonas* sp. have been reported to degrade organophosphate compounds and neonicotinoids (Doolotkeldieva et al. 2018; Uqab et al. 2016). Immobilization of bacteria on alginate and other matrix have been used to achieve degradation of various pesticides under different flow rates and environmental conditions (Javaid et al. 2016).

In case of fungi, they make minor changes in the structure of these compounds during degradation, making them more accessible for degradation by other microbes. The fungal species *Flammulina velutipes, Stereum hirsutum, Coriolus versicolor, Dichomitus squalens, Hypholoma fasciculare, Auricularia auricula, Pleurotus ostreatus, Avatha discolor* and *Agrocybe semiorbicularis* have exhibited the ability to degrade pesticides such as chlorinated organophosphorus compounds triazine, dicarboximide and phenylurea (Uqab et al. 2016). Reports on white rot fungi especially *Phanerochaete* such as *Phanerochaete chrysosporium*, *Phanerochaete sordida*, *Pleurotus ostreatus*, *Phellinus weirii* and *Polyporus versicolor* have shown the ability to degrade aldrin, chlordane, mirex, gamma-hexachlorocyclohexane (g-HCH), heptachlor atrazine, terbuthylazine, lindane, metalaxyl, dieldrin, diuron, dichlorodiphenyltrichloroethane (DDT), etc. *Aspergillus* sp., *Fusarium oxysporum*, *Penicillium chrysogenum* and *Trichoderma* sp. have shown effective biodegradation of organophosphate pesticides (Frazar 2000; Uqab et al. 2016). *Aspergillus* sp. have also been reported to actively degrade endosulfan (Bhalerao and Puranik 2007). Oliveira et al. (2015) reported the fungal species *Penicillium citrinum*, *Aspergillus fumigatus, Aspergillus terreus* and *Trichoderma harzianum* that could tolerate and degrade chlorfenvinphos.

A fungal-bacterial consortium of *Mortierella* sp. LEJ701 and *Aminobacter* sp. MSH1 was used for the degradation of 2,6-dichlorobenzamide (BAM) and it was observed that the mineralization of the compound proceeded faster than when these strains were used individually. Degradation of agro-chemicals has been found to be most effective on using the bacterial and fungal consortiums than using the microorganisms individually. Biosorption by *Aspergillus niger* and *Mycobacterium chlorophenolicum* has been studied for the removal of polychlorinated phenols (PCP) from aqueous solutions and was found to be pH dependent.

Algal cells such as *Chlamydomonas* sp., *Chlorella* sp., *Chlorococcum* sp., *Cylindrotheca* sp., *Dunaliella* sp., *Euglena gracilis, Scenedesmus obliquus, Selenastrum capricornutum* have been reported to degrade agro-chemicals (Table 11.5) (Ardal 2014).

The algae either metabolize these toxic pollutants using them as energy source or utilize cytochrome P450, a specialized family of monooxygenase enzymes to oxidize herbicides and pesticides. Biotransformation of these agro-chemicals has been reported in *Chlorella* sp. using the cytochrome P450. The presence of P450 has also been demonstrated in the presence of herbicide Metflurazon in the algae *Chlorella fusca* and *Chlorella sorokiniana.* Research on green algae degrading phenol, lindane, DDT, chlordimeform has also been reported (Priyadarshani et al. 2011).

Bacterial consortiums have been preferred for bioremediation of soils contaminated with mixed pesticides. *Bacillus* sp. and *Chryseobacterium joostei* have been used together to treat soils contaminated with lindane, methyl parathion and carbofuran. Abraham and others (Abraham et al. 2014) reported the use of a ten strain bacterial consortium containing *Alcaligenes* sp. JAS1, *Ochrobactrum* sp. JAS2, *Sphingobacterium* sp. JAS3 isolated from chlorpyrifos contaminated soil; *Enterobacter ludwigii* JAS17, *Pseudomonas moraviensis* JAS18 and *Serratia marcescens* JAS16 isolated from monocrotophos containing soil and *Klebsiella pneumoniae* JAS8, *Enterobacter cloacae* JAS7, halophilic bacterial strain JAS4, *Enterobacter asburiae* JAS5 isolated from endosulfan contaminated soil in the biodegradation of organophosphorus and organochlorine pesticides. Similar studies using a consortium isolated from chlorpyrifos contaminated soil containing the bacteria *Pseudomonas putida* (NII 1117), *Klebsiella* sp., (NII 1118), *Pseudomonas stutzeri* (NII 1119), *Pseudomonas aeruginosa* (NII 1120) in biodegradation of chlorpyrifos have been reported (Sasikala et al. 2012). The bacterial consortium using *Acinetobacter* sp., *Bacillus* sp., *Citrobacter freundii, Flavobacterium* sp., Pseudomonads (*Pseudomonas putida, Pseudomonas aeruginosa* and *other Pseudomonas sp*). *Stenotrophomonas* sp., *Proteus* sp., *Proteus vulgaris* and *Klebsiella* sp. was seen to be effective in degradation of methyl parathion and p-nitrophenol (Pino et al. 2011).

11.10 Microorganisms Used in Bioremediation of Dye Compounds

Rapid urbanization and industrialization have led to an increase in the use of fast dyes in industries such as textiles, plastic, food, etc. About 50% of the dye used is released in the industrial effluent. Azo dyes are a potential hazard to the environment due to their bio-recalcitrant, toxic, carcinogenic and mutagenic effects on living organisms. Commonly applied techniques for the removal of the dye involve physical, chemical and decolourization processes which pose a cost issue. Green technologies using microorganisms such as bacterial and fungal biomass provide a low-cost solution.

Various bacteria capable of degrading dyes have been reported. These include lactic acid bacteria, *Pseudomonas, Staphylococcus arlettae, Micrococcus luteus, Listeria denitrificans* and *Nocardia atlantica, Bacillus megaterium*. Basidiomycetous fungi such as *Trametes pubescens* and *Pleurotus ostreatus* and other fungal species such as *Aspergillus tamarii, Aspergillus ochraceus, Aspergillus niger, Fusarium oxysporum, Penicillium purpurogenum* and *Trichoderma lignorum* have also been identified for their role in biodegradation of dyes (Table 11.6) (Patel and Gupte 2016; Rani et al. 2014).

Significant findings have also been reported using consortium of bacteria containing two aerobic strains of bacteria and *Pseudomonas putida* (MTCC1194) in degradation of a mixture of azo dyes from textile effluents (Senan and Abraham 2004). Bacterial consortium of *Neisseria* sp., *Vibrio* sp., *Bacillus* sp., *Bacillus* sp. and *Aeromonas* sp. reportedly showed a degradation of the dyes that ranged from 65% to 90% with decolourization of the dye. This was significantly more than when the monocultures were used proving that bacterial consortium is more efficient in treating dye effluents (Karim et al. 2018).

11.11 Bioremediation of Toxic Pollutants Using Genetically Modified Microorganisms

Xenobiotic compounds cannot be easily degraded by the naturally occurring autochthonous population of microorganisms. These toxic pollutants persist in nature owing to their hydrophobic nature which makes it difficult for the microorganisms to take it up as they lack the uptake transport pathways for such compounds. Recombinant DNA technology involves introducing the desired gene by gene manipulation and plasmid DNA resulting in the development of strains of genetically modified microbes that are efficient in bioremediation. Many genetically modified strains have been used in bioremediation of various complex and toxic anthropogenic compounds especially from the genera *Pseudomonas* and *E. coli* (Table 11.7). This is due to the simple nature of *E. coli* and easy ability to manipulate its genome. While *Pseudomonas* sp. have a natural ability to degrade complex compounds, the genome can be further modified to yield more efficient strains. Marine bacteria have been efficiently transformed by inserting gene coding for

Table 11.6 Microorganisms used in bioremediation of dye compounds

Dye compound degrading microorganisms		
Microorganism	Compound	Reference
Bacteria		
Acinetobacter baumannii	Azo dyes effluents	Kumar et al. 2016a
Bacillus firmus	Vat dyes, textile effluents	Adebajo et al. 2016
Bacillus macerans	Vat dyes, textile effluents	Adebajo et al. 2016
Bacillus pumilus HKG212	Textile dye (Remazol black B), Sulphonated di-azo dye reactive red HE8B, RNB dye	Das et al. 2015
Bacillus sp. ETL-2012	Textile dye (Remazol black B), Sulphonated di-azo dye reactive red HE8B, RNB dye	Shah 2013
Bacillus subtilis strain NAP1, NAP2, NAP4	Oil-based based paints	Phulpoto et al. 2016
Bacillus cereus	Azo dyes effluents	Kumar et al. 2016a
Exiguobacterium indicum	Azo dyes effluents	Kumar et al. 2016a
Exiguobacterium aurantiacum	Azo dyes effluents	Kumar et al. 2016a
Pseudomonas aeruginosa	Textile dye (Remazol black B), Sulphonated di-azo dye reactive red HE8B, RNB dye	Das et al. 2015
Klebsiella oxytoca	Vat dyes, textile effluents	Adebajo et al. 2016
Listeria denitrificans	Textile azo dyes	Hassan et al. 2013
Micrococcus luteus	Textile azo dyes	Hassan et al. 2013
Nocardia atlantica	Textile azo dyes	Hassan et al. 2013
Staphylococcus aureus	Vat dyes, textile effluents	Adebajo et al. 2016
Fungi		
Myrothecium roridum IM 6482	Industrial dyes	Jasinska et al. 2015
Pycnoporus sanguineous	Industrial dyes	Yan et al. 2014
Phanerochaete chrysosporium	Industrial dyes	Yan et al. 2014
Penicillium ochrochloron	Industrial dyes	Shedbalkar and Jadhav 2011
Trametes trogii	Industrial dyes	Yan et al. 2014

Table 11.7 Genetically modified microorganisms used in bioremediation processes

Genetically modified bacteria used for bioremediation		
Microorganism	Pollutant	Reference
Bacteria		
Corynebacterium glutamicum	As	De et al. 2008
Deinococcus geothermalis	Mercury (II), Fe (III)-nitrilotriacetic acid, Uranium (VI), and Chromium (VI).	Brim et al. 2003
Deinococcus radiodurans	Toluene, ionic Mercury	Brim et al. 2003
Deinococcus radiodurans DR1-bf +	Uranium and heavy metals	Manobala et al. 2019
E. coli	*cis*-1,2-dichloroethylene	Kumar et al. 2013
E. coli JM109	Cd	Deng et al. 2007
Escherichia coli ArsR -ELP153AR	As	De et al. 2008
Escherichia coli	Polychlorinated benzene (PCB), benzene and toluene	Kumamaru et al. 1998
Escherichia coli FM5/pKY287	Trichloroethylene (TCE) and toluene	Winter et al. 1989
Nocardia sp.	Crude oil	Balba et al. 1998
Pseudoalteromonas haloplanktis TAC125	Aromatic compounds	Papa et al. 2009
Pseudomonas aeruginosa PA142 *P. aeruginosa* JB	2-chlorobenzoate	Kumar et al. 2013
Pseudomonas putida DLL-1	Methyl parathion	Kumar et al. 2013
Sphingomonas sp. CDS-1	Methyl parathion	Kumar et al. 2013
Sphingomonas sp. *CDS-1*	Organophosphate and carbamate-degrading	Kumar et al. 2013
Sulphate-reducing bacteria (SRB)	Chromate	Das and Dash 2014
Synechococcus sp.	Heavy metals	Das and Dash 2014
Thalassospira lucentensis	Hydrocarbons	Das and Dash 2014
Fungi		
Fusarium solani	DDT	Kumar et al. 2013
Gliocladium virens	Paraoxon and diisopropylfluorophosphate	Kumar et al. 2013
Pichia pastoris	Azo dyes, anthraquinone dyes	Kumar et al. 2013
Trichoderma atroviride	Dichlorvos pesticide	Kumar et al. 2013
Yeast		
Saccharomyces cerevisiae CP2 HP3	Cd, Zn	De et al. 2008

(continued)

Table 11.7 (continued)

Genetically modified bacteria used for bioremediation		
Microorganism	Pollutant	Reference
Algae		
Chlamydomonas reinhardtii	Cd	De et al. 2008; Kumar et al. 2013; Igiri et al. 2018
Chlorella sorokiniana ANA9	Heavy metals	Kumar et al. 2013
Laminaria japonica	Pb	Kumar et al. 2013
Nitella pseudoflabellata	Chromium (VI)	Kumar et al. 2013
Phaeodactylum tricornutum	PET	Moog et al. 2019

metallothionein. This has been successfully used in bioremediation of metal contaminated environments. Genetically modified marine Antarctic bacterium, *Pseudoalteromonas haloplanktis* TAC125 has reportedly shown promise in bioremediation of aromatic compounds (Table 11.7). A genetically modified strain of *Pseudomonas putida* ENV2030 was obtained by mutation and was reported to degrade an organophosphorus compound paraoxon by utilizing it as a sole source of carbon and nitrogen. The strain from *Acinetobacter* sp. YAA was mutated by several rounds of mutagenesis to increase the activity of aniline dioxygenase against aniline, 2,4-dimethylaniline and 2-isopropylaniline. *Burkholderia cepacia* strain V350F and V350M are mutants that produce the enzyme 2,4-dinitrotoluene dioxygenase that is reported to have significant activity against m-nitrophenol, o-nitrophenol, o-methoxyphenol and o-cresol. The bacteria *Agrobacterium radiobacter* AD1 was reported to efficiently degrade TCA at contaminated sites. Genomic shuffling has increased the degradation potential of *Sphingobium chlorophenolicum* ATCC 39723 for the pesticide pentachlorophenol. The most significant application for bioremediation involves protein engineering for large subunit of the hybrid enzyme of biphenyl dioxygenase from *Pseudomonas pseudoalcaligenes* KF707 and *Burkholderia cepacia* LB400 that results in enhanced degradation of polychlorobiphenyls (Kumamaru et al. 1998; Kumar et al. 2013). Toxic mercury-degrading gene from terrestrial bacteria has been used to transform marine bacteria for their applications in field for bioremediation of mercury contaminated environments (Das and Dash 2014). *Deinococcus radiodurans* is genetically modified bacteria and the most radiation resistant bacteria that has been designed to digest toluene and ionic mercury from nuclear wastes (Brim et al. 2003). The plasmid from *Deinococcus radiodurans* has been reportedly used to transform *Deinococcus geothermalis,* another radiation resistant bacterium that can reduce Mercury (II), Fe (III)-nitrilotriacetic acid, Uranium (VI) and Chromium (VI). A recombinant strain of *Deinococcus radiodurans* DR1-bf + has gained importance as a potential bacterium for the bioremediation of uranium and heavy metals due to its ability to form biofilms (Manobala et al. 2019). Genes for metallothioneins and phytochelatins from fungi and plants have been cloned in *Escherichia coli* which demonstrates an enhanced binding of heavy metals. Genetically engineered bacteria such as *E. coli* JM109, *Mesorhizobium huakuii, Pseudomonas putida* and *Caulobacter crescentus* that bioaccumulate Cd^{+2} by presence of phytochelatins and metal-binding proteins have been reported. Other bacteria that have been engineered and are being studied for bioremediation have been mentioned in Table 11.7. Modifications in the active sites of enzymes of microorganisms such as *Pseudomonas putida*, *Bacillus megaterium*, *Burkholderia cepacia* strain LB400, *Comamonas testosteroni* B-365 and *Rhodococcus globerulus* P6 by genetic manipulation has resulted in increased efficiency of these enzymes in degrading the target pollutant. *Halobacteriaceae* family protein MBSP1that had biosurfactant activity when used to transform *E. coli Rosetta* ™ (DE3) demonstrated significant increase in hydrocarbon degradation (Araújo et al. 2020).

Saccharomyces cerevisiae has been genetically modified to express P450 cytochrome complexes to express genes to degrade dioxins. Another yeast, *Hansenula polymorpha* has been genetically modified for bioremediation of chromate. The fungi *Fusarium solani* has been genetically modified to improve production of dehalogenase enzyme that is crucial in degradation of DDT. Other fungi that have been genetically modified for the degradation of target pollutants are included in Table 11.7.

A brown algae *Laminaria japonica* from the marine ecosystem was chemically modified for the removal of lead from the wastewaters. The green algae, *Chlorella sorokiniana* ANA9 was used in removal of heavy metals from soil. It was reported to play a crucial role in preventing the diffusion of toxic Cd^{+2} in the soil. The toxicity of chromium (VI) in contaminated waters can be reduced by using *Nitella pseudoflabellata.* To enhance ability of *Chlamydomonas* to bind metals, a foreign metallothionein gene was expressed in *Chlamydomonas reinhardtii.* This enhanced the ability of the strain to absorb Cd by two-fold in comparison to the wild strain in damp soils and aquatic ecosystems (Kumar et al. 2013). Marine microalgae, *Phaeodactylum tricornutum*, has been modified to carry polyethylene terephthalate, PETase gene from *Ideonella sakaiensis* is an eco-friendly method for recycling strategies (Moog et al. 2019).

11.12 Bioremediation of Toxic Pollutants Using Microbial Biosurfactants and Bioemulsifiers

Bioemulsifiers and biosurfactants are surface active compounds which are amphiphilic in nature and promote emulsification of two immiscible phases. These biomolecules are produced by microorganisms such as yeast, bacteria and fungi. They find potential applications in environmental bioremediation, industrial processes and food processing industries.

Although the terms biosurfactants and bioemulsifiers have been used interchangeably with each other, they differ based on their physicochemical properties of interaction and the physiological role they play in bringing the miscibility of the two phases. Bioemulsifiers and biosurfactants both by virtue of being amphiphilic biomolecules possess hydrophilic and hydrophobic structural moieties which allow them to dissolve in polar and non-polar solvents.

Biosurfactants can be either glycolipids which includes rhamnolipids, sophorolipids or trehalose lipids, wherein the sugars are linked to β-hydroxy fatty acids. Lipopeptides biosurfactants such as iturin and fungicin contain cycloheptapeptides with amino acids linked to fatty acids of different chain lengths. Other biosurfactants include polymeric and particulate surfactants. The surface activity of biosurfactants is due to their ability to lower the surface and interfacial tension between the two phases (liquid- air), (liquid- liquid), (liquid- solid). This is carried out by adsorption onto the different surfaces stimulating more interaction and mixing of the immiscible phases. Biosurfactants possess critical micelle concentration (CMC) that form stable emulsions. CMC is the minimum concentration of biosurfactant that is needed to reduce the surface tension to a minimum level and forms micelles. Biosurfactants have low toxicity, high biodegradability and exhibit diversity. Thus, they find potential applications as wetting, foaming and solubilizing agents in industrial processes (Uzoigwe et al. 2015).

A marine strain of *Pseudomonas aeruginosa* isolated from oil-contaminated sea water was found to produce biosurfactant that was effective in degrading hydrocarbons such as 2-methylnaphthalene, tetradecane, hexadecane, octadecane, heptadecane and nonadecane. Hydrocarbonoclastic bacteria that are ubiquitous in the marine environment have the ability to degrade aliphatic and aromatic fractions of crude oil. A mixture of biosurfactants produced by these bacteria stimulate the degradation of these hydrocarbons. Biosurfactant producing strains *Acinetobacter haemolyticus* and *Pseudomonas* ML2 showed a significant reduction in hydrocarbons up to 75%. A lipopolypeptide from *Bacillus subtilis* was found to be stable at varying temperatures, pH and salt concentrations and therefore exhibited potential in applications for bioremediation of hydrocarbons in the marine environment. Biosurfactants such as surfactin, lichenysin and rhamnolipids are found to be effective in hydrocarbon degradation. The biosurfactants produced by *Acinetobacter venetianus* ATCC 31012 exhibited removal of 89% of the crude oil by emulsification (Uzoigwe et al. 2015).

The biosurfactants from *Candida sphaerica* exhibited a bioremediation efficiency of 95% for iron, 90% for zinc and 79% for lead. The surfactant interacted with the heavy metal ion resulting in their detachment from the soil. *Candida* sp. could bioaccumulate nickel and copper by producing biosurfactants (Luna et al. 2016). Heavy metal removal was found to be productive when biosurfactants like surfactin, rhamnolipid, sophorolipids were used for bioremediation of copper and zinc. *Rhodotorula mucilaginosa* was studied for the removal of metal with an efficiency up to 95% due to its ability to form biofilms. The production of biofilm plays a crucial role in bioremediation as biofilms are a direct result of EPS formation which contains molecules that possess surfactant or emulsifying properties (Grujić et al. 2017; El-Masry et al. 2004). The biosurfactant EPS isolated from *Vibrio* sp. emulsified the hydrocarbon hexadecane and xylene by reducing the surface tension between the two immiscible phases (Kharangate-Lad and Bhosle 2014).

In microbial cells, apart from special components produced by cells, many EPS produced by yeast, bacteria and fungi are bioemulsifiers in nature. *Halobacillus trueperi* has been reported to produce an EPS that possesses bioemulsifying properties with the hydrocarbon hexadecane (Kharangate-Lad and Bhosle 2015). This EPS bioemulsifier on characterization was found to be glycopeptide in nature. Bioemulsifiers efficiently emulsify two immiscible liquids and form stable emulsions at low concentration. Significantly, it is important to understand that though all biosurfactants bioemulsify all bioemulsifiers do not reduce surface tension. Therefore, it can be suggested that though all biosurfactants are bioemulsifiers, all bioemulsifiers are not biosurfactants.

Research has shown that efficient stabilization property of bioemulsifiers is a function of their chemical composition. It has been reported that in *Acinetobacter* sp. RAG-1 (Table 11.8), the utilization of alkane is dependent upon the presence of fimbriae. Microorganisms producing biosurfactants and bioemulsifiers that have potential applications in the field of bioremediation have been listed in Table 11.8. An alanine-containing bioemulsifier has been reported in *A. radioresistens* KA53. Alasan is a complex of alanine in association with polysaccharides and proteins. It is a secreted by the cell and remains cell bound and has the ability to emulsify a wide range of hydrocarbons such as long chains alkanes and aromatics, solubilization of polyaromatic hydrocarbons (PAHs) and paraffins and crude oils (Uzoigwe et al. 2015). *Acinetobacter* sp. also exhibited a bioemulsifier that was composed of 53% protein, 42% polysaccharide and only 2% lipid. Owing to the significant ability of this bioemulsifier to emulsify hydrocarbons and solvents, it showed potential for bioremediation studies. *Stenotrophomonas maltophilia* UCP 1601 showed production of bioemulsifier that had excellent dispersion capacity and formed stable oil in water emulsions. The EPS produced by *Halomonas eurihalina*, which was rich in uronic acid and was composed of smaller fractions of carbohydrates and protein components had significant ability to bioemulsify and detoxify hydrocarbons. Similar bioemulsifiers produced by *Klebsiella* sp. were seen to exhibit bioremediation potential.

Relatively a smaller number of filamentous fungi have been identified for the production of biosurfactants. These fungi include *Aspergillus niger, Cunninghamella echinulate, Fusarium* sp., *Penicillium chrysogenum* SNP5*, Rhizopus arrhizus* and *Trichoderma* sp. (Silva et al. 2018). Filamentous fungi are less extensively used in bioremediation due to their slow growth. However, they are excellent producers of biosurfactants and bioemulsifiers and promote dispersion of hydrophobic compounds that aids in bioavailability and biodegradation of these compounds (Table 11.8).

Mannoproteins are glycoproteins that are produced by the yeast in their cell walls. Mannoproteins of *Kluyveromyces marxianus, Saccharomyces cerevisiae* exhibit significant emulsifying properties. These mannoproteins could form stable emulsions with hydrocarbons, solvents and waste oil suggesting potential application in bioremediation. Other yeasts which have been reported for the production of biosurfactants are *Rhodotorula glutinis*, *Candida* sp., *Yarrowia lipolytica*,

Table 11.8 Biosurfactant and bioemulsifier producing microorganisms used in bioremediation processes

Microorganisms producing biosurfactants and bioemulsifiers used in bioremediation			
Microorganism	Biosurfactant/ bioemulsifiers	Pollutant	Reference
Bacteria			
Acinetobacter calcoaceticus BD4 13	Emulsan (polysaccharide-protein bioemulsifier)	Oil in water emulsion stabilization	Uzoigwe et al. 2015
Acinetobacter radioresistens KA53	Alanine (alanine-based glycoprotein bioemulsifier)	Oil in water emulsion stabilization	Uzoigwe et al. 2015
Acinetobacter sp. ATCC 31012 (RAG-1)	Emulsan (Glycolipopeptide bioemulsifier)	Insoluble toxic pollutants, heavy metals, hydrocarbon emulsification	Ron and Rosenberg 2001
Arthrobacter sp.	Trehalose, corynemycolates	*n*-alkane	Uzoigwe et al. 2015
Bacillus licheniformis	Lichenysin	Oil recovery	Uzoigwe et al. 2015
Bacillus subtilis K1	Lipoprotein Subtilisin	Oil recovery	Pathak and Keharia 2014
Halomonas eurihalina	Uronic acid rich glycopeptides	Emulsification and detoxification of hydrocarbons	Martínez-Checa et al. 2002
Klebsiella sp.	Uronic acid rich glycopeptides	Emulsification and detoxification of hydrocarbons	Uzoigwe et al. 2015
Nocardia farcinica BN26	Trehalose	Toxic pollutants	Uzoigwe et al. 2015
Pseudomonas aeruginosa DS10-129	Rhamnolipid	Toxic pollutants	Uzoigwe et al. 2015
Rhodococcus erythropolis	Trehalose	Dissolution of hydrocarbons (*n*-alkanes)	Uzoigwe et al. 2015
Rhodococcus sp.	Mycolates, corynemycolates	Oil recovery	Uzoigwe et al. 2015
Rhodococcus wratislaviensis BN38	Trehalose	Toxic pollutants	Tuleva et al. 2008
Fungi			
Aspergillus niger	Glycolipid	Hydrocarbon degradation	Silva et al. 2018
Aspergillus ustus	Glycolipoprotein	Hydrocarbon degradation	Silva et al. 2018
Cunninghamella echinulate	Carbohydrate-protein-lipid complex	Hydrocarbon degradation	Silva et al. 2018
Fusarium sp.	Trehalose	Hydrocarbon degradation	Silva et al. 2018

(continued)

Table 11.8 (continued)

Microorganisms producing biosurfactants and bioemulsifiers used in bioremediation			
Microorganism	Biosurfactant/ bioemulsifiers	Pollutant	Reference
Penicillium chrysogenum SNP5	Lipopeptide	Hydrocarbon degradation	Silva et al. 2018
Ustilago maydis	Glycolipid	Hydrocarbon degradation	Bhardwaj et al. 2013
Yeast			
Candida lipolytica	Lipopolysaccharide	*n*-alkane dissolution	Uzoigwe et al. 2015
Kluyveromyces marxianus	Mannoproteins	Hydrocarbon emulsification	Uzoigwe et al. 2015
Saccharomyces cerevisiae	Mannoproteins	Hydrocarbon emulsification	Uzoigwe et al. 2015
Torulopsis sp	Sophorolipids	Hydrocarbon emulsification	Uzoigwe et al. 2015
Algae			
Cyanobacteria	Trehalose dicorynomycolate, lipid based bioemulsifier	Hydrocarbon biodegradation	Alizadeh-Sani et al. 2018
Diatoms	Lipid based bioemulsifier	Hydrocarbon biodegradation	Alizadeh-Sani et al. 2018
Phormidium sp.	Lipid-protein-carbohydrate bioemulsifiers	Hydrocarbon biodegradation	Alizadeh-Sani et al. 2018

Pseudozyma rugosa, Trichosporon asahii, *Wickerhamomyces anomalus* and *Kurtzmanomyces* sp. (Bhardwaj et al. 2013; Silva et al. 2018).

A variety cyanobacteria belonging to *Oscillatoriales* produce bioemulsifiers. *Phormidium* sp. ATCC 39161 have been successfully used to yield hydrocarbon and oil emulsions in water. The bioemulsifier showed fractions of lipid, proteins and carbohydrates and showed significant stability of oil in water emulsions (Alizadeh-Sani et al. 2018). Marine algae and diatoms are increasingly being explored for their potential to produce bioemulsifiers. These bioemulsifiers are EPS based lipid bioemulsifiers that have potential application in bioremediation and industries.

11.13 Conclusion

Microbial bioremediation, although a cost effective and eco-friendly technique for biodegradation of recalcitrant toxic compounds, faces issues due to the biotic and abiotic factors affecting biodegradation. In the natural environment, constant fluctuations in oxygen, nutrient, pH and temperature occur that hinders and reduces the efficiency of microbial bioremediation. Despite these limitations the advantages outweigh the disadvantages and bioremediation using microbes and their components have been successfully implemented in cleanup of many toxic contaminants. Naturally occurring microbes and genetically designed microbes are important tools for successful cleanup of contaminated sites using green technology. However, considering the lacunae in the efficiency of microbial cell mediated bioremediation, integrated approaches involving microorganisms, nanoparticles and physical methods are now being explored.

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Microbial Scavenging of Heavy Metals Using Bioremediation Strategies

12

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Abstract

In the last years, increasing the population growth followed by an acceleration of the industrial process costs the quality of our ecosystem. Large waste quantities of industrial activities deposit risk concentrations of toxic materials like heavy metals. Heavy metal pollution has been distinguished as serious contaminants with worldwide risk since the industrial modern revolution. Environment depositions of these contaminants intimidate all the biological life forms for its high toxic characteristics. Chemical, physical, and mechanical strategies proved its low efficiency for its high energy needs, high costs, and even leave other secondary wastes to pass through the environment that raising another contaminant issue. Bioremediation through biological scavenging of heavy metals by microorganisms offers simple, low costs, low energy, and eco-friendly strategy for heavy metal elimination. Microorganisms developed extracellular (adsorption) and intracellular (accumulation) ways to bind metal ions through its viable or dead cells in a magnificent biosorption strategy. These strategies prop up as natural cell self-defense mechanisms for the elimination of the toxic effect of these hazardous materials. The whole bioremediation practicability affected by diverse factors such as microbial strain sensitivity, biomass concentricity, pH, surrounded temperature, and many else agents controls the metal ion bioavailability and the fast speed of the biosorption process.

Keywords

Bioremediation · Biodegradation · Heavy metals · Pollutants · Microbes

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12.1 Introduction

Metals stand as a significant constituent of our ecological system with concentrations and availability related to its cycling, through various ecosystems geological and biological processes (Ehrlich 2002). Heavy metals (HM) distinguished as metallic trait elements with 420 atomic number that exist through industrialization activities and urbanization with critical or toxic environment levels (Jing et al. 2007). It is present naturally as an intrinsic micronutrient for plentiful organisms involving plants, fungi, algae, yeast, bacteria, and animals unless its concentration exceeds specific level, these metals generate biochemical, physiological, and genotoxic thirties through all living forms (Emamverdian et al. 2015; Mahmoud et al. 2020a; Ibrahim and Mahmoud 2020).

Industrial revolution generates large quantities of contaminants which enter through the environment by accidents or even misusing the elimination protocols (Mahmoud and Bagy 2019). Throughout the last century, electroplating, smelting, tanneries, pesticides, fertilizer, electronic, paper, and petroleum manufactures exonerate large amounts of HM through our natural ecosystem each year, which disrupted the biological systems and its physiological functions (Arivalagan et al. 2014; Mahmoud et al. 2015a, 2015b; Taiwo et al. 2016). It impulse multiple health troubles that injury the human pancreas, lung, liver, kidney, causing also multiple functional disorders. These heavy metals could cause critical issues that reach to DNA damage (Kumar et al. 2017). Heavy metal contamination also occurs naturally by leaching it through atmospheric deposition, metal corrosion, groundwater, sediment, and water resources metal evaporation (Weerasundara et al. 2017; Francová et al. 2017). In soil they could precipitate through the layers and staying for many years, (Manafi et al. 2012), however in water environments they could settle in the bottom and accumulate in the deposits (Kang and So 2016).

Environmental common hazardous HM includes Lead (Pb), Aluminum (Al), Copper (Cu), Chromium (Cr), Nickel (Ni), Mercury (Hg), Arsenic (As), Zinc (Zn), and Cadmium (Cd) representing key pollutants in anthropogenic regions causing serious issues to various organisms and even humans (Islam et al. 2007; Dhanarani et al. 2016; Karthik et al. 2017). It enters the environment system via natural and/or anthropogenic practicability and deposited in water, soils, or even transmitted and present in the surrounded air (Chen et al. 2015; Kuppusamy et al. 2017). It can mobile through the aquatic ecosystems generating toxic effects to higher and smaller life forms, which prioritized them as major inorganic environmental contaminants (Khan et al. 2008). The sources of HM through human activities include the discharging of toxic level wastes from electroplating, mining, refining, metallurgical, and chemical industries, while HM releases by biological processes related to the geological weathering (Basta et al. 2004; Monteiro et al. 2009; Kumar et al. 2015b). Several physicochemical methods were established for HM abstraction as chemical reactions for precipitation, solvent extraction, ion exchange reactions, and oxidation reactions, however, all these frameworks required large operational charges, high levels of energy input, and spaced capital investment (Gupta and Rastogi 2008; Singh et al. 2018).

High concentrations of HM effects on the microbiota societies through two lines, metabolic function deactivation and genetic materials modulation (Yuan et al. 2015). Heavy metals caused distribution of the viable membranes of the cells (Karthik et al. 2016), ordinary cell division (Banfalvi 2011), cell enzyme activity (Khan et al. 2009), protein deformations (Banfalvi 2011), genetic material damaging (Sobol and Schiestl 2012) and even could deactivate all the transcription active process (Gundacker et al. 2010). Bioremediation processes could name as biosorption, biological biotransformation, biomineralization, and microbial bioaccumulation that carries through the microorganisms, however, phytoremediation is established by multiple plants in a metal-polluted environment (Arivalagan et al. 2014).

Bioremediation technology introduced affordable, applicable, economic, and low energy consuming ways for heavy metal remediation. Living and even non-living bacteria, algae, fungi, and yeast have proven high metals uptake and binding reflecting its potentiality for remediation of heavy metal pollutants from various ecosystem types (Shanab et al. 2012; Abdel-Ghani and El-Chaghaby 2014). Heavy metal affects on the biological life forms through inhibiting its enzyme activity, changing its protein conformations and even its nucleic acid. However, microorganisms developed various intracellular defense mechanisms assist them to reduce or cancel the heavy metal toxic effect (Haferburg and Kothe 2007), also established extracellular detoxify systems that prevents the entrance of heavy metals into the viable cells, while the intracellular system mechanisms protect only the intracell system from the chock of excess highly toxic metals entrance (Bellion et al. 2006).

Metal uptake included two stages, adsorption and cell bioaccumulation process by viable or dead microorganisms defined as biosorption process. First, metal ions adsorbed on the viable or non-viable cell surface for little time may be seconds or even minutes; then start to enter the cells slowly through its cell membrane and finally accumulated within the cell. Microbiota cell wall is responsible for the metal-binding through specific binding groups (Siddiquee et al. 2015). Adsorption process promoted by binding special groups like OH^-, PO_4^{3-}, SH^-, COO^-, NO_3^-, RO^-, etc. (PeralesVela et al. 2006). Bioaccumulation process restricted to the living cells, including metal ion transport through the cell membrane and binds to the cytoplasmic polysaccharides or proteins, or polyphosphate bodies, or cellular organs like vacuoles (Micheletti et al. 2008; De Philippis et al. 2011; Markou et al. 2015). The microbial responses towards HM through the bioremediation practicability rise from normal cell self-defense strategies in it which includes changes in the cell surface and cause cells agglomeration to eliminate the toxic impact of the heavy metals (Jacob et al. 2018).

12.2 Bioremediation Strategies of Heavy Metal Pollutants

Microorganisms assist in the mineralization of harmful elements completely into carbon dioxide (CO_2) and water (H_2O) or partially into less toxic compounds that could be utilized by other organisms until complete degradation. Bioremediation could perform also by the transformation of available toxic heavy metal into unavailable form which is known as metal detoxification (Ma et al. 2016). Different reactions of heavy metal bio-removing were conducted including immobilization, oxidation, binding, transformation, and even volatilizing the heavy metals (Verma and Kuila 2019). All these reactions depend on the existence or absence of oxygen (O_2); in aerobic biodegradation oxygen contributory as electron acceptor and the organic toxic pollutants oxidized by the reduction of the electron acceptors, however in anaerobic biodegradation microorganisms could utilize other organic compounds like ferrous (Fe^{+3}) or manganese (Mn^{+4}) as electron acceptor (e^{-}) (Lovley and Phillips 1988). Availability of alternative electron acceptors is critical for the anaerobic declination of pollutants (Spormann and Widdel 2000).

There are various techniques applied for HM bio-removal process. Bioremediation utilizes adsorption: this type concentrated on the extracellular substances associated with the microbial cell wall that will affects directly on the metal element adsorption process (Guine et al. 2006). These polymeric substances have high metal and binding capabilities towards heavy metals using the proton exchange in the microorganism's cell walls (Fang et al. 2010).

12.2.1 Bioremediation Using Bioaugmentation

Addition of specialized microorganisms (exogenous or indigenous insertion) in the site of pollution to eat the contaminant is called bioaugmentation. To upgrade the microbial growth good nutrients, air (for aerobic degradation), electron acceptors, and convenient organic substrates are required. This bioremediation method considered as effective, affordable, and highly fast remediation process treated the problem in its location and highly applicable in site managers (EPA 2006).

12.2.2 Bioremediation Using Biosorption

Biosorption means the adsorption of metal contaminant to a biological matrix by chemical interactions like ions and protons displacement, physical interactions with electrostatic forces, complexation, and chelation especially at neutral pH that the microbial surface will contain the anionic moieties which will work as binding sites for the cationic heavy metals (Fomina and Gadd 2014). Using biosorption practicability in heavy metal abstraction lean basically on the balanced between a biosorbent (microorganism) and sorbate (metal ions) (Das et al. 2008). Various natural microbial species and also engineered species were used in the biosorption process (Ueda 2016). The kinetics of the sorption practicability, utmost sorption capability, regeneration, bound metals elimination needed to analyze for estimation of the utilized microorganism stability as a biosorbent (Verma and Kuila 2019). Selected biosorbent should prepare by low costs, reusable, easy to separate from the pollutant solution (in the aquatic environment), and it must be fast removal (Bae et al. 2003). Aquatic heavy metal biosorption strategies include exo-polysaccharides production, using dead biomass for the cleaning or living cultures as biosorbent (Verma and Kuila 2019).

Despite all the previous advantages; biosorbtion encounters many challenges like pH dependence, ionic strength, and biosorbent that has specific lifespans especially with dead biomass which will degrade by the time with unavailable binding sites (Fomina and Gadd 2014). Contrast, the bioaccumulation way is a pushing metabolic operation that the microorganisms enter the heavy metals into membrane intracellular space with a translocation lane via the lipid bilayer. After that, the HM sequestered using various peptide and protein ligands (Mishra and Malik 2013; Diep et al. 2018).

Microorganisms could grow speedily giving high biomass yield which is very adequate to the remediation process of HM polluted areas (Aryal and Liakopoulou-Kyriakides 2015). For achieving high HM remediation high adsorption capacity is needed. This could be obtained naturally in the microbial biomass without pretreated; however, acid or alkali pretreatment raises the adsorption capacity. Throughout acid medication, the microbial growth is protonated with positive (+) charge density improving resulting in much more binding sites with high electrostatic force amidst microorganisms and HM with negatively charged (Yin et al. 2019). The addition of polyacrylic acid to *Corynebacterium glutamicum* raised cadmium Cd(II) removing by 3.2 times (Mao et al. 2013). Alkali treatment using sodium, ammonium and calcium hydroxides, and carbonates treatments also increases the negative charge microorganisms surface and augments the electrostatic force for positive (+) heavy metal. Khalil et al. (2016) reported that alkali medication raised the uranium (U) biosorption by mycotic mycelia than untreated samples. Yan and Viraraghavan (2000) reported that alkali treatment of *Mucor rouxii* biomass improved its adsorption efficient.

12.3 Bioremediation of Heavy Metals by Bacteria

Bacteria characterized by particular genetic mechanisms play roles in the mitigation of the environmental hazardous (Jacob et al. 2018). The functional binding sites of bacteria include carboxyl, sulfonate, hydroxyl, phosphonate, and amide groups that involved strictly to the metals uptake process (Huang and Liu 2013). Microbial responses to heavy metal as biosorbent materials generated as natural self-defense mechanism of the cell that includes changes through the cell morphology and physiology, for example, the wall of bacterial cells in Cr(VI) contaminated media appeared irregular to form clump/adherence while in normal medium appeared as smooth surface elongated cell wall (Jacob et al. 2018).

There are two mechanisms through bacterial cells by which the hazards of heavy metal pass to the bacterial cell; non-specific technique that works on energetic transport without ATP dependent that produces fast transportation HM directly through the bacterial growth. Latest mechanism is ATP-subordinate by the bacterial cells which made it the slower speed and highly substrate-dependent (Ahemad 2012). In bacteria, heavy metals accumulated in the cell wall chemical groups, peptidoglycan layer determines the bacterial metal-binding capability, Gram (+ve) positive bacteria found to aggregate higher HM concentrations on their walls than Gram (−ve) negative bacteria (Rani and Goel 2009). Extracellular polysaccharides participated in heavy metals accumulation depending on the bacterial species (Yee and Fein 2001).

Bacterial biomass proved its potentiality for the heavy metals uptake from various polluted sites or media (Table 12.1) especially *Streptomyces*, *Citrobacter*, *Pseudomonas*, and *Bacillus* species that utilize heavy metal by biosorption strategies and transfer these metals to their biomass matrix (Dhanarani et al. 2016). *Pseudomonas* and *Bacillus* sp. have been utilized widely in heavy removal from soils and wastewater sites for their richly metal ions attaching alliance (Ullah et al. 2015). Bacterial cell wall is taking charge of the metal-attaching process, for its anionic nature that enables it to attach the cations throughout the electrostatic energy (Siddiquee et al. 2015). Gram (+ve) positive contains rustic cell walls that contain teichoic, peptidoglycan biomolecules, and teichuronic acids, while Gram (−ve) negative bacteria contain thin peptidoglycan layer which assumed that other positive bacterial type are much dynamic in metal ions trapping technique (Karthik et al. 2017; Jacob et al. 2018).

Escherichia coli and *Bacillus idriensis* were utilized in arsenic (Ar) bioremediation (Singh et al. 2008; Liu et al. 2011). *Achromobacter* species, *Acidithiobacillus ferrooxidans*, *Arthrobacter viscosus*, *Bacillus cereus*, *Deinococcus radiodurans*, *Pseudomonas aeruginosa*, and *Staphylococcus epidermidis* used in mercury (Hg) bioremediation (Brim et al. 2000; Sasaki et al. 2005; Kiyono et al. 2009; Ng et al. 2009; Sinha et al. 2012; Yin et al. 2016; Hlihor et al. 2017; Quiton et al. 2018).

Bacillus coagulans, *Bacillus licheniformis*, *Bacillus megaterium*, *Desulfovibrio desulfuricans*, *Kocuria rhizophila*, and *Pantoea agglomerans*, utilized in chromium (Cr) bioremediation (Srinath et al. 2002; Zouboulis et al. 2004; Sikander et al. 2012; Kim et al. 2015; Haq et al. 2016). *Bacillus firmus*, *Desulfovibrio desulfuricans*, *Lactobacillus* sp., and *Micrococcus luteus* utilized in copper (Cu) bioremediation (Salehizadeh and Shojaosadati 2003; Schut et al. 2011; Puyen et al. 2012; Kim et al. 2015).

Alcaligenes sp., *Bacillus firmus*, *Bacillus subtilis*, *Enterobacter cloacae*, *Geobacillus thermocatenulatus*, *Pseudomonas fluorescens*, *Micrococcus luteus*, and *Staphylococcus saprophyticus* utilized in lead (Pb) bioremediation (Huang et al. 2001; Salehizadeh and Shojaosadati 2003; Bondarenko et al. 2008; Jencarova and Luptakova 2012; Samarth et al. 2012; Puyen et al. 2012; Kang et al. 2015; Jin et al. 2017).

Bacillus firmus, *Brevibacterium* sp., *Rhodobacter capsulatus*, *Pseudomonas putida*, *Streptomyces rimosus*, and *Thiobacillus ferrooxidans* utilized in zinc (Zn) bioremediation (Mameri et al. 1999; Taniguchi et al. 2000; Salehizadeh and Shojaosadati 2003; Chen et al. 2005; Nagashetti et al. 2013; Magnin et al. 2014). *Escherichia coli*, *Desulfovibrio desulfuricans*, *and Pseudomonas* sp. used in nickel (Ni) bioremediation (Liu et al. 2004; Sulaymon et al. 2012; Kim et al. 2015).

Table 12.1 Common bacteria utilized as heavy metal scavengers in bioremediation process

Biosorbent	Metals	References	Biosorbent	Metals	References
Escherichia coli	Arsenic (Ar)	Singh et al. (2008)	*Bacillus firmus*	Copper (Cu)	Salehizadeh and Shojaosadati (2003)
Bacillus idriensis	Arsenic (Ar)	Liu et al. (2011)	*Desulfovibrio desulfuricans*	Copper (Cu)	Kim et al. (2015)
Achromobacter sp.	Mercury (Hg)	Ng et al. (2009)	*Micrococcus luteus*	Copper (Cu)	Puyen et al. (2012)
Acidithiobacillus ferrooxidans	Mercury (Hg)	Sasaki et al. (2005)	*Lactobacillus* species	Copper	Schut et al. (2011)
Bacillus cereus	Mercury (Hg)	Sinha et al. (2012)	*Bacillus firmus*	Lead	Salehizadeh and Shojaosadati (2003)
Deinococcus radiodurans	Mercury (Hg)	Brim et al. (2000)	*Enterobacter cloacae*	Lead (Pb)	Kang et al. (2015)
Pseudomonas aeruginosa	Mercury (Hg)	Yin et al. (2016)	*Bacillus subtilis*	Lead (Pb)	Huang et al. (2001)
Pseudomonas sp.	Mercury (Hg)	Kiyono et al. (2009)	*Pseudomonas fluorescens*	Lead (Pb)	Bondarenko et al. (2008)
Arthrobacter viscosus	Mercury (Hg)	Hlihor et al. (2017)	*Geobacillus thermocatenulatus*	Lead (Pb)	Samarth et al. (2012)
Staphylococcus epidermidis	Mercury (Hg)	Quiton et al. (2018)	*Staphylococcus saprophyticus*	Lead (Pb)	Jencarova and Luptakova (2012)
Pantoea agglomerans	Chromium (Cr)	Sikander et al. (2012)	*Micrococcus luteus*	Lead (Pb)	Puyen et al. (2012)
Bacillus coagulans	Chromium (Cr)	Srinath et al. (2002)	*Alcaligenes* species	Lead	Jin et al. (2017)
Bacillus licheniformis	Chromium (Cr)	Zouboulis et al. (2004)	*Bacillus firmus*	Zinc	Salehizadeh and Shojaosadati (2003)
Desulfovibrio desulfuricans	Chromium (Cr)	Kim et al. (2015)	*Brevibacterium* sp.	Zinc (Zn)	Taniguchi et al. (2000)

(continued)

Table 12.1 (continued)

Biosorbent	Metals	References	Biosorbent	Metals	References
Kocuria rhizophila	Chromium (Cr)	Haq et al. (2016)	*Rhodobacter capsulatus*	Zinc (Zn)	Magnin et al. (2014)
Bacillus megaterium	Chromium (Cr)	Srinath et al. (2002)	*Pseudomonas putida*	Zinc	Chen et al. (2005)
Salmonella typhi	Cadmium (Cd)	Basha and Rajaganesh (2014)	*Thiobacillus ferrooxidans*	Zinc (Zn)	Nagashetti et al. (2013)
Bacillus cereus	Cadmium (Cd)	Huang et al. (2013)	*Streptomyces rimosus*	Zinc (Zn)	Mameri et al. (1999)
Ochrobactrum sp.	Cadmium (Cd)	Khadivinia et al. (2014)	*Desulfovibrio desulfuricans*	Nickel (Ni)	Kim et al. (2015)
Bacillus licheniformis	Cadmium (Cd)	Zouboulis et al. 2004	*Pseudomonas* sp.	Nickel (Ni)	Liu et al. (2004)
Pseudomonas putida	Cadmium (Cd)	Wu et al. (2006)	*Escherichia coli*	Nickel (Ni)	Sulaymon et al. (2012)
Enterobacter species	Cadmium	Lu et al. (2005)	*Pseudomonas* sp.	Cobalt (Co)	Nanda et al. (2011)
Kocuria rhizophila	Cadmium (Cd)	Haq et al. (2016)	*Bacillus licheniformis*	Ferrous (Fe)	Karakagh et al. (2012)
Mesorhizobium species	Cadmium	Sriprang et al. (2003)	*Pseudomonas* sp.	Arsenic (Ar)	Nanda et al. (2011)

Genetically modified bacterial strains upgraded their catabolic properties and used highly throughout the bioaugmentation practicability (Mrozik et al. 2011). Emenike et al. (2017) utilized bacteria consortium like *Lysinibacillus* species, *Bacillus* species, and *Rhodococcus* species in the bioaugmentation and concluded that reduced the HM concentrations with 88% in copper, 41% in cadmium, and 71% in lead. Fauziah et al. (2017) stated that the microbial consortium of *L. sphaericus*, *B. thuringiensis*, *and R. wratislaviensis* reduced nickel contamination with >50%. However bacterial biostimulation utilizes bacterial strains with providing suitable conditions to increase the bacterial resistant potentiality against toxic metals and ultimately enhance overall the bioremediation process (Atagana 2008), like addition nitrogen, phosphorus, oxygen, and carbon as nutrients to enhance the bacterial growth (Bundy et al. 2012).

12.4 Bioremediation of Heavy Metals by Fungi

Fungi are remarkable by their ability to live under elevated concentrations of toxic heavy metals pollutants that made it utilize as HM scaviours. Fungi used as heavy metal scavengers owing to their unique cell wall structure with high cell/surface ratio, which gives them a high tendency to contact these metals (Jacob et al. 2018). It detoxified heavy metal effects through transformation, precipitations, and uptake process (Thatoi et al. 2014). Chitin, polysaccharides, glucuronic acid, and phosphate in mycological cells performed critical part throughout bioremediation process of HM including ion exchange process (Purchase et al. 2009) also the working groups of carboxyl (COO^-), hydroxyl (OH^-), amine (NH_2), and phosphate (PO_4) action on the mycological removing capability of fungi to the heavy metals.

The acidic surface of *Termitomyces clypeatus* cells utilize chromium metals with the active groups assist of carboxyl (COO^-), phosphate (PO_4), imidazole ($C_3H_4N_2$), and hydroxyl (OH^-) (Ramrakhiani et al. 2011). The high content of carboxyl throughout the mycotic cell wall polysaccharides augments highly the HM biosorption operation (Raja et al. 2015). Owing to the lineal interaction by the cell wall and toxic HM; fungal morphology deformations observed in several fungal species (Mahmoud et al. 2020a). However, these heavy metals in very small concentrations could utilize as antifungal agents (Abdelhamid et al. 2020). Many fungal species used to remove various types of heavy metals included in Table 12.2.

Pleurotus platypus used in silver (Ag) bioremediation (Das et al. 2010); *Pleurotus sapidus* and *Rhizopus arrhizus* used in mercury (Hg) bioremediation (Tobin et al. 1984; Yalcinkaya et al. 2002); *Aspergillus niger*, *Aspergillus fumigatus*, *Ganoderma lucidum*, *Penicillium chrysogenum*, *Rhizopus arrhizus*, *Rhizopus nigricans*, and *Termitomyces clypeatus* utilized in chromium (Cr) bioremediation (Merrin et al. 1998; Sudha Bai and Abraham 2001; Muter et al. 2002; Dursun et al. 2003; Tan and Cheng 2003; Ramrakhiani et al. 2011; Mondal et al. 2017; Dhal and Pandey 2018). *Aspergillus niger*, *Aspergillus oryzae*, *Mucor rouxii*, *Pleurotus sapidus*, *and Trichoderma* sp. utilized in cadmium (Cd) bioremediation (Huang

Table 12.2 Common fungi and yeast utilized as heavy metal scavengers in bioremediation process

Biosorbent	Metals	References	Biosorbent	Metals	References
Pleurotus platypus	Silver (Ag)	Das et al. (2010)	*Aspergillus niger*	Copper (Cu)	Gunasekaran et al. (2003)
Pleurotus sapidus	Mercury (Hg)	Yalcinkaya et al. (2002)	*Rhizopus oryzae*	Copper (Cu)	Fu et al. (2012)
Rhizopus arrhizus	Mercury (Hg)	Tobin et al. (1984)	*Ganoderma lucidum*	Copper (Cu)	Muter et al. (2002)
Ganoderma lucidum	Chromium (Cr)	Muter et al. (2002)	*Lepiota hystrix*	Copper (Cu)	Kariuki et al. (2017)
Penicillium chrysogenum	Chromium (Cr)	Tan and Cheng (2003)	*Saccharomyces cerevisiae*	Copper (Cu)	Amirnia et al. (2015)
Aspergillus niger	Chromium (Cr)	Dursun et al. (2003), Mondal et al. (2017)	*Rhizopus arrhizus*	Copper (Cu)	Tobin et al. (1984)
Aspergillus fumigatus	Chromium (Cr)	Dhal and Pandey (2018)	*Penicillium citrinum*	Copper	Verma et al. (2013)
Rhizopus arrhizus	Chromium (Cr)	Merrin et al. (1998)	*Penicillium spinulosum*	Copper (Cu)	Townsley et al. (1986)
Rhizopus nigricans	Chromium (Cr)	Sudha Bai and Abraham (2001)	*Aspergillus niger*	Zinc (Zn)	Gunasekaran et al. (2003)
Termitomyces clypeatus	Chromium (Cr)	Ramrakhiani et al. (2011)	*Penicillium chrysogenum*	Zinc (Zn)	Fourest et al. (1994)
Pleurotus sapidus	Cadmium (Cd)	Yalcinkaya et al. (2002)	*Rhizopus arrhizus*	Zinc (Zn)	Tobin et al. (1984)
Trichoderma sp.	Cadmium (Cd)	Bazrafshan et al. (2016)	*Rhizopus nigricans*	Lead (Pb)	Volesky and Holan (1995)
Aspergillus niger	Cadmium (Cd)	Tsekova et al. (2010)	*Mucor rouxii*	Lead	Yan and Viraraghavan (2001)
Aspergillus oryzae	Cadmium (Cd)	Huang et al. (1988)	*Penicillium chrysogenum*	Lead (Pb)	Niu et al. (1993)

M. rouxii	Cadmium	Yan and Viraraghavan (2001)	*P. chrysogenum*	Nickel	Tan and Cheng (2003)
Ganoderma lucidum	Lead (Pb)	Muter et al. (2002)	*M. rouxii*	Nickel	Magyarosy et al. (2002)
A. niger	Lead	Dursun et al. (2003)	*M. rouxii*	Nickel	Yan and Viraraghavan (2001)
Lepiota hystrix	Lead (Pb)	Kariuki et al. (2017)	*Saccharomyces cerevisiae*	Manganese	Fadel et al. (2017)
Penicillium simplicissimum	Lead	Fan et al. (2008)	*Rhizopus arrhizus*	Manganese (Mn)	Tobin et al. (1984)

et al. 1988; Yan & Viraraghavan 2001; Yalcinkaya et al. 2002; Tsekova et al. 2010; Bazrafshan et al. 2016).

Aspergillus niger, *Ganoderma lucidum*, *Lepiota hystrix*, *Rhizopus nigricans*, *Mucor rouxii*, *Penicillium chrysogenum*, and *Penicillium simplicissimum* used in lead (Pb) bioremediation (Niu et al. 1993; Volesky and Holan 1995; Yan & Viraraghavan 2001; Muter et al. 2002; Dursun et al. 2003; Fan et al. 2008; Kariuki et al. 2017). *Aspergillus niger*, *Ganoderma lucidum*, *Lepiota hystrix*, *Rhizopus oryzae*, *Rhizopus arrhizus*, *Saccharomyces cerevisiae*, *Penicillium citrinum*, and *Penicillium spinulosum* utilized in copper (Cu) bioremediation (Tobin et al. 1984; Townsley et al. 1986; Muter et al. 2002; Gunasekaran et al. 2003; Fu et al. 2012; Verma et al. 2013; Amirnia et al. 2015; Kariuki et al. 2017). *Aspergillus niger*, *Penicillium chrysogenum*, and *Rhizopus arrhizus* used in zinc (Zn) bioremediation (Tobin et al. 1984; Fourest et al. 1994; Gunasekaran et al. 2003). *Mucor rouxii* and *Penicillium chrysogenum* used in nickel (Ni) bioremediation (Yan & Viraraghavan 2001; Magyarosy et al. 2002; Tan and Cheng 2003). *Saccharomyces cerevisiae* and *Rhizopus arrhizus* used in manganese (Mn) bioremediation (Tobin et al. 1984; Fadel et al. 2017).

Metal ion uptake using living fungal cells depends on the cell age, absorption time, pH level, temperature, etc. Biosorption of Cu, Cd, Zn, and Pb using living cells of *Penicillium*, *Aspergillus*, and *Rhizopus* takes from 1 to 4 h depending on all the previous conditions (Mullen et al. 1992). This process kinetics represented by a rapid initial phase that contributes up to 90% biosorption and takes about 10 min then the second slower phase lasts to about 4 h depending on the used fungal strain. Volesky and May (1995) stated that twelve hour old *Saccharomyces cerevisiae* was able to absorb heavy metals 2.6 times more than 24 h yeast cells.

12.5 Bioremediation of Heavy Metals by Algae

Algae are photosynthetic microorganisms found in various water types like freshwater, saltwater, and special water environments. Algae used in polluted water HM bioremediation and stated the capability of algae for HM utilization. Algae used various peptides as cell defense against heavy metal toxicity to protect the algae (Bilal et al. 2018). *Fucus vesiculosus* and *Cladophora fascicularis* were found as lead biosorbents (Deng et al. 2007; Demey et al. 2018). *Cystoseira crinitophylla* and *Sargassum* have been reported as copper Cu (II) biosorbent from water solutions (Christoforidis et al. 2015; Barquilha et al. 2017). *Desmodesmus* sp., *Sargassum fusiforme*, and *Saccharina japonica* utilized as copper (Cu^{+2}), cadmium (Cd^{+2}), nickel (Ni^{+2}), and zinc (Zn^{+2}) biosorbents (Rugnini et al. 2018; Poo et al. 2018).

12.6 Agents Affecting on HM Bioremediation

Bioremediation process represents a complex biological process affects by many control factors (biotic - abiotic) that impacts on the microbial expansion and the metabolic process. Microorganisms could decrease HM bioavailability through acids production, oxidation, reduction, and complexing agent's productions (Gadd 2010).

12.6.1 Biotic Factors

Biotic factors affect mainly the microbial growth, cell size, and the metabolite formations. Using the right biomass quantity represents one of the critical successful points of the biosorption processes. Biomass concentration affects significantly on the heavy metal removal, increasing the biomass quantities enhanced the metal ions absorption for the high availability of metal-binding sites, however very high concentrations have a reverse effect with lower heavy metal removal capacity due to the aggregation of biomass that leads to lower metal-binding sites availability (Monteiro et al. 2012). Biomass concentration represents an important biological factor; low biomass have high intercellular space and higher metal removal efficiency (Park and Choi 2002).

Romera et al. (2007) stated that the ultimate biosorption potentiality is established by the lowest microbial mass quantities. Many researchers stated that low biomass inoculums give high removal efficiency in *Saccharomyces cerevisiae*, *Pseudomonas aeruginosa*, and *Bacillus subtilis* (Fadel et al. 2017). Higher biomass concentrations restrict the interaction process to only the microbial superficial binding sites and generate the shell effect on the microbial cell surface (Romera et al. 2007; Abbas et al. 2014).

Higher biomass also diminishes the inside cell spaces bring in efficiently decreasing of metal hazard elimination (Fadel et al. 2017). Gong et al. (2005) reported decreasing in metal uptakes in high biomass concentration (20-40 g/l). However, at equilibrium levels, heavy metals adsorbed efficiently and also could enter the cells by the metal concentration gradient (Vasudevan et al. 2002).

12.6.2 Abiotic Factors

Abiotic factors related to the climatic conditions like temperature, humidity, wind speed, and physicochemical parameters like pH, oxygen, metal concentration, nutrient availability, and water content.

12.6.2.1 Temperature

Temperature affects on almost all rates of the chemical reaction, a higher temperature much favors for the high metal ions solubility which decreased the metal ions microbial sorption process (Lau et al. 1999). Optimum temperature for the microbial biosorption varies by the kind of metal ion and the microbial biosorbent species (Gupta et al. 2010). Temperature higher than optimum levels decreased the bioremediation process by inducing modifications in the protein synthesis however lower temperatures decreased the membrane fluidity and the transport systems (de Groot and Ventura 2006).

In algae as biosorbent, Gupta and Rastogi (2008) stated that cadmium adsorption through *Oedogonium* sp. was decreased at elevated temperatures. In bacteria as biosorbent, *Acinetobacter* species (Panda and Sarkar 2012), *E. aerogenes* (Fu et al. 2012), *B. cereus* (Naik et al. 2012), and *Rhizobium* species (Karthik et al. 2016) revealed maximum heavy metal bioremediation efficiency in mesophilic conditions. In fungi as biosorbent, *A. niger* (Gu et al. 2015) and *R. oryzae* (Fu et al. 2012) showed high remediation of heavy metal also in mesophilic conditions.

12.6.2.2 pH

Many studies revealed that the biosorption of HM ions is correlated to the surrounding pH that affects on metal solubility and toxicity especially in water environment (Brinza et al. 2007). pH has the potency to vary the microbial biomass, metal chemistry complexation, enzyme effectiveness, and manner of functional groups in the cell outer surface (Gupta and Rastogi 2008). pH affects the toxicity availability degree of these metals through the water ecosystem affecting in the chemistry of water and the water microbial ecosystem (Brinza et al. 2007).

Acidic pH alters the characteristics of surface functional groups and their interaction with metal ions (Jacob et al. 2018). Alkaline pH conditions generated hydroxo-metal complexes and increase the microbial logarithmic phase which reduces the bioremediation process (Govarthanan et al. 2016). In bacteria as biosorbent, like *Bacillus* species (Naik et al. 2012), *Escherichia coli* (Samuel et al. 2012), *M. luteus* (Puyen et al. 2012), and *P. aeruginosa* (Oves et al. 2013) the bioremediation efficiently was the highest in neutral pH range.

Fungi like *Pleurotus* species (Das et al. 2010) and *Trichoderma* species (Mohsenzadeh and Shahrokhi 2014) prefer a neutral pH range. For algae as microbial sorbent, since the preponderance of metal ion attaching sites is acidic (especially carboxyl) the biosorbent process regarded as pH-dependent (Han et al. 2006). Optimal pH for Cesium, Cu, Cr, and Cd biosorption by *Durvillaea potatorum*, *Padina* sp., *Sargassum* sp., *Padina australis* was pH 2 and even lower (Yu et al. 2000; Jalali et al. 2004). For uranium accumulation by *C. vulgaris* was pH 3–6 (Gunther et al. 2008), Cr accumulation by *C. miniata* was pH 3–4.5 (Han et al. 2006).

12.6.2.3 Metal Ion Concentration

Lower levels of heavy metals could involve directly in various metabolic processes of the microorganisms, however, by elevated the levels it starts to affect on the growth and physiological process of the microorganisms even with biosorption ability (Singh et al. 2010). Metal ion concentration affects on the biosorbent microorganisms highly as each microorganism has specific bioremediation rate. *Aspergillus niger* eliminates copper 15.6 mg/g after 1 h (Dursun et al. (2003), however, *Micrococcus luteus* eliminates 408 mg/g by 12 h (Puyen et al. 2012), and *Desulfovibrio desulfuricans* eliminates only 98.2 mg/g by 168 h (Kim et al. 2015).

Fusarium chlamydosporum, *Fusarium solani*, *and Aspergillus niger* were highly affected by copper present in the medium than *Alternaria alternata* and *Trichoderma harzianum* (Ibrahim and Mahmoud 2019). Also, by increasing cadmium concentration to high levels growth inhibition and morphological disturbances cleared in *Cladosporium cladosporioides*, *Fusarium oxysporum* and *F. solani* (Ibrahim et al. 2020). High heavy metal toxicity induced various physiological changes in microorganisms, e.g. biomass reduction, cellular functions disturbance, and microbial enzyme inhibition (Oves et al. 2016). Much heavy metal intensity react via microbial viable membrane resulting irreversible unstoppable membrane destruction, enter the cytoplasm, and disrupt the enzymes and could cause genetic modifications (Fashola et al. 2016).

12.6.2.4 Nutrients and Oxygen Availability

Nutrients or oxygen availability related directly to the bioremediation site and the microbial bioremediation requirements. Good microbial growth needs carbon, nitrogen, and phosphorus that are directly involved through the microbial metabolism and reflected on the growth for both fungi and bacteria. The previous three components involved in organic compounds, protein, ATP, and nucleic acid biosynthesis (Xu et al. 2015; Mohamed and Mahmoud 2018) and found in almost all growth media of bacteria, yeast, and fungi (Mahmoud et al. 2019; Abdel-Hakeem et al. 2019). Optimum carbon and nitrogen sources will affect straightly through the whole microbial growth (Nafady et al. 2015; Mahmoud et al. 2020b) which will reflect on the metal removal efficiency (Venil et al. 2011). Preponderance of microbial scavengers needs oxygen for the bioremediation process as they grow aerobically and it is used in energy yielding (Jacob et al. 2018).

12.7 Harmful Effect of Heavy Metals

Heavy metals have different effects on various life forms related to its concentration in the environment. Heavy metals even in low concentrations affect badly in human health and lead to serious disease that could end by human death. Heavy metal toxicity could lessing the human rational, nervous actions, and harmful the lungs, skin, liver, pancreatic, and kidneys (Vardhan et al. 2019). Plants uptake necessary minerals from soil using the expanded root; these minerals classified as essential nutrients and non-essential nutrients, also the essential nutrients classified as macronutrients as nitrogen, potassium, phosphorus, silicon, calcium, sulfur, magnesium and micronutrients needed in tiny amounts as sodium, nickel, chlorine, molybdenum, manganese, boron, zinc, copper, and iron (Xun et al. 2018). Micronutrients as Ni, Zn, and Cu required to plant metabolism only with very small amounts, however, other micronutrients even in low concentrations are toxic to plants, e.g. mercury, chromium, cadmium, lead, and silver (Muszynska et al. 2018). High HM concentrations incorporated with plant chlorosis, leaf rolling, senescence, low biomass, shriveling, and low seeds quantities (Shahid et al. 2017; Shi et al. 2018). Higher lead concentration throughout the soil generated plants with irregular morphology (Kushwaha et al. 2018). Higher nickel concentration results in nutrient imbalances and cell membrane scatters of its capacities (Mendez et al. 2014). Chromium affects on the plants photosynthesis process and enzyme activities resulting of putrefaction and shrinking of leaves (Kumar et al. 2015a; Kumari et al. 2018). The effects of heavy metals on microorganisms depend on the microorganism sensitivity and the metal concentration. According to Ibrahim et al. (2020) and Mahmoud et al. (2020a) elevated concentration of cadmium caused microbial growth inhibition with various degrees depending on the microbial strain and morphological deformation in mycelia, phialid, conidia and also cause speeding in chlamydospores formation which reflect the huge stress of cadmium heavy metal on the microbial cells. Copper also showed inhibition effects on several phytopathogenic fungi especially in high concentrations with cellulase enzyme inhibition (Ibrahim and Mahmoud 2019).

12.8 Conclusion

Heavy metal violation turns out as one of the prime pollution affair that threatens human, biological and animal lives. This problem arises from industrial speeding with low safety procedures for wastes disposal. Many heavy metal remediation techniques have been used, however, bioremediation listed as the low cost and safest remediation strategy. Microbial scavenging of heavy metals is characterized as low energy, low cost, speedy, and eco-friendly technique having potential for application in large contaminated sites. Microbial scavenge requires efficient microbiome as bacteria, yeast, cyanobacteria, fungi, and algae with efficient biomass and powerful activity to degrade, or absorb, or adsorb, or convert heavy metal from hazard toxic forms into almost un-harmful forms. Success of these technique focuses mainly on picking the right scavenger microbe as per the contaminated site chemicals, the prevailing environmental conditions. Providing the required optimum growth conditions for microorganisms in the contaminated sites will increase HM degradation process with less harmful effects on the environment.

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Plant–Microbe Interaction in Attenuation of Toxic Wastes in Ecosystem

13

Kingsley Erhons Enerijiofi and Beckley Ikhajiagbe

Abstract

The use of plant–microbial interactions in mitigating the effect of toxic waste in the environment has increased tremendously as a result of the high success rate. This could be attributed to various survival mechanisms of plants–microbes in contaminated environment. However, important factors such as plants ability to produce biomass, active root proliferation and/or root activities with root symbiosis establishment and others determine the efficacy of phytoremediation technology which has proved to be effective. More rapidly growing plants with high phytoextraction abilities should be identified for the remediation of pollutants from soil. Plant–microbial interactions are very crucial for the sustenance of environmental sustainability through toxic waste attenuation.

Keywords

Bioremediation · Ecosystem · Plant · Microbes · Toxic wastes

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13.1 Introduction

Higher Plants live together with other biotic and abiotic components of the environment, thereby participating in a number of relationships. This is so as they cannot live in complete isolation from each other. The biotic components are the living forms of life which include microorganisms and higher animals, while the abiotic are the non-living things made up of the physical, chemical, and cultural features (Enerijiofi 2014). However, the interactions between plants, microorganisms, and other environmental constituents are quintessential for continuous survival of plants on earth as well as balance of the environment.

13.2 Plant Interaction with Soil

The interaction between plants and soil occurs in the region known as rhizosphere. However, Hiltner (1904) was first to draw attention to the scientific domain of the word rhizosphere which involves the promotion of microbial growth round the roots of leguminous plants. There exist different meanings of rhizosphere (Marschner 1995; Uren 2001). Uren (2001) defined rhizosphere as the interface between the soil and plant root which is characterized by lots of mineral nutrients, pH, redox processes, root exudates as well as lots of microorganisms which results from increased activities of microorganisms. The rhizosphere region of plants is made up of two regions; ectorhizosphere and endorhizosphere. The ectorhizosphere is the layer of soil that immediately surrounds the roots of plants while in the endorhizosphere, microorganisms colonize the internal tissues of the root. The health of soil determines the health of plant as well as humans, due largely to the dependence on its products for survival (Enerijiofi 2014). Mycorrhizae perhaps encompass the best conspicuous and nearby forms of mutualistic plant–fungal relationships (Fester et al. 2014).

13.3 Plant Interaction with Microbes

Though plant–microbial interactions are not visible to the human eye, they interact at different facets and levels. Almost, all plant organs undergo interactions with microbes at one phase or the other in their life and it is not essentially a harmful one for the plant. Plants as well as other living and non-living components make up a great chunk of diverse environments for microorganisms. The specific environments may include noxious combinations of compounds in which there may be inadequate supply of nutrients which are important in supporting the growth of microorganisms (Fester et al. 2014). The various classes of microbes like the prokaryotes and eukaryotes undergo interactions with plants and sustain their wellbeing in a variety of ways. These include enhancement of the growth of plant and harvest, control of diseases, ability to survive and recover from hostile ecological disorders such as lack of water, etc. (Adesemoye et al. 2009; Reid and Greene 2012).

They are associated with millions of other microbes. The functions of the aforementioned plant-associated microorganisms are still under investigation, though they are known to support plants which enable them withstand the abiotic and biotic stresses, thereby aiding the host in water and assimilation of other nutrients as well as the production of plant hormones, siderophores and inhibitory allelochemicals (Weyens et al. 2009a, b; Bulgarelli et al. 2013). However, under extreme contamination conditions, plants have a resilient influence on the microbial communities of soil and they are regularly in control of the building and power-driven firmness of a given system. Though in real situations, plants in association with microorganisms always seem to be the actual actors intervening the impact of plant on the transformation of contaminants (Ingham et al. 2011).

13.4 Positive Interactions Between Plant and Microbes in Soil

Series of microbes are famous in the colonization of the rhizosphere area. Though, members of the *Streptomyces* species are distinctive in a range of ways. Their pattern of growth is filamentous, colonise soil as well as plant roots and its aerial parts, dynamically yield antibiotics and save plants from attack by disease causing bacteria species, production of unsound biological compounds that are accountable for the exceptional bouquet of new forest soils. They could also be utilized as natural control mediators in numerous agrarian practices. The actual ingenious *Streptomyces* species are made use of as biofertilizer in improving the growth of plants due to their intrinsic growth-promoting proficiencies. Their ability to form endospore gives them comparative advantage in extant severe soil situations contrary to the non-spore formers in the soil. Also, *Streptomyces* species possess innate capability to produce diverse forms of lytic enzymes which provides them the ability to break caked organic mixtures which secrete nutrients that can be used by plants (Vurukonda et al. 2018). Plant growth-promoting bacteria (PGPB) can similarly be utilized in the reduction of heavy metal polluted soils. *Helianthus tuberosus* is rich in biomass and used in the production of bio-ethanol. However, when it is exposed to a specific PGPB that is secluded from plants on heavy metal polluted soil, its ability to withstand high concentrations of heavy metals increases. The bacteria were revealed to grow endophytically in the root ensuing substantial upsurge in cadmium absorption by the plant. More so, the plant exhibited a reduction of metal-induced pressure and an enhanced growth in the presence of bacteria. Thus, these PGPB can aid in remediation and in sustainable biomass production (Montalbán et al. 2017).

Perennial ryegrass, *Lolium perenne* is an essential cool-season grass specie for fallow, silage and turf with a high yield has increased harvest and upright grass excellence as well as a compact system of root, greater tillering and fast capability to regenerate itself can easily withstand drought or to high salt concentration but PGPB are known to fully support its forbearance to dearth of water and high salinity (Su et al. 2017; He et al. 2018). Su et al. (2017) opined that valuable bacterium in soil like *Bacillus amyloliquefaciens* GB03 in a relationship with water absorbent mediator which consist in super permeable hydrogels can be used for controlling erosion in soil thereby significantly improving the ability of perennial ryegrass to withstand drought conditions. This holds true when linked to tender single components that previously were considered to improve the ability of the plant to resist drought relative to the control. In the same distinguishing method, an innovative isolated bacterium from a C4 persistent juicy xerohalophyte tree with exceptional ability to stand long absence of water and high salt concentration was made use to meaningfully enhance development and salinity forbearance of the perennial ryegrass. In addition, is the sequencing of the bacterial genome and identification of several genes supposedly associated with promoting traits during plant growth and decreasing of abiotic stress (He et al. 2018). PGPB can support the ability to withstand drought and high salinity.

Zhang et al. (2018) studied the affirmative role of *Rhizophagus irregularis* CD1 fungus as it affect growth and proliferation of plant and the Verticillium wilt resistance of cotton. They were able to study the synergistic proficiency of 17 cotton varieties to *R. irregularis* with the most efficient being Lumian 1 which was utilized in field trial for 2 years. Nevertheless, the existence of the mycorrhizal fungus considerably amplified growth of the plant and also ability to withstand plant malady against *Verticillium dahliae* wilt. However, the negative impact on *V. dahliae* presence possibly will be as a result of mycorrhiza-induced resistance which revealed that the growth of *R. irregularis* may proportionately prevent the growth of *V. dahliae* by letting loose as yet anonymous volatiles. Consequently, microbes are utilized to absolutely alter the growth abilities of plants in order to put them at a vantage position to be able to stand against biotic and abiotic pressures like lack of water and high salinity which might probably take place far more frequently with increasingly abating change in climatic conditions.

13.5 Plant–Microbial Interaction—An Overview

Plants have just lately been known as a metaorganism with a distinct microbiome and adjacent synergistic interactions with closely related microbes (Mendes et al. 2013). They are shielded by microorganisms with some pathogens while others display a helpful effect on plant growth and development. Hitherto, a few abound merely with no clear cut function in studies of microbial ecology. The plant roots are confined by a dense cover of microorganisms in the rhizosoil. Also, plant seeds are linked with the microorganisms and are famous for having intense effect on development of plant, since they are available all through seed germination which could also have a rich outcome on the ecosystem, wellbeing, and yield of plants. The microbiome of seed consists in endophytic and exophytic (Hawkins and Crawford 2018). Microorganisms are known to be powerfully effective in motivating series of important roles in soil ecosystem (Enerijiofi 2020). Microorganisms are relevant building blocks in the recycling of major nutrients and are associated with plant roots for fruitful nutrients supply as well as reducing the effect of pathogens, thereby giving support particularly for plant and animal health and generally for life on planet earth. The exceptional act and natural ingenuity of microorganisms particularly round the growing root of plants give credibility to the series of possible valuable microbes for the growth experienced in biotechnological field. This is relevant in improving crop yield, pathogens of plants, controlling of weeds, and more feasible methods of cleaning up polluted soils. This benign and extensive use of microorganisms has lots of prowess for making chemical methods extinct. This is found to be the relevance and its profound constituent of soils. Microorganisms are also used as soil quality indicators and in good working of the ecosystem (Enerijiofi 2020; Sherwood and Uphoff 2000).

13.6 Factors Affecting Interactions

Plant–microbial inter-relationship is implicated in the degradation of bulky quantities of contaminated waste arising from their possession of genetic metabolic machinery and their capability to withstand punitive environments. Consequently, they are a main actor in the cleanup of sites polluted with toxic wastes. Nevertheless, their potential to perform is reliant on various factors, though not limited to contaminant concentration and its chemical constituents, ability of plant–microbe interaction, and physicochemical characteristics of the location (Joutey et al. 2013). So, dynamics that affects the level of contaminants breakdown by interaction between plant and microbes is linked to plant–microbe and their nutritive supplies or related with the surrounding factors (Joutey et al. 2013).

13.6.1 Soil Factors

One of the chief ecological duties carried out by soil is filtration, others are buffering and transformation of contaminants of either organic or inorganic pollutants. This very important role guarantees worthy quality of underground water and safe production of food. When contaminants find their way to soil, they undergo series of reactions such as physicochemical, microbiological, and biochemical processes that keep, diminish, or lower their destructive capabilities. Essential characteristics of soil that affect the behaviour of pollutants encompass soil texture, quantity of soil organic matter, pH, levels of moisture, and temperature. The characteristics of soil pollutants besides are important. These include size, solubility, charge distribution, and molecular structure.

13.6.2 Plant Factors

Soils play host to series of minute forms of life. These include all classes of microorganisms viz-a-viz bacteria, fungi, nematodes, viruses, etc. The rhizosphere region, where the root of plants interacts with soil is known to contain the highest quantity of bacteria species (Ho et al. 2017). Nevertheless, the diversity of soil bacteria affects soils in any of the three means. The inter-relationship existing between soil bacteria and soil may be helpful, detrimental, or unbiased (Weyens et al. 2009a, b). The PGPB include the free living, those with explicit harmonious inter-relationships with plants, e.g. *Cyanobacteria*. PGPB can support the growth of plant openly by empowering the capacity to have a hold on controlling the levels of plant hormone and secondarily by decreasing the resistance impact of pathogenicity and plant growth by standing in as proxies of biocontrol (Glick 2012).

13.6.3 Climate Factor

The change in global climatic condition is linked with lots of factors including increase in atmospheric temperature and high concentration of carbon (iv) oxide (Srivastava et al. 2014). The community of microbes in soil environment is known to play important function in cycling of carbon as microorganisms have enlarged potential to degrade organic matter in soil at high carbon (iv) oxide and nutrient concentration which are primarily affected by biotic and abiotic factors. There are no proof that can be traced to the influence of change in climatic condition on bioremediation except the physicochemical parameters which have influence on the metabolic process of the microbial community thereby affecting bioremediation (Sowerby et al. 2005; Castro et al. 2010; Srivastava et al. 2014). The extracellular enzymes production by microorganisms could be attributed to the microbial activities and physicochemical characteristics of the soil environment which are affected by the climatic conditions (Sowerby et al. 2005; Enerijiofi 2020). A study reported that an increase in temperature arising from change in climatic conditions positively boosts the community of microorganisms to properly utilize recalcitrant compounds in soil (Bardgett et al. 2008; Frey et al. 2013). Also, increase in the concentration of carbon (iv) oxide is directly proportionate to the bacterial richness and indirectly proportionate to the fungal richness (Frey et al. 2008; Castro et al. 2010). The reduction in fungal biomass at elevated temperature and during dry seasons is responsible for the reduction in the fungal/bacterial biomass ratio in soil (Sowerby et al. 2005). This showed reduced degree of organic matter recycling in the environment which in addition distorts the normal course of degradation by indigenous microorganisms that are skilled at cometabolic reaction in breaking down precarious compounds made possible by the availability of natural carbon. Baldrian et al. (2013) predicted that metabolic activities of microbes rise significantly if the temperature of soil increases arising from change in global climatic conditions.

13.6.4 Microbial Factors

The catabolic and anabolic abilities of microorganisms are referred to as microbial factor. The biotic factors influencing microorganism destructive activities of biological combinations have uninterrupted hindrance to enzymatic activities and multiplication routes of microbes involved in the degradation process. For example, inhibition can take place when there is struggle between microbes for limited resources like carbon, hostile inter-relationships between microbes, or the predation of microbes by bacteriophages and protozoa (Riser-Roberts 1998). The extent of breakdown of precarious waste is mainly due to the quantity of the toxic material as well as the catalytic agent that is available for the process to take place. In furtherance of the aforementioned, the extent to which the toxic waste is degraded is mostly due to the capability of the specific enzymes implicated, affinity for the toxic waste as well as the degree of the bioavailable fractions (Enerijiofi 2020). Also, adequate quantities of oxygen and nutrients should be present in readily available form as well as in precise amounts as this support the substantial growth and multiplication of microorganisms (Riser-Roberts 1998).

13.6.5 Environmental Factors

The soil type and the concentration of organic matter play important function in the capability of the noxious waste to adsorb to the compact surface of the soil. In absorption which is a corresponding procedure, toxic waste infiltrates into the major mass of the soil medium. However, both adsorption and absorption reduce the accessibility of the toxic waste to a greater chuck of plant and microbes interactions at the rhizosphere region and the degree of element absorbed is directly condensed. In the soil matrix, the ability of passing on gases like oxygen, carbon (iv) oxide, and methane is reduced in finely coarse soils and sediments and also when soils are water logged which arises from poor porosity. They also affect plant and microbial growth which regulates the degree and kind of biodegradation that occurs. The reduction–oxidation prowess of a soil is the ability of its electron compactness of the system. Energy is gained through the breakdown of compounds in which electrons are conveyed from one oxidized compound to another during electron transport chain known as electron acceptors. A low electron mass with Eh $>$ 50 mV specifies breaking down and aerobic situations, while high electron mass (Eh $<$ 50 mV) points to reduction and anaerobic conditions. Series of other additional environmental factors that affect biodegradation rate of toxic waste are temperature, pH, and moisture. Biological enzymes that have an important function in degradation pathway need an optimum temperature for best performance, below or above the optimum temperature is a proportionate degradation metabolic rate (van der Heul 2009). According to Riser-Roberts (1998), the degree of breaking down declines approximately by 50% for each 10 °C diminution in temperature. In terms of pH, breakdown takes place in a wide range, but, a pH range of 6.5–8.5 is mostly best for biodegradation process in most terrestrial and aquatic environments. The water content performs a very important function in the metabolism of toxic waste in the ecosystem because it regulates the solubility, type, and amount of decipherable materials as well as the growth of the microorganisms that partake in the process, osmotic pressure as well as pH of both aquatic and terrestrial ecosystem (Cases and de Lorenzo 2005).

13.6.6 Biological Factors

These are only noticeable when bioremediation techniques are being implemented. However, there exist many intrinsic characteristics of microorganisms that perform roles in the degradation of substrate. Example is plasmid-encoded genes that make available the exact enzyme for the specific substrates but, naturally, it has been known that microorganisms mostly bacteria have different specificity for diverse nutrients (Mars et al. 1997). The control of chemotaxis by bacterial cells places them at a vantage position to be able to degrade obstinate biological molecules (Pandey and Jain 2002). It is worthy to note that the use of single isolate is not as active as microbial communities in accomplishing comprehensive degradation of xenobiotic compounds. The microbial communities required for bioremediation is mostly reliant on complex interactions. Maphosa et al. (2010) posited that metagenomics which encompasses genome sequencing aid in making data available regarding the species of microorganisms that contribute to substrate degradation. More so, the peak of microbial growth conditions cannot be determined (Ingham et al. 2007). Microbes are important in ensuring proficiency in the working of ecologies on earth and issues influencing growth, development, arrangement, and richness of microorganisms and microbial populations may perturb the biomes (Nweke et al. 2007). Chakraborty et al. (2012) posited that Allelopathic response of plants in the terrestrial environment on the community of microorganisms may affect the degradative abilities of soil microorganisms negatively. Aerobic degradative actions of microbes are restricted by organic carbon solubility and lack of oxygen. However, certain microorganisms can utilize supplementary sources of biological carbon, electron acceptor, and energy as cometabolic substrates in so doing degrading the recalcitrants compounds, e.g. *Mycobacterium gilvum* can breakdown pyrene in the presence of oxygen in the rhizosphere of *Phragmites australis* concurrently with the breakdown of benzo(a)pyrene (Toyama et al. 2011). Pandey and Jain (2002) opined that injurious pressure applied by toxics on microorganisms quickly modifies their enzymes which play vital function in microbial degradation of refractory compounds.

13.7 Microbial Diversity Implicated in Plant Interactions

A lot of studies have documented a number of microorganisms that are implicated in plant–microbe interactions (Montesinos et al. 2002; Garbeva et al. 2004; Vimal et al. 2017). Microbes found in soil are important in the preservation of soil role in both regular and succeeded agrarian soils arising from their involvement in significant practices like soil structure formation, decomposition of organic compounds, toxins elimination, and recycling of nutrients like carbon, etc. (van Elsas and Trevors 1997). Also, microbes perform important function in subduing soil borne diseases of plant, encouraging plant growth and fluctuations in flora.

Though microbiologists had studied the influence of different microorganisms on the firmness of environment role since the 1960s, Harrison et al. (1968) stated that there is now intensified attention of its influence on functioning and resilience of the ecology to turbulences in soil ecosystems. Microorganisms have established quite a number of approaches to ensure successful acclimatization to the environment of the plant, together with helpful or harmful interrelationships. Valuable interrelationships are triggered by synergetic or non-synergetic bacteria and by a very specific kind of fungi, the mycorrhizae. The harmful interrelationships of microorganisms with plants comprise different microbial types with contagious diseases upsetting the kingdom Plantae. In agricultural soils, perhaps 80% of the nitrogen fixed biologically originates from an extensive variety of soil bacteria like the *Rhizobium*, *Sinorhizobium*, and *Allorhizobium* of the family Rhizobiaceae in relationship with leguminous root of plants (Vimal et al. 2017). These endophytes generally invade the root structures of leguminous plants giving rise to nodules thereby stimulating the growth of plants unswervingly or incidentally (Zimmer et al. 2016).

The genetic basis of plant–microbial interaction is sturdily clarified by the gene-for-gene elicitor-receptor model. On this premise, numerous investigations have utilized plant pathogenic bacteria of the genera *Pseudomonas* and *Xanthomonas*. A group of genes have been rapt comprising of the hypersensitivity reaction (HR) and pathogenicity (hrp) which impact the limit of bacteria to create HR in non-host plants (Montesinos et al. 2002). Majority of plants are not proficient in gathering enough biomass for obvious steps of remediation within the sight of high degree of contaminants (Harvey et al. 2009; Chakraborty et al. 2005). The cleanup route of polluted ecosystem is restricted and delayed due to inadequate nutrient level. Soil microorganisms are assumed to exercise affirmative influence on the wellbeing of plant through mutualistic associations between them. Conversely, microorganisms are subtle to contamination and reduction in their population through the types as well as biomass which regularly take place in such polluted soils (Shi et al. 2002). A stress in the biotic or abiotic conditions through a little change in the physicochemical and natural characteristics of rhizospheric soils may prompt exceptional impact on plant–microbial interaction. The utilization of Plant growth-promoting microorganisms as inocula in rhizosphere is gaining more ground as its prospects is on the increase in phytoremediation process; though, it partially subject to the capacity of the plant to withstand the toxic nature of the metal and give adequate harvest. The exudates at the plant roots are utilized by microbes in the rhizosphere region as nutrients for growth and subsequent multiplication. It is projected that the amount of the remaining photosynthetic carbon transported to plant roots varies amid 30–60% and 10–20% of root requirements originates from rhizodeposition (Marschner 1995; Salt et al. 1998). The exudates are basically made up of low as well as high molecular weight organic acids. Their total amount determined in plant roots falls within the range of 10–20 mM, by and large consisting of acetate, lactate, succinate, oxalate, fumarate, malate and aconitate while the remainder of biological solutes in roots are sugars (90 mM) and amino acids (10–20 mM) (Jones 1998).

Bioremediation is the practice of eliminating environmental pollutants utilizing living organisms which are mostly microbes. This is one of the most reliable methods for cleanup and restoration of polluted ecosystems. The frequent use of some plants for cleanup of precarious toxins in the ecosystem in a recently developed method is known as phytoremediation. They are known as hyperaccumulators which grow optimally in heavy metals rich soil. Alkorta and Garbisu (2001) have reported phytoremediation to be real, in situ, artistically attractive, reduced effort socially acknowledged technique for the cleanup of contaminated soil. These cleanup may be through phytostabilization, rhizofiltration, phytoextraction, and phytovolatilization. It is not only cleanup of the ecosystem contaminations but plant–microbe inter-relationship also adds to viable improvement of agriculture. These days, there exist a major issue in production of crops with decreased utilization of pesticides and inorganic fertilizers. So the use of PGPR to improve yield of harvests has demonstrated to be an earth benevolent technique as a substitute to such issues.

As soon as a site becomes contaminated, the masterpiece of the autochthonous microbial population in the site as well as the underground water will acclimatize to the new condition. The microbial species that are able to use the pollutants as foundation of substrates for growth will proliferate and turn out to be dominant (Liu and Suflita 1993; Gkorezis et al. 2016). The normal, non-planned process of xenobiotic breakdown by the native microbial species is known as normal diminution and it is considered the modest method of bioremediation. The Environmental Protection Agency (EPA, United States) describes innate remediation as a combination of degradation, dispersion, dilution, sorption, volatilization, chemical and biochemical balance of pollutants. Though, in earlier times, this "treatment" technique was regularly talk about as an important method, it gradually has become a vital instrument to remediate polluted sites. Natural attenuation is already a success for BTEX compounds which is associated with underground water (USEPA 2001). It has been useful mostly on locations with "low" public worth, especially when there is enough time, since cleanup could last a while when other kind of restoration technologies are not appropriate. Normal cleanup is not allowed at sites near home with great ecological worth, such as natural resorts. Time is also a restraining influence because the ability of native microorganisms to adapt could take decades, contingent on the nature of the xenobiotic that is available (Ojuederie and Babalola 2017). The by-products that arise from incomplete breakdown of other contaminants can be lethal. For example, toxic 1-napthol arises from oxygenic conversion of naphthalene, while the actual carcinogenic compound vinyl chloride comes from anaerobic conversion of tri-chloroethylene (Liu et al. 2007). Heavy metals are recalcitrant so they cannot be damaged by normal degradation; nevertheless, they are subjected to volatilization. Also, microorganisms that have appropriate catabolic genes may not be present on the site for all xenobiotic compounds, which is confirmed by the buildup of hazardous and obstinate mixtures found in the ecosystem (Vimal et al. 2017).

13.8 Plant–Microbial Interaction During Remediation

The interaction between plant and microorganisms can be accomplished through various immediate: nutrient transfer (originating from nutrient or siderophore production, air nitrogen fixation, enzymatic deterioration of organic matter in soil, or transformation of inorganic minerals to dissolvable constituents, particularly phosphorous), direct encouragement of growth through phytohormones, (for example, ethylene or indole acetic acid), antipathy towards pathogenic microorganisms, and mitigation of salt stress. The soil is exceptional in possessing a life-dependent structure and offers ecosystem services that are vital for global roles, comprising principally production, regulation of biogenic gases, earth's climate, biogeochemical and water cycling, as well as biodiversity maintenance (Magdoff and Es 2000; Welbaum et al. 2004). A substantial quantity of the land is polluted arising from different human influences and a steady upsurge of this level is anticipated in years ahead. The microorganisms inhabiting the soils form a very vital component of living things. The relationship between bacteria and plants in the different ecological niches including the rhizosphere contributes to the rise in promoting the growth by directly affecting plant anabolic and catabolic reactions in the absence of most important pathogen. These bacteria fit into different genera, including *Acetobacter, Achromobacter, Anabaena, Azotobacter, Bacillus, Hydrogenophaga, Kluyvera, Pseudomonas,* and *Rhizobium* (Bashan et al. 2008).

There are important factors that determine the efficiency of phytoremediation. These include setting up of important plants with the ability to produce biomass, vigorous root as well as root activities with the root network, aiding cleanup using plants in the rhizosphere region. Likewise, the association of different groups of microorganisms can be of advantage to the plant. In addition to the numerous positive interrelationships, there exists competition of resources between plants and microorganisms (Kaye and Hart 1997). Arising from the restrictions of scarce nutrients and its struggle, which usually take place at contaminated locations, the proliferation of microorganisms as well as biodegradability could be restricted (Joner et al. 2006; Unterbrunner et al. 2007). Though, supply of too much nutrients can be responsible for appropriate conditions for encouraging heterotrophic and pollutant bacteria that have become acclimatized, this may not essentially result in realizing improved rates of phytoremediation. This has been reported in the degradation of hydrocarbon in oil contaminated ecosystems. The degradation of the contaminant was not influenced or subdued by nutrient addition (Chaineau et al. 2005).

The microbial communities found in soil that show diverse competences of hereditary capabilities and endeavours can differ widely in soils which may also impact on the functioning capacities of soil, arising from their involvement in important metabolic reactions (Nannipieri et al. 2003). The relationship that exists between microorganisms is constrained by precise compounds and is accountable for significant natural processes, such as organic matter decomposition, and safeguarding of plant wellbeing just as soil quality (Barea et al. 2004). The development of enormous amounts of metabolically active inhabitants of useful microorganisms in soil is required for distinctive bioremediation (Metting Jr

1992). In the aforementioned microorganisms, the motivating aspects are high ability to acclimatize to different environmental conditions, fast growth rate, and biochemical resourcefulness to fully utilize different types of normal and xenobiotic chemicals for an entrenched ecosystem (Narasimhan et al. 2003).

13.9 Role of Plant Growth-Promoting Rhizobacteria

Plant growth-promoting rhizobacteria play critical function in the promotion of plant growth leading to viable agricultural development. They assist plant growth promotion by direct and indirect machineries. The direct consist in fixing of nitrogen in the atmosphere, solubilization of phosphorus, siderophore production for iron chelation, and providing siderophore–iron complex to plant resulting in the synthesis of different plant hormones. While indirect method includes control of pathogenic plant pathogens via antibiotics production, reduction of iron in the soil, and eventually encouraging the growth of plants. Plant growth-promoting Rhizobacteria are classified into two based on their association with host plant: (1) cooperative rhizobacteria, which assault and colonize the inward piece of the plant cell to endure, e.g. bacteria forming nodule, and (2) free-living rhizobacteria that exist outside the plant and are likewise popular as extracellular PGPR, e.g. *Azotobacter, Burkholderia*, and *Bacillus* (Babalola 2010; Khan 2006). Microbes like PGPR can improve the supply of supplements in the rhizosphere (Choudhary et al. 2011; Kumar et al. 2017). For instance, nitrogen, the best controlling variable related with the development of plant is not promptly open for plant use, yet *Azospirillum* existing in grain biological system can fix free nitrogen accordingly, advancing the yield of harvests (Tejera et al. 2005). Besides, phosphate is likewise provided in the accessible form by PGPR (Vacheron et al. 2013), making it to be promptly used by plants. Vejan et al. (2016) posited that Lavakush Yadav et al. (2014) completed a trial on PGPR strain like *Pseudomonas putida* and *Pseudomonas fluorescens* relating to their impact on take-up of uptake of nutrient during the growth of rice.

Certain rhizospherical strains possess the capability to give up a variety of substrates such as antimicrobials, hydrocyanic acid, indoleacetic acid (IAA), siderophores which is integral to expanding the bioavailability and admission of hefty metals by plant root, for both fundamental (e.g. Fe and Mn) and superfluous (e.g. Cd) nutrients (Barber and Lee 1974; Crowley et al. 1991; Salt et al. 1998). An examination was completed which indicated connection between metal opposition and metal activation capacities of rhizobacteria under weighty metal pressure. Phosphate solubilizers had the most extensive level of the biochemical movement of all segregates and against metal opposition; trailed by siderophore makers and in conclusion acid producers. This points to the fact that the aforementioned group of microorganisms is utilized by rhizobacteria and be responsible for metals mobilization in soil (Abou-Shanab et al. 2005). The take up and movement of non-essential elements might differ significantly and regularly influenced by different genera and form of minor elements. To the varying degree, the various metals display different rates of mobility, and the conscription rate might remain higher for some than others for a specific metal inside a plant.

13.10 Hormones in Enhancing Growth During Remediation

Some rhizospheric microorganisms produce plant hormones which support root growth and in so doing discharge root secretions. The plant secretions incorporate carbohydrates, amino acids, lipophilic mixes, and chelating specialists secreted from the roots of plants and set forth constructive outcomes to keep up an assortment of microbial networks in the rhizosphere (Anderson et al. 1993). Plants that are low in phosphorus try to summon phosphorous components that are accessible in soil by expanding citrus extract level in root exudates (Hooda 2007). A coagulated oil alluded to as mucigel is needed for root entrance which is emitted by it cells and adds to expanding the root mass apically during growth in the soil. The microbes in soil use these mixes for development to create the plant rhizosphere (Anderson et al. 1993). The survival of plants in contaminated and nutrient limiting environments is stimulated via inter-relationships existing between microorganisms associated with plant roots and plants itself in the rhizosphere. Several metal ions have low bioavailability due to their reduced solubility in aqueous solution and resilient affinity for soil particles which render them immobile thereby hampering utilization by plants. However, microbes that colonize the roots of plant can contribute to increased metal uptake by increasing the bioavailability (Hooda 2007).

13.11 Role of Endophytes and Mycorrhiza

The degradation of contaminants has also been implicated in endophytic microorganisms as well as those involved in plant–microbial interactions. The endophytic bacteria colonize internal plant tissues without necessarily impeding plant development (Lodewyckx et al. 2002; Schulz et al. 2006). Plant–endophyte interactions are such that plants provide nutrients and shelter for the endophyte, whereas the latter provide growth enhancement conditions for the plant through the production and release of useful metabolites (Bacon and White 2000; Garbeva et al. 2001; Tan and Zou 2001). Generally, many common easily grown endophytic species are *Pseudomonaceae, Burkholderiaceae*, and *Enterobacteriaceae* (Mastretta et al. 2006). This association has also been exploited in remediation of contaminants. The photoautotrophic capacities of plants make for the possibility that associating rhizospheric microorganisms would have the capacity to biodegrade and/or utilize petroleum hydrocarbons even when they are poorly soluble in water. Haichar et al. (2008) earlier reported that the soils with enhanced plant cover usually had more diverse microorganisms and as such are most likely to be easily remediated. Plants release exudates, mucilages, lysates, vitamins, organic acids, ligands, enzymes, or otherwise rhizodeposits (Olson et al. 2003). These are carbon sources that enhance soil microbial proliferation and eventual biodegradative capacities (Chaudhry et al. 2005).

13.12 Mechanism of Rhizoremediation

The ability of plants to cleanup contaminants from either terrestrial or aquatic environments relies basically on its rooting capacities. The root is the major organ for nutrient absorption, adsorption, and accumulation. Plant capacities to associate with soil microorganisms that are critical for plant development also rest, to a very large extent, on the roots. Therefore, bioremediation of contaminants is better appreciated at rhizospheric levels. There are a number of mechanisms of contaminant remediation in the roots—this however depends first on the types of contaminants. Whereas inorganic contaminants are basically absorbed or adsorbed either by direct flow or upon enhancement by ligand and chelators, organic contaminants are degraded or sequestered around the rhizosphere or rhizoplane. The role of microorganisms in achieving these capacities is imperative. The process of bioremediation can be carried out either using oxygen or not, according to the requirement of the organism involved. This means bioremediation can be of two form, aerobic or anaerobic (Malik and Ahmed 2012). It is however common to ascribe the mechanism of remediation to aerobic route due to the overly abundance of aerobic organisms involved in bioremediation. Below are the equations for bioremediation.

Aerobic biodegradation:

$$\begin{aligned}&\text{Biota} + \text{Hydrocarbon compound} + \text{Oxygen } (\mathrm{O_2}) \pm \text{Enzyme(s)}\\&\quad = \text{Biota} + \text{Water} + \text{Residue(s)}\end{aligned}$$

Anaerobic biodegradation:

$$\begin{aligned}&\text{Biota} + \text{Hydrocarbon compound} + \text{Carbon (iv) oxide} \pm \text{Enzyme(s)}\\&\quad = \text{Biota} + \text{methane } (\mathrm{CH_4}) + \text{Water} + \text{Residue(s)}\end{aligned}$$

Many genera of bacteria have been reported to be useful in bioremediation. Among the aerobic bacteria involved are *Bacillus, Micrococcus, Sphingobium, Rhodococcus*, those of the anaerobic are *Pelatomaculum, Desulphovibrio, Desulfotomaculum, Aromatoleum aromaticum, Dechloromonas aromatica*, *Desulfitobacterium hafniense* (Cao et al. 2009), and *Syntrophus* (Shimao 2001; Jayasekara et al. 2005).

The process by which the microorganism carry out remediation can be ascribed to mineralization, a process whereby the pollutant is converted into intermediate substance, usually according to the pathway the organism uses in remediation. The whole process involves absorbing the pollutant into the cell, followed by the release of enzymes and organic acids such as citric acid, and malic acid, etc., which acts on them thereby converting them into intermediate product. However, before absorption the pollutants are converted into less toxic compound by complete oxidation using an electron acceptor, oxygen in the case of aerobic respiration.

13.13 Enzymes and Genetic Implications of Hydrocarbon Biodegradation

In most cases of hydrocarbon pollution, the process of remediation is usually preceded by the release of extracellular enzymes such as oxygenase. This is usually observed in fungi which are known to degrade their substrate extracellularly before taking it in using enzymes such as lignin peroxidases (LiP), laccases, etc. (Asemoloye et al. 2017). These enzymes are typically involved in the breakdown of substrate by cleaving to the bond and metabolizing hydrocarbon contaminant into phenols or trans dihydrodiols (Bogan and Lamar 1995). The functionality of these enzymes has been reported to be affected by the length and complexity of the hydrocarbon chain of the pollutant. However, some microbes have cytochrome P450 enzymes which are capable of converting long chain hydrocarbon into isoforms. Such enzymes have been isolated from *Candida* species which were able to utilize long chain aliphatic hydrocarbon. A typical example is the alkaneoxygenase which is able to oxidize alkane and some other methane monooxygenases which contain copper (Scheller et al. 1998; Van Beilen and Funhoff 2005).

13.14 Synergistic Rhizosphere Mechanisms for the Removal of Hydrocarbons in Polluted Soils

Biodegradation requires reduced energy and it involves the use of life organisms in the cleaning up of contaminated soils (Segura and Ramos 2013). It is a generally accepted technology because of its cost effectiveness and more ecofriendly when compared to other conventional remediation methods. Using this method, one major challenge is the ability to establish the plant in the remediation process, due to the toxic property of the pollutant. The roots of plants are important in the remediation of both land and soil but with increase in the rooting ability of the plant in the land or water to be remediated there is increase the rate of remediation by way of reducing the amount of contaminant left in the field (Gunawardana et al. 2011). Some level of pollution will however inhibit the rate of rooting in plants, this has been the major problem in rhizoremediation (Abhilash et al. 2012; Li et al. 2013; Ukaegbu-Obi and Mbakwem-Aniebo 2014). Ways have been looked into, to be able to increase root proliferation in this type of situation, such as trying different form of techniques. Treatment of root of plants in hydrocarbon polluted soils with organic fertilizers and selected microbes is known to improve plants abilities to remediate polluted soils. The microbes which can be native or introduced have been said to symbiotically promote root system of the plant (Escalante-Espinosa et al. 2005; Huang et al. 2004;

Johnson et al. 2005; Joner et al. 2006; Leigh et al. 2006; Gerhardt et al. 2009; Weyens et al. 2009a, b; Glick 2010; Guo et al. 2014).

13.14.1 Biosurfactants

Most microbes, including bacteria, yeast, and the filamentous fungi have been reported to synthesize several biomolecules. Many of these biomolecules produced by these organisms have shown surface activity, because they comprise both hydrophilic and lipophilic properties. These compounds are made up of a water loving acids, peptide positive and negative charged ions, and a hydrophobic moiety of unsaturated or saturated hydrocarbon chains or lipids (Banat et al. 2010). They can be of two type, the first being the low mass compounds called biosurfactants, known for reducing surface and interfacial tensions, and they include lipopeptides, glycolipids, and proteins (Nguyen and Sabatini 2011; Banat et al. 2014; Dobler et al. 2016; Santos et al. 2016). The high mass are the bioemulsifiers such as the lipopolysaccharides, polysaccharides. Bioemulsifiers balance out oil-in-water emulsions and possess reduced ability to bring down surface pressure than biosurfactants (Neu 1996; Smyth et al. 2010a, b; Uzoigwe et al. 2015). The aforementioned properties have been attributed to enhance microbial growth by expanding the surface territory among oil and water through emulsification, as well as through expansion of the pseudosolubility by apportioning into micelles (Volkering et al. 1997). The whole procedure will enhance the bioavailability of the contaminant to degradation by microorganisms (Mulligan 2009; Pacwa-Plociniczak et al. 2011; Lawniczak et al. 2013).

Typical examples have been reported, like the case of *Bacillus circulans* which produces lipopeptide and *Pseudomonas aeruginosa* which produces both lipopeptides and protein-starch-lipids have increased biodegradation (Bordoloi and Konwar 2009; Das et al. 2008). Another is the comparative study between Triton X-100 and the commercial rhamnolipid JBR-515 (Jeneil Biosurfactant Company, USA) using *Burkholderia multivorans* (NG1) shows that Triton X-100 increased bioavailability by emulsification and sustained interfacial take-up, while the rhamnolipid mixture JBR-515 considerably did not emulsify hydrocarbons, improving bioavailability in its place by solubilization of the micelle (Mohanty and Mukherji 2013). Colores et al. (2000) have however posited that the presence of surfactants of biological origin and that of non-biological origin may be inhibitory to the process of biodegradation. This is because the Micelle cores formation which will trap the organic contaminants can create a hydrophilic barrier between the organic contaminant and the hydrophobic microorganisms making it less available for degradation (Colores et al. 2000).

Another case observed in *Pseudomonas aeruginosa* is the use of a mechanism not so different to pinocytosis for the uptake of rhamnolipid-coated hexadecane droplets which can be referred to as the internalization of biosurfactant layered hydrocarbon droplet. Some microbes have been reported to even emulsify hydrocarbons without absorbing the hydrocarbon. This have prompted the attention to the surface property of the cell to be associated with emulsification, due to the connection of the oil–water interface by broad hydrophobic communications as opposed to explicit acknowledgment of the substrate. It is said that the microorganisms cells may serve as fine strong units at interface, meaning that stationary-phase or hydrophobic microorganisms can settle oil–water emulsions by clinging to the oil–water interface because of the cell surface hydrophobicity in a population of different microbes, the production of biosurfactants by the microbes or the plants or the one introduced into the medium may be suitable substrate for species that naturally degrade hydrocarbon, thus reducing the remediation yield. Biosurfactant of external and internal origin is however poisonous to certain microorganisms by impairing permeability of the membrane, hence meddling with chemotaxis driven motility, and upsetting the formation of biofilm.

Biofilms, bacterial networks encompassed by self-produced polymeric matrices reversibly committed to a passive surface are a survival strategy against harsh physicochemical environments, to aid exchange of cations, gene transfer, and regulation of redox ability of their ecosystem (Costerton et al. 1995; Gorbushina and Broughton 2009; Shemesh et al. 2010). Biofilm milieus are made up of extracellular polysaccharides (EPSs), deoxyribonucleic acids, and proteins (Sutherland 2001; Branda et al. 2005; Rinaudi and Gonzalez 2009), with EPS influencing the water holding capacity, thickness, moisture content, and mechanical firmness of biofilms (Flemming and Wingender 2010).

Biofilms, however, have the property of enhancing PHC bioremediation courses by aggregating the accessibility of the contaminant (Wick et al. 2002; Johnsen and Karlson 2004). The production of high molecular weight compounds is usually proportional to the formation of production of biofilm; therefore, in the event that release of polymers by microbes is trailed by production of biofilms on the superficials of inexplicable hydrocarbons. This put those microbes particularly well prepared for the management of unruly combinations due to their great microorganism biomass inside biofilm. However, biofilm formation enhances remediation process by preserving best situations of pH, limited concentrations of solute as well as redox ability in the presence of the cells.

13.15 Environmental Factors Affecting Bioremediation of Contaminants by Plant–Microbe Interactions

Competition for resource and interference by chemicals lead to harmful associations among plants. Also, exudates from plants root are a possible factor that can affect the three instruments of intervention. For some species of plant, the exudates from root perform vital function as phytotoxins (i.e. allelopathy). Also, these exudates are crucial for improvement of interrelationships among some plants parasite and their hosts. Lastly, release from the roots also performs crucial secondary roles in the struggle for resources, this is done by interfering with soil chemistry, various soil processes, and the population of microorganisms. Root exudates sometimes control positive interactions between plants. In some situations, root exudates induce plant defence that helps decrease vulnerability to infections from pathogen, but in opposite conditions, these immunities result in the manufacture and discharge of green volatiles which attracts killers of plant adversaries. Also, the different influences of releases from the root positively impact on the soil processes, and population of microorganisms as well as the surrounding plants.

Allelopathy or chemical enhanced plant interference is one method used by plants to have a lead on their rivals. Plants do this by producing and releasing potent phytotoxins to inhibit or diminish the instituting, growth, or existence of vulnerable plant neighbours, this will help reduce or eliminate competition and then increase the availability of resources. Some of the phytotoxins released could be located in rotten foliage and root matter that might have been discarded by the plant. These phytotoxins show differences in their chemical structures, mechanisms of activity and influence on plant growth and metabolism. The various phytotoxins present in root exudates affect various processes like the production of metabolites, photosynthesis, root growth, etc.

Root exudates are critical factors required for establishing important relationships between microorganisms and plant roots or even between other biota and plant roots. Plant capacity for survival also rests on this. Plant association with other biota may not necessarily be always beneficial. Whereas some associations are synergistic, others could be parasitic, neutral, or commensalistic. Root exudates can influence better association.

13.16 Conclusion

This paper reviewed toxic waste, plant–microbial interactions, survival mechanisms of plants–microbes and their interactions in contaminated environment. It also took a cursory view on the genetic implications of plant–microbes interactions involved in the conversion of toxic waste in the ecosystem. Environmental factors affect enzyme responses during ecosystem cleanup. These can be as little as can induce free radical activity that would change the course of enzyme activity that would ultimately influence remediation capacities and performance. It re-echoes the overwhelming importance of synergistic relationship between plants and their counterpart rhizospheric microbes during the conversion of toxic waste making it a better and sustainable alternative for the elimination of poisonous wastes (organic and inorganic) within the surrounding. Microbes and plants have innate natural machineries that support their survival under environmental conditions and eliminate the toxics from the ecosystem. Additional fast developing plants with great phytoextraction potentials need to be identified for the cleanup of contaminants in soil.

13.17 Future Perspectives

There are new ways of studying plant–microbial interactions. These are chromatography, sequencing, microscopy, mass spectrometry, phospholipid fatty acid (PLFA), real-time PCR (RT-PCR), etc. Additional development in this genomic age will open up avenues for improved knowledge of the inter-relationships of endophytes, plant–pathogen and plant protection. There is need for improved remediation techniques to meet the challenge of pollution. In plants, together with their microbiomes, lies huge unexploited potential for purifying both environmental pollution particularly soil.

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PGPR in Management of Soil Toxicity

14

Jupinder Kaur

Abstract

Intensive agricultural practices, development of industries and several other human activities are adding significant amount of pollutants in soil. When these pollutants are present in soil beyond their normal concentration then they act as danger to soil health, human health and environment. Such pollutants which can result in soil toxicity include heavy metals, non-metals (like ammonia) and various other organic compounds (chlorinated as well as non-chlorinated compounds). To overcome the problem of soil toxicity, low cost, efficient and nature friendly remediation techniques are needed. Most of the remediation techniques face limitations due to the toxic nature of pollutants. The battle of soil toxicity can be conquered by using the plant growth promoting rhizobacteria (PGPR). PGPR possess many functional activities, some of which can be used as a tool for remediation of soil toxicity. So, these rhizobacteria not only play role in plant growth promotion and biological control of diseases but they may also help in reducing the toxicity of various pollutants in soil. The use of PGPR for curing soil toxicity is gaining much interest as it offers environment friendly, economical and natural aesthetic benefits.

Keywords

Heavy metals · PGPR · Rhizobacteria · Soil contamination · Soil toxicity

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14.1 Introduction

Soil is a dynamic and biologically active medium in which soil constituents, soil organisms and plants interact with each other. It acts as a major sink for pollutants released by various natural and human activities (Adriano 2001). The worldwide intensive agricultural practices, industrialization and various other anthropogenic activities like mining release toxic substances such as heavy metals, various non-metals, organic pollutants, etc. which lead to contamination of soil. Toxicity of soil negatively impacts the soil structure and growth of plants resulting in stress and consequently leading to agricultural losses (economic). These problems of soil toxicity can be managed by used of microbes as the various transformations occurring in the soil are associated with the biological activities (microbes) of soil–plant systems (Adriano et al. 2004). Microorganisms perform a wide variety of functions in plant soil ecosystems. A wide range of transformation reactions are carried out by bacteria that cannot be carried out easily by any other species (Rovira et al. 1983). The ability of microbes to adapt and live in various habitats and their vital role in various biogeochemical cycles and other transformations made microbes a suitable candidate for the elimination of various toxic pollutants. Free living rhizobacteria that trigger plant growth and exert other beneficial effects are known as Plant Growth Promoting Rhizobacteria (Kloepper et al. 1989). These soil beneficial bacteria facilitate the growth of plant directly as well as indirectly (Glick 1995). Fixation of atmospheric nitrogen, solubilization of insoluble phosphorous, production of phytohormones, sequestration of iron by siderophore production, etc. are some of the direct mechanisms used by plant growth promoting rhizobacteria for stimulation of plant growth, whereas the protection of plant from diseases by acting as biocontrol agent is the indirect mechanism of PGPR to boost plant productivity (Glick and Bashan 1997). Microorganisms are responsible for the transformation of at least one third elements of the periodic table. The activities of these microbes are affected by environmental factors also (Kaur and Gosal 2015; Kaur and Gosal 2017). The inoculation of PGPRs with diverse functional activities also help the plant to withstand various stresses like salt stress, osmotic stress, heavy metals stress, etc. These transformation reactions help the microbes to metabolize the soil pollutants also. The processes of microbes like assimilation or incorporation into cell biomass, dissimilation to obtain energy or detoxification, etc. act as remediation processes for various soil pollutants (Stolz and Oremland 1999; Upadhyay et al. 2017). This means PGPRs adapt even in the conditions of soil toxicity. So, the activities of microorganisms present in soil are not a prerequisite only for healthy and fertile soil but these microbes are indispensable for degradation of various substances also (Alexander 1999). So, in this chapter we will discuss about sources of soil toxicity, their classification and management of soil toxicity using rhizobacteria.

14.2 Soil Toxicity and Soil Health

Soil is thin layer of loose soil particles covering the rocky surface of Earth. Dirt, mud and ground are the other names of it. Soil is composed of inorganic (fragment of rocks) and organic materials (derived from decaying remains of plants and animals) apart from air, water and various organisms residing in it. Due to its heterogeneity, it is considered as one of the complex system. Soils are formed over many years by the decomposition of parent bed rock and organic matter. It is the basis of agricultural productivity. The productivity of crops for feeding of human and animals are dependent on soil (Belluck et al. 2003). Composition of parent bed rock, climatic conditions and influence of various other factors affect the soil properties like the ability to retain water, cycling of nutrients, micro- and macro-biota it can inhabit, etc. Soil contains various chemical elements as part of the soil minerals. All the soil nutrients and various reactions occurring in soil contribute towards soil health. 'Soil health' term is often used interchangeably with 'soil quality' by the farmers. Soil is considered as healthy if it has good structure, proper amount of organic matter and diverse range of organisms (Brevik et al. 2013). To get maximum productivity of any agricultural crop, soil must be healthy and fertile. As soil is a universal sink, thus it bears the burden of pollution. To maintain soil health, fertility and productivity of agricultural ecosystem, soil pollution needs to be controlled. Moreover, the health of the soil also determines the fate of soil contaminants.

Any soil element or any other chemical which is present at higher concentration than its normal concentration is considered as pollutant. Pollutants adversely affect the non-targeted organisms and can result in toxicity of soil. Presence of pollutants in soil is the worst example of contamination as it causes irreversible damage due to build-up of toxicity. Soil toxicity may be referred to as the higher quantity of any chemical beyond its threshold limit that lead to undesirable physio-chemical and biological changes in properties of soil which disturb various biotic and abiotic components of ecosystem. There are number of ways in which soil can be polluted. The chemical or substances which are responsible for soil toxicity can be natural as well as anthropogenic. The natural sources of waste such as dead plants, remains of animals, rotten fruits and vegetables, only add to the soil fertility. But, the waste produced from anthropogenic sources is full of chemicals and cause soil pollution. Human activities have intentionally added many harmful contaminants in the soil. Heavy metals and pesticides are the most important contaminants encountered in soil. Presence of these toxic substances in soil can adversely affect the soil health and fertility (Upadhyay et al. 2017). Soil toxicity can be considered as hidden danger as it is difficult to perceive it visually and cannot be directly assessed.

14.3 How Toxic Compounds Reach Soil

Presence of toxic compound in soil interferes with the various transformation reactions occurring in soil and can adversely affect the soil properties. Most of the toxic substances enter into the soil environment by accidental discharge of sewage,

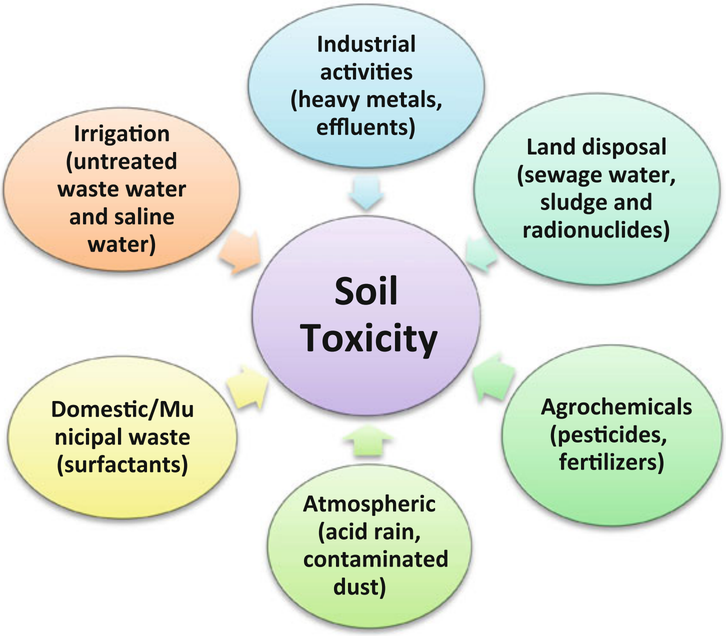

Fig. 14.1 The various causes of soil pollution resulting in soil toxicity

industrial or domestic effluents and sometimes they are part of some beneficial products. There are many ways in which soil become polluted leading to its toxic nature (Fig. 14.1). The release of these pollutant chemicals into the soil is either accidentally (leaching from landfills) or intentionally (fertilizers, pesticides, sewage sludge application, irrigation with untreated waste water). Pollution from anthropogenic sources may work in conjunction with pollution from natural sources resulting in increasing the levels of toxicity in soil. The various routes for entry of toxic compounds into soil are described below.

14.3.1 Industrial

Chemicals are integral part of industries. Industrial activities have been the biggest contributors towards the pollution problems. Industrial activities release various substances or chemicals which pollute soil, air and water. The agricultural waste containing inorganic residues poses serious threats to ecosystem. These inorganic residues contain heavy metals which have high potential for causing soil toxicity. The effluents released from industries also emit a large quantity of sulphur dioxide and arsenic dioxide (Richardson et al. 2006). Soil can become very acidic due to the sulphur dioxide released by industrial effluents. In the atmosphere of phosphoric acid, superphosphate, steel, aluminium and ceramic industries, fluorides are found.

The presence of these metals in the atmospheric waste can destroy vegetation and lead to leaf injury also.

The other metals like cadmium, nickel, arsenic, lead, copper mercury reach the soil through industrial effluents and mine washings. These metals accumulate in soil and cause soil toxicity. Soil particles adsorb the smoke released from automobiles, which is toxic to growth of plants (Van 1996). Radionuclides and gaseous pollutants released from industries reach soil via atmosphere (acid rain/atmospheric deposition). Improper storage of chemicals and direct discharge of industrial waste into soil also lead to soil toxicity. Soil salinity is also a problem in areas near to industries involved in soap and detergent production, ceramic manufacturing, production of textile, glass and rubber, metal processing, animal hide processing and leather tanning, etc. (Saha et al. 2017). The expansion of lead based industries also contributes towards soil toxicity (Zahran et al. 2013). The fertilizer manufacturing industries are among the leading users of heavy metals (mercury, cadmium, arsenic, lead, copper and nickel) and natural radionuclides (^{238}U, ^{232}Th and ^{210}Po). The by-products of industries dealing with mineral extraction are mostly contaminated. These by-products if not disposed properly, will linger on soil surface and this, contribute towards its toxicity.

14.3.2 Land Disposal

The incrementation of human population at an alarming rate consequently results in increased waste production. This is becoming a dangerous situation due to the lack of municipal services dealing with waste management. So, the way of our waste disposal is a main concern in soil toxicity problem. Usually this waste is managed either by disposal in landfills or by incineration. But in both cases, pollutants (heavy metals, pharmaceutical compounds, polyaromatic hydrocarbons, etc.) and their derivatives accumulate in soil (Swati et al. 2014) in the form of landfill leachate or ash fallout from incineration plants which lead to soil pollution and thus, contribute towards its toxicity (Mirsal 2008). By urine or faeces, human also produce certain amount of waste. Part of this waste is directly dumped to landfills and part of it moves to sewage, which ultimately ends at the landfill. The toxins or chemicals present in waste seeps into the land and result in soil toxicity. Sewage sludge is also the chief source of soil pollution. It is the source of various heavy metals like zinc, copper, nickel, lead and chromium toxicity in soil (Wang et al. 2016). If sewage sludge is repeatedly applied to soil in large quantities, then heavy metal accumulation occur in soil and consequently soil can even become unable to support plant growth.

Radionuclides existing in the environment have both natural as well as anthropogenic origin (Mehra et al. 2010). After any radioactive incident, radionuclides become the part of land disposals. Radionuclides have long half-lives.^{40}K,^{238}U, ^{232}Th, ^{90}Sr and ^{137}Cs are among the frequently occurring radionuclides in soil with natural and anthropogenic basis (Wallova et al. 2012).

Nuclear accidents, fallouts during the nuclear weapon testing, mining of radioactive ores, nuclear waste handling and mineral fertilizers, etc. (Ulrich et al. 2014) are main anthropogenic sources of radionuclides. After reaching in soil, these radionuclides are taken up by plants and thus reach various trophic levels through food chain (Zhu and Shaw 2000). These radionuclides remain bioavailable in soils for long time (Falciglia et al. 2014). It is not possible to remove the top layer after any radioactive accident (as it will generate large amount of radioactive waste) so, agricultural countermeasures (like abandoning the soil for years) should be followed to restrict the entry of radionuclides into various level of our food chain (Vandenhove and Turcanu 2011).

14.3.3 Agrochemicals

To get higher productivity of agricultural crops, vast range of chemicals are used. Agrochemicals such as fertilizers, manures and pesticides are source of soil pollution and contribute towards its toxicity. Metals such as arsenic, copper, lead, cadmium and mercury released from these agrochemicals result in soil toxicity. This soil toxicity due to these metals decreases the productivity of crops by impairment with the metabolism of plants. Fungicides used in agricultural production also contain copper and mercury, thus contribute towards soil toxicity. Spillage of agrochemicals during their transport and storage or spillage of hydrocarbons in agricultural soils used as fuel for machine are also among the point sources of pollution contributing towards soil toxicity (Prakash et al. 2014).

More than recommended dose of application of fertilizers or manures or injudicious use of macronutrients like nitrogen, phosphorous can result in mineral toxicity in soil (Kanter 2018). Excessive application of fertilizers pollutes the soil and has negative impact on soil microflora. This can also result in soil salinity, accumulation of nitrate, eutrophication of water bodies which negatively impacts environment as well as act as big threat to human health. Adequate management and handling of fertilizers is the utmost need to prevent the soil from mineral toxicity (Stewart et al. 2005). Instead of inorganic fertilizers, biofertilizers, compost and animal residues can be used as these are good source of nutrients. These provide nutrients and increase organic matter content thus, decrease the dependence on agrochemicals and save the environment and soil from negative impacts (Shiralipour et al. 1992).

Pesticides also contribute towards soil toxicity. Pesticides are the chemical formulations or their combinations used to restrict, eliminate, or lessen the damage caused by any pest. Use of pesticides helps in good security as their application protects the crop from any damage caused by any pest. But, the application of pesticides has negative impacts on soil, environment as well as on human health (FAO and ITPS 2017). Some pesticides are highly persistent, so residues of such pesticides remain in soil for long time thus interfering with the soil properties. Improper storage of pesticide stocks result in its leakage to surroundings thus, polluting the soil, water and environment.

14.3.4 Atmospheric (Acid Rain, Contaminated Dust Such as Sulphur Dust)

Atmosphere also contributes towards the soil toxicity. The gaseous pollutants released from the industries mix up in the air. This air when come in contact with the rain water it reaches soil and cause soil pollution. Acid rain is the most common example. Acid rain occurs when pollutants (like H_2S gas) present in air mix up with the rain (leading to formation of sulphuric acid) and falls back on earth. This polluted rain water on reaching the soil will change the soil properties and contributes towards its toxicity. The chemicals that can travel more easily through air as fine particulate matter are highly risky. The toxic and foul gases emitted from the landfills also pollute the air leading to dust contamination. Contaminated dust also causes serious problems. It also produces the unpleasant smell creating inconvenience. Such chemicals which adhere to dust or move as fine particulate matter are very resistant to degradation and can bio accumulate in living organisms. Construction dust easily spread through air. Due to its lower particle size, it is highly dangerous (as it cause respiratory illness and even cancer). Demolition of older buildings release asbestos, a toxic chemical that poisons the soil.

14.3.5 Domestic/Municipal

Increase in population also lead to generation of more waste. Organic waste of various types causes soil toxicity. When municipal sewage and domestic garbage is inadequately disposed, it affects soil, plant, animals and human health. This waste contains large quantities of detergents, borates and phosphates. If this waste is disposed without any treatment, it can cause soil toxicity.

14.3.6 Irrigation (Untreated Waste Water and Saline Water)

If the untreated waste water, sewage water or saline water is used for irrigation, then it can also cause soil pollution. The presence of toxic substances such as heavy metals, excess of inorganic elements like nitrogen, phosphorous not only causes soil toxicity, but also disturbs, water quality and human health and food security once they enter the food chain (FAO and ITPS 2015).

14.4 Classification of Soil Toxic Compounds

The pollutants present in soil responsible for its toxicity usually originates from anthropogenic processes. Although some substances are present naturally in soil yet human interventions are main contributors towards soil toxicity. The most common toxic substances generally encountered in soil can be classified on the basis of their persistence as well as their chemical nature (Fig. 14.2). Apart from these two main

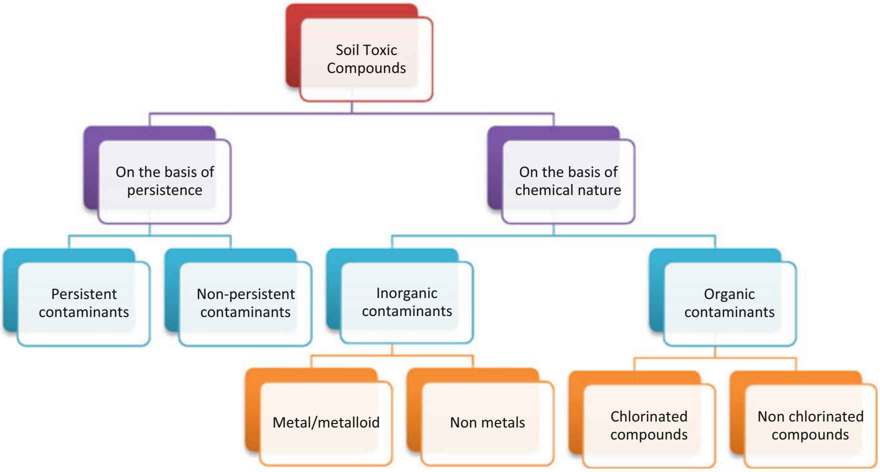

Fig. 14.2 Classification of contaminants responsible for soil toxicity

categorizations, pollutants can be classified on some other basis also but that can result in the overlapping among various classification groups.

14.4.1 On the Basis of Persistence

On the basis of persistence, soil toxic compounds can be persistent or non-persistent. The term persistent or non-persistent refers to how long a pollutant stays in soil.

14.4.1.1 Persistent Pollutants

Persistent pollutants are those which are resistant to degradation. These pollutants accumulate in the food chain and impose negative impact on soil, water quality and human health (UNEP 2018). A number of factors may be responsible for persistence nature of pollutants such as structure that is resistant to microbial degradation, strong sorption or hydrophobicity. Persistent organic pollutants are very common as they are used in agricultural as well as in many industries. Persistent organic pollutants include chlorinated as well as brominated aromatics, polychlorinated biphenyls, organochlorine pesticides such as DDT, etc. Other toxic chemicals like dioxins (polychlorinated dibenzo-p-dioxins and –furans), which are produced from industrial activities and during the ignition of waste, also exist in this category for their long-term persistence. These organic pollutants are hydrophobic in nature which increases their affinity for the lipid membranes of cells and thus allows them to persist in the fatty tissues of living organisms (Jones and de Voogt 1999). They keep on accumulating in the food chain as they move from one organism to the next (Biomagnification). The Stockholm Convention has registered around 20 POPs so far (Stockholm Convention 2018) (Vasseur and Cossu-Leguille 2006). Persistent pollutants persist in soil and contribute towards its toxicity.

14.4.1.2 Non-persistent Pollutants

Non-persistent pollutants are those pollutants which stay in soil for a brief period after their release. These pollutants are biodegradable in nature. Although, the damage caused by non-persistent pollutant is reversible but these pollutants have more immediate toxic action than persistent pollutants. Once the non-persistent pollutants undergo degradation, they no longer cause toxicity in soil and are not a threat for soil, environment and human health. The half-life of these pollutants is also very short (hours to weeks at most). Domestic sewage, fertilizers, chlorinated hydrocarbons such as endosulfan and organophosphates such as malathion are among the examples of non-persistent pollutants.

14.4.2 On the Basis of Chemical Nature

Categorization of chemicals on the basis of their chemical nature was proposed by Swartjes (Swartjes 2011). This is the most systematic way of categorization of pollutants and is very useful in understanding them.

14.4.2.1 Inorganic

The inorganic pollutants include metals, metalloids and non-metals which are described in detail as under:

Metal

Heavy metals are defined as group of metals or metalloids possessing high density (usually greater than 4.5 g cm^{-3}). The metals such as lead, zinc, cadmium, copper, mercury and tin; along with some non-metals such as arsenic, selenium and antimony are also included in this group due to their density and toxic nature (Kemp 1998). Most heavy metals appear in uncontaminated soils during the weathering of parent bed rock. The concentration of heavy metals remains very low in soil under natural conditions. Plants and animals require these elements in trace amounts.

Heavy metals cause phytotoxicity, when present in high concentration. In soil, these metals get strongly adsorbed on organic or inorganic colloidal particles. Being persistent in nature, the remediation of heavy metals is difficult. Due to non-biodegradable in nature, these accumulate in the tissues of living organisms thus; they are threat to soil quality, crop productivity and human health. Among the various metals responsible for soil toxicity, zinc, nickel, cobalt and copper are more toxic to plants whereas cadmium, mercury, lead, arsenic and chromium are more toxic to animals (McBride 1994). Arsenic, lead, cadmium, mercury and selenium are main contaminates of food chain.

The main sources of heavy metals toxicity in soil are anthropogenic such as urban and industrial aerosols, atmospheric deposition, fuel combustion, heavy metal waste disposal, spillage from petrochemicals, animals and human derived solid or liquid material, mining effluent and agrochemicals, etc. (Alloway 2013). Arsenic is introduced in soil with the application of agrochemicals; livestock based manures and mining activities. Weathering of parent bed rock can also result in high arsenic concentration in soil. Metals such as copper reach the soil due to pesticides (Komarek et al. 2010).

Nonmetal (Cyanide, Ammonia, Sulphur)

Apart from metals, some nutrients or compounds like cyanide, ammonia and sulphur, etc. also affect the soil ecosystem. These nutrients or compounds are added into soil through natural as well as anthropogenic methods. The decrease as well increase in concentration of these nutrients above a certain limit can result in toxic nature of soil. Ammonia fertilizers are added to agricultural soil for the provision of nitrogen to the growing crop. But these fertilizers are often added to soils in high dosage in order to get higher productivity. High amount of mineral nitrogen in soil is not appropriate for good soil health. Excess of ammonia in soil also enhances the process of nitrification which is the process of soluble nitrates formation from the elemental atmospheric nitrogen or ammonia and this process contributes towards soil toxicity as high level of nitrate in soil is toxic to plants as well as organisms. These nitrates also contribute towards water pollution as the nitrates leach out from soil and contaminate groundwater. So, inorganic nitrates and phosphates are responsible for soil contamination as well as result in eutrophication. The decomposition or organic material in soil can release sulphur compounds.

14.5 Organic Compounds

Apart from inorganic compounds, the organic compounds such as chlorinated as well as non-chlorinated compounds are also main contributors towards soil toxicity.

14.5.1 Chlorinated

The chlorinated compounds which contribute towards soil toxicity include alkenes, dioxins, polychlorinated biphenyls, chlorinated pesticides, etc. Dioxin is chemically 2,3,7,8-tetrachlorodibenzoparadioxin (TCDD). Generally, the group of chemicals structurally and functionally related to polychlorinated dibenzo-para-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) the named as ‘dioxins’.

Sometimes, compounds with the same toxicity like polychlorinated biphenyls (PCBs) are also categorized as ‘dioxins’. So far 419 chemical compositions have been grouped under dioxin-related compounds, but only 30 among these are found toxic, with TCDD being the most toxic. These are persistent organic pollutants that are highly toxic in nature. Dioxins undergo biomagnification and keep on accumulating in food chain. Highest level of dioxins is found in animals, which are at the top of food chain. Dioxins can cause developmental and reproductive problems, can cause cancer, interfere with hormones and can also decrease the immunity (WHO 2013).

Other carbon based organic pollutants include persistent organic pollutants (POP’s) which are not easily degradable in the environment. POP’s include

Table 14.1 General description and environmental behaviour of some organic pollutants

POPs	Half–lives	Environmental behaviour in soil
Aldrin	10,000–30,000	Persistent
Chlordane	10,000–30,000	Persistent
DDT	10,000–30,000	Persistent
Hexachlorobenzene	>30,000	Persistent
Mirex	>30,000	Persistent
PCBs	>10,000	Persistent
Polychlorinated dioxins	3000–10,000	Persistent
Polychlorinated furans	10,000–30,000	Persistent
Phenanthrene	2.5–4400	Mineralization
Flouranthrene	2.5–4400	Persistent
Benzopyrene	1368–13,000	Persistent

polycyclic aromatic hydrocarbons (PAH), polychlorinated dibenzofurans (PCDFs), polychlorinated biphenyls (PCBs), polybrominated biphenyls and pesticides such as organophosphorous and carbamates (ex DDT), etc. There are only few studies which deal with the toxicity of these organic pollutants in soil (Burgess 2013). Polycyclic aromatic hydrocarbons (PAHs) pollutants in soil are of major concern due to their recalcitrant and carcinogenic properties (Wilson and Jones 1993). Incomplete combustion of organic material in volcanic activities, burning of fossil fuels, forest fires and hydrothermal wells are important natural sources of PAHs.

Polychlorinated biphenyls are wide spread in all environments due to their use as additives in plastics, electrical insulators, in pesticides, etc. PCBs are introduced into soil through various routes such as application of pesticides or deposition of air particles, etc. Pesticides such as DDT (Dichlorodiphenyltrichloroethane) are also hazardous to soil health due to their persistent nature and their ability to undergo bioaccumulation via process called biomagnification. The general description, half-lives and environmental behaviour of some organic pollutants is given in Table 14.1.

These organic pollutants have structural composition with atoms (such as bromine, sulphur or and chlorine) placed at some unusual positions not commonly found in nature. Due to their persistent nature, these synthetic organic chemicals do not break down easily and consequently prove toxic to living creatures. Hence, these pollutants build up over time in body tissues, or become magnified along food chains. The industries create these compounds in very large quantities; many POPs are actually by-products of these processes.

14.5.2 Non-chlorinated

Apart from, chlorinated compounds, non-chlorinated chemicals also contribute towards soil toxicity. These compounds include volatile organic compounds mainly. Non-chlorinated compounds are diverse and ubiquitous. The main non-chlorinated compounds which play role in soil toxicity are alkenes such as ethane; aliphatic such benzene, ethyl benzene, xylene or toluene.

14.6 Solution to Soil Toxicity

Soil is the most valuable resource of the nature. As soil is a source of human food also so, healthy and productive soil is essential for the survival of mankind. But, modern agricultural practices, rapid industrialization and many other anthropogenic activities contribute a significant amount of pollutants to soil resulting in soil toxicity. Soil toxicity has many negative effects as it affects soil biological activities as well as soil physico-chemical properties. It is threat to soil fertility and crop productivity as it changes the original nature of soil. With the widespread awareness regarding adverse impacts of soil toxicity, there has been increasing interest in techniques that carry out remediation of soil toxicity. There are many strategies used as a solution to soil toxicity. The strategies in which total concentration of pollutant must be lowered are termed as 'Clean up technologies'. While the strategies that do not aim to lower the pollutant concentration but aims to measure the exposure to pollutant along with taking into consideration the health and environmental risks are called 'Containment technologies'. All these strategies can broadly be categorized into four classes (Fig. 14.3). These classes are described below:

14.7 Thermal Methods

Thermal methods (Fig. 14.4) hold a significant position in remediation of soil pollution as they meet the clean-up standards. Thermal methods remediate the soil pollution site very efficiently and quickly. There are many thermal operations which are used for remediation of toxic soil. These methods are described under:

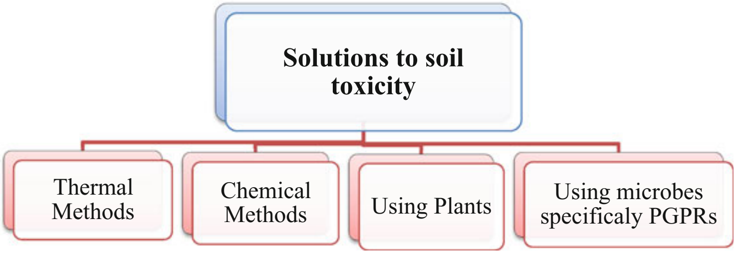

Fig. 14.3 The various solutions for the management of soil toxicity

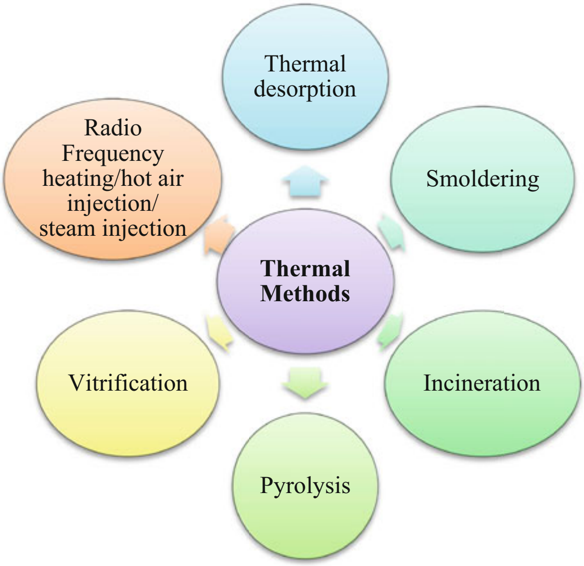

Fig. 14.4 Thermal methods for the management of soil toxicity

14.7.1 Thermal Desorption (TD)

This method involves heating of toxic soil so that the toxic pollutants present in soil either volatilize or get desorbed. The pollutants after volatilization or desorption are removed by vacuum or gas stream. Then these are destroyed by carbon adsorption or incineration (Roberts 1998). There are two variations of TD; one is LTTD and other is HTTD.

- *LTTD*: It refers to low temperature thermal desorption. In this temperature are 100–300 °C.
- *HTTD*: It refers to high-temperature thermal desorption. In this temperature varies from 300 to 550 °C.

Thermal desorption can be carried out ex situ as well as in situ. In ex situ thermal desorption, contaminated soil is excavated and then subjected to thermal desorption units such as rotary drums or thermal screws for heating. Desorbed pollutants are incinerated or disposed using activated charcoal after they are swept away from heating unit. In situ TD involves, use of vacuum wells or dual heaters to desorb and remove soil toxic pollutants using vapour extraction. Gases evolving during the process can be collected for reuse or disposed. Both the methods are highly effective and remove contaminants quickly and efficiently. The cost for TD depends on the contaminated soil. This technique is highly useful for removal of volatile or semi-volatile toxic pollutants.

14.7.2 Smoldering

Smoldering is the exothermic flameless combustion process. Heat, water and carbon dioxide are the final end products after the combustion process. The average temperature in smoldering process ranges from 600 to 1100 °C (Hasan et al. 2015). This process is widely used for oil contaminated sites. During the early phase, combustion is initiated by providing air injection and heating. After ignition, heating can be stopped but air injection will continue as long as the remediation process is not completed. Conduction and convection heat up the soil. This lead to desorption of contaminants as the temperature rises. Pyrolysis can also occur. Therefore, smoldering is a process of exploiting a self-sustained flaming wave to destroy soil pollutants. Off gases are collected for disposal or reuse. Smoldering is useful in treating soils that are hampered with heavy hydrocarbons. Studies have claimed successful removal of significant levels of hydrocarbons through smoldering.

14.7.3 Incineration

Incineration refers to the complete removal of contaminants from polluted soil through combustion at very high temperature. This technology has been found suitable to remove toxic hydrocarbon, municipal and many other hazardous wastes. Depending upon the site of action, it can be on-land or onsite incineration with no excavation of contaminated soil. However, this method of on-land or open burning is problematic, unpredictable and expensive. Therefore, more reliable is the ex situ incineration technology that involves the excavation of contaminated soils followed by combustion in controlled incineration units (Fingas 2010).

Incineration demands the maintenance of high temperature for a continuous period which makes it an expensive technology. Despite, it is a widely used remediation technology owing to its efficiency and effect on a broad range of target contaminants. It can also destroy nearly flammable pollutants.

14.7.4 Pyrolysis

Pyrolysis is defined as the heating of impacted soils in anoxic atmospheres, typically to 400–1200 °C for a variety of hazardous waste. When applied to soils, pyrolysis can function in two different ways. If soil temperature is increased gradually, the pollutants with low molecular weight will first undergo thermal desorption when heated to their boiling temperature. Later, at temperature >250–300 °C, the high energy chemical bonds of the contaminant destroy and it may generate reactive radicals. These bonds and the order in which they are cleaved usually involve C-heteroatom (i.e., C–S) bonds, followed by C–H and then C–C bonds. The reactive radicals may continue their self-destruction reactions (beta-scission) or may initiate a chain of aromatic condensation reactions that results information of a carbonaceous material (char) with very low H/C ratio (Shearer 1991).

Pyrolysis can remove the soil contaminants at low temperature. It saves energy and sequesters carbon in the form of char.

14.7.5 Vitrification

In vitrification, contaminants are heated to very high temperatures (1600–2000 °C), melted and fused with soil to form a glass-like solid. Radioactive wastes are mostly treated by using this method. It works on the principle that contaminant solid in its molten state develops properties similar to an obsidian and with strength ten times greater than concrete (Shearer 1991). Further, rapid cooling of these molten contaminants prevents crystallization and it develops into stable glass from the non-volatile materials. Soils rich in a variety of organic contaminants such as petroleum or those receiving hazardous inorganic wastes such as heavy metals are best cured by vitrification.

14.7.6 Radio Frequency Heating/Hot Air Injection/Steam Injection

Heating the contaminant by high frequency radio waves (RFH, i.e., microwave heating) can serve as one of the remediation techniques that enhance the efficiency of other processes such as air sparging, bioremediation and enhanced vapour recovery. RFH removes low molecular weight hydrocarbons by causing their volatilization and desorption, improves bioavailability, decreases viscosity and speeds degradation by microbes (Price et al. 1999).

Hot air injection is a soil vapour extraction remediation which functions by increasing mobility and extraction efficiency of the contaminant. More often, steam is used as an additional component with hot air for more efficient transmission of desorbed organics into the vacuum well. The heating capacity of steam is higher than hot air, therefore provides more efficient means for heating soils; when easily accessible (Roberts 1998).

Despite such advantages, thermal methods have disadvantages also. In thermal operations, heating the toxic soil is quite labour intensive and it is very costly also. High temperature used during thermochemical operations can destroy soil organic matter, soil minerals and even soil microbial biota. So although, thermochemical methods efficiently remove the contaminants from soil, yet they are not so much desirable due to their negative impact on soil and plant growth.

14.8 Chemical Methods

Technicians are putting continuous efforts in developing strategies that are environment friendly, simple and economical to maintain and restore quality of soil. A number of chemical based technologies are prevalent to treat polluted soils. These include the small scale remediation approaches with simpler technology; as well as those occurring at a large scale that often encounter more difficulties due to complexity, high costs and several side effects. Chemical treatments (Fig. 14.5) commonly used for the remediation of polluted soil are discussed below:

14.8.1 Encapsulation

In this chemical treatment method, contaminated soils are isolated through low permeability walls or caps to prevent the infiltration of precipitation. The commonly used polymers as barrier for encapsulation are polyethylene, EIA (ethylene interpolymer alloy) and PVC (Poly vinyl chloride). The method of encapsulation for the treatment of toxic soil is economical and simple method. This method has some disadvantages like there is no complete destruction of the contaminant, i.e. it remains at the site of remediation, also the efficiency of this method is limited by time. A number of other factors like properties of the contaminated site and depth of contaminant also influence this remediation process (Mulligan et al. 2001).

14.8.2 Chemical Oxidation

This method relies on a redox reaction involving the formation of stable organometallic complexes through the percolation of organic and inorganic reagents by reduction of metals to their lowest valence state. The most effective oxidizing agents for both inorganic and organic contaminants are chlorine dioxide, hydrogen peroxide and potassium permanganate. Although chemical oxidation is low-cost method

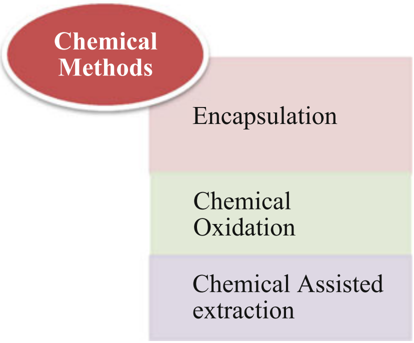

Fig. 14.5 Chemical Methods for the management of soil toxicity

yet it is rather expensive in the case of high-contaminant concentrations (FRTR 2002).

14.8.3 Chemical Assisted Extraction

This method involves the action of chemicals like EDTA (ethylene diaminetetraacetic acid) for abstraction of metals during vigorous mixing. These function as metal chelators that cause the removal of metals from the contaminated soil via extraction. This method is cost effective and even efficient for high dose of metals; but it has been found that the chelator itself may persist long in soil and have harmful effects on plants and other soil biota (Tandy et al. 2004).

14.9 Use of Plants in Toxicity Removal

Traditionally used thermal or chemical soil remediation methods are costly and often result in several harmful side effects. Application of biological methods as a solution to soil toxicity problems is the most desirable and cost effective approach as it has many benefits over thermochemical methods. Green technologies involving phytoremediation have gained popularity due to its environment friendly nature. This technique utilizes green plants for the remediation of pollutants from the environment (Bisht et al. 2014a). It is quite popular and acceptable among the society due to its environment sustainability and aesthetic appeal. Phytoremediation is an autotrophic system, simple to handle with very less requirement of nutrients. There are many plants which are capable of accumulating much diverse range of toxic pollutants into their vegetative or reproductive parts. There are many features which are desirable in plant for its use in phytoremediation. These desirable features are listed below:

- Plant should be fast growing.
- It should have high biomass production.
- It should be native species with extensive root system.
- It should be highly tolerant and capable of accumulating various toxic pollutants.

Phytoremediation of heavy metal polluted soils can be achieved via different mechanisms which include phytoextraction, phytostabilization and phytovolatilization. The first step in phytoremediation is the extraction of soil pollutant from the soil solution (Bisht et al. 2014b). This is followed by the mobilization of pollutant towards surface of roots. The toxic pollutants then bind to root cells and are uptake by roots after recognition and then these pollutants are transported to aerial parts of plants. Transporter proteins along with vascular system are involved in this transportation process.

Being a cost effective, environmental friendly approach, this technique is quite successful when the toxicity levels are low. But, when there is high amount of toxic

Table 14.2 Variations of phytoremediation technique

Phytoextraction	• It is the most common form of phytoremediation • It includes pollutant accumulation; especially heavy metals, in the roots and shoots of phytoremediating plants (can cause problem in food chain). These plants are later harvested and incinerated • Plants used for phytoextractions should have high growth rate, high biomass, extensive root system, and ability to tolerate high amounts of heavy metals
Phytostabilization	• It involves immobilization of metals by plants, resulting in reduced metal bioavailability via leaching and erosion • It is often practiced when phytoextraction is not desirable or even possible • Phytostabilization is the result of metalvalence reduction, precipitation, sorption, or complexation • The plants used for phytostabilization should necessarily have (1) ability to tolerate variable soil conditions, (2) dense root system, (3) rapid growth to provide adequate ground coverage, (4) ease of establishment and maintenance underfield conditions, (5) longevity and (6) ability to self-propagate
Phytovolatilization	• Phytovolatilization is when the plants are allowed to take up pollutants from the soil and then these pollutants undergo transformation into volatile compounds which are transpired into the atmosphere through aerial parts of the plant
Phytodegradation	• It involves the role of plant associated microbes that degrade metal rich organic contaminants
Rhizofiltration	• Plant roots serve as filters to absorb metals from waste in soil

pollutants, the growth of plants retards with less biomass yield. There are many variations in phytoremediation which are described in Table 14.2.

14.10 Use of Microbes Specifically PGPR's in Toxicity Reduction

The limitation of phytoremediation technique, in high toxicity level necessitates the need of other biological sources. The disadvantage of phytoremediation can be overcome using rhizobacteria for the remediation of soil toxicity. PGPR represent a wide array of soil bacteria which, when allowed to grown in association with plant roots, causes the stimulation of the host growth (Vessey 2003). PGPR can impose a positive effect on plant growth by two mechanisms: direct and indirect. During direct growth promotion, these bacteria synthesize various phytohormones, reduces the root membrane potential for better nutrient absorption, synthesize enzymes like ACC deaminase that influence plant hormone production, fixes atmospheric N, produce organic acids to solubilize of inorganic phosphate, mineralize organic phosphorus compounds, mobilize phosphorous to the plants. Indirect promotion of plant growth by PGPR involve activities that induce plant stress response through hormonal signaling or those reducing the deleterious effect of pathogenic microorganisms like synthesis of antibiotics or siderophores.

Apart from the plant growth promoting mechanisms, PGPR strains reduce the toxicity of by converting the pollutants into less toxic form, helping in disease management, modulating bioavailability and help in mitigation of soil toxicity. Several PGPR (*Pseudomonas putida, Bacillus subtilis* and *Enterobacter cloacae*) have been effectively used for the remediation of heavy metals. Some bacteria also enhance the efficiency of phytoremediation by promoting plant growth, alleviating pollutant phytotoxicity, altering bioavailability of pollutants in soil and increasing translocation within the plant.

Use of PGPR in the remediation of soil pollutants is emerging as one of the most effective ways as microbes possess the ability to use these compounds as carbon and nitrogen source.

14.11 Mechanism of PGPR Action

Bacteria remediate organic contaminants through unique degradation pathways of their metabolism (Boopathy 2000). However, bacterial bioremediation may limit in terms of rate and efficiency when the polluted in soil is specifically recalcitrant hydrocarbons (Grishchenkov et al. 2000). PGPR along with the assistance of plants helps in remediation of various toxic pollutants. For example: the plant rhizosphere is rich in root exudates which serve as substrate for microbial growth and metabolism; as well as it maintains soil pH to favour microbial activities (Kumar et al. 2017) The various mechanisms used by PGPR (Fig. 14.6) for the management of soil toxicity are described below:

14.11.1 Acting as a Metal Chelator

In natural environments, the pollutants which are soluble in soil solution like metals are readily absorbed by plant. Whereas, those pollutants present in insoluble

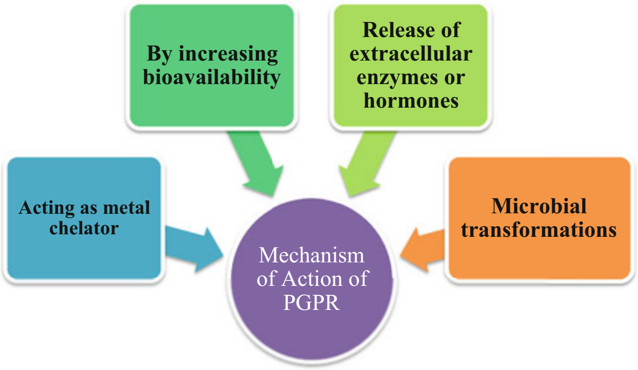

Fig. 14.6 Various mechanisms of PGPR action

precipitate form are unavailable for plant uptake. These recalcitrant pollutants are made available to plants by the application of chelators that causes precipitation and sorption by forming metal chelate complexes. This improves the availability of these pollutants in soil solution (Marques et al. 2009). Addition of chelates has been found an effective approach for improved transport of metal pollutants through the precipitate dissolution and desorption (Norvell 1984). PGPR also release chelating agents to increase the biological availability of pollutants. Examples of chelates include EDDHA (ethylenediamine-di-o-hydroxyphenylacetic acid), EDTA (ethylenediaminetetraacetic acid), EDDS (SS-ethylenediaminedisuccinic acid), HEDTA (N-hydroxyethylenediaminetriacetic acid) and DTPA (diethylenetriaminepentaacetic acid).

PGPR are known to produce organic acids like malic and citric acid; which have an effective chelating ability and therefore; can improve phytoextraction of pollutants from soils. The main disadvantage of using chelates for pollutant bioavailability is the risk of their leaching and the groundwater contamination (Lombi et al. 2001).Synthetic chelates are also available but these may have toxic effect on plants and disturb soil microbial dynamics if used in concentration too high (Chen et al. 2004).

14.11.2 Increases Bioavailability

Bioavailability refers to the amount of element which is available for organism to uptake or adsorption across cellular membrane. In soil toxicity context, it refers to the availability of contaminants. Toxic pollutants can only be taken up if they are in available form (dissolved in water). But, the contaminants are not always present in available or dissolved form. Organic contaminants may become sorbed or sequestered in organic matter. Heavy metals get precipitated into the solid phase. Volatile compounds can be lost as aerosols to the atmosphere. So, in all these forms pollutants are not available for uptake by microbes or plants. So, these toxic contaminants must be dissolved in soil solution to become biologically available. PGPR increase the bioavailability of various pollutants for their degradation.

14.11.3 Release of Extracellular Enzymes/Hormones

Many enzymes are produced by microbes (Kaur et al. 2020). These enzymes also act as indicator of soil health (Kaur et al. 2014). Enzymatic breakdown mediated degradation of pollutants is one of the most important mechanisms used by PGPR. Many hydrolytic enzymes are released by PGPR. These enzymes serve as an essential factor in biocontrol and nutrient recycling. Microbial hydrolytic enzymes can easily hydrolyse the various toxic pollutants. Pollutant rich in cellulose can serve as substrate for microbial cellulose enzyme while keratin for keratinase and chitin for chitinase. Kraft pulp degradation is observed in the presence of both xylanase and β-xylosidase, and sewage sludge is acted upon by protease and phosphatase.

Similarly, synthetic insoluble pollutants like nylon can undergo hydrolysis by enzymes like Mn-dependent peroxidase (MnP), polyacrylate by cellobiose dehydrogenase, polyurethane by esterase, poly-l-lactic acid by depolymerase and alkaline protease (Gramms et al. 1999).

Mostly the bacteria which are used as PGPRs can also produce these enzymes. Understanding the role of PGPRs with activities like ACC deaminase; in mitigating plant stress conditions is currently the focus of researchers. Pollutants having inorganic nitrogen and phosphorous, are utilized by PGPR having nitrogenase and phytase enzyme, respectively. Dehalogenase enzyme hydrolyses chlorine and fluorine from halogenated aliphatic and aromatic hydrocarbons. Laccase, peroxidases and dioxygenase help in the degradation of various organic pollutants. Nitrilase enzyme remove cyanide group from nitriles whereas the nitroreductase enzyme removes nitro group from various nitro compounds (Pieper et al. 2004).

14.11.4 Through Microbial Transformation

Many substances used by microbes are structurally similar to pollutants (Singer 2006). This structural similarity (analogy) favours the accidental uptake of pollutants by microbes called microbial co-metabolism. The oxidative breakdown of a non-growth substrate in the presence of another other growth substrate is termed as co-metabolism. It is observed as a major pathway behind the microbial transformation of pollutants or other complex substrates in environment. Biotransformation refers to the structural modification in chemical compounds (pollutants) that may lead to the formation of new molecules with less toxicity. This mechanism has been developed by microbes to acclimatize to environmental changes and it is functional in a wide range of biotechnological processes. Examples of major microbial transformation are as under:

1. Steroids and sterols.
2. Non steroid compounds.
3. Antibiotics.
4. Pesticides.
5. Other pollutants.

14.12 Role of PGPR in Managing Soil Toxicity

PGPRs are an intact part of bioremediation clean up strategies which aim to reduce the whole proportion of toxic pollutant in soil through various degradative activities of microbes. These microbial groups participating in soil toxicity reduction are also categorized as degraders. These degraders use the pollutants as a source of nutrients and energy. Enrichment of polluted site with specific strains of degrader microbes to boost the remediation process is also practiced as technique named bioaugmentation. A number of remediation trials using non-indigenous strains of degrader PGPRs have been reported by researchers at site with varying degrees of pollution. However, so far; no strong evidence has been documented indicating significant remediation by non-native microorganisms for tested situations.

The benefit of using PGPR in soil toxicity remediation is that they can are very cost effective. However, microbial bioremediation is more time consuming than other thermochemical or phytoremediation treatments. This is because microbial activities are more sensitive to even minute changes in the degrading environment, nature and dose of the pollutant. Although, not all soil pollutants are amenable to be managed by PGPR yet, but successful results has been observed for soils polluted with petroleum hydrocarbons, wood preservatives, pesticides, solvents and other organic or inorganic chemicals.

14.12.1 Use of Inorganic Compounds

The genus *Bacillus;* specifically *B. subtilis,* has been found with ability to reduce nonmetallic compounds. Garbisu et al. (1995) recorded reduction of toxic selenite to a less toxic product by application of *B. subtilis*. More interestingly, chelating effect of *B. thuringiensis* and *B. cereus* has also been reported for the increased bioavailability of Cd and Zn in soil polluted with waste from metal industry(Mohideena et al. 2010). The chelators facilitating extraction were the siderophores produced (Fe complexing molecules) by these bacteria in soil. It was emphasized that presence of heavy metals must have induced the production and release of siderophore by bacteria which consequently improved metal bioavailability (Lelie et al. 1999). Another bacteria with sulphate reducing ability (*Desulfovibrio desulfuricans*) can also remediate polluted soils; indirectly by bioprecipitation. It reduces the sulphate sulphur to hydrogen sulphate which further reacts with heavy metals such as Cd and Zn to form of metal sulphides.

14.12.2 Use of Organic Compounds

Plant Growth Promoting Rhizobacteria plays a key role in the degradation or removal of contaminants and provides an environmental friendly zone for the plant to thrive (Schwab and Banks 1994). Rhizobacteria are extensively used for remediating soils with organic pollutants. However, results are found more efficient with the synergistic action of plants and microorganisms. The combined approach offers greater efficiency because plant roots can penetrate through the varied substrates and layers of soil and expose the entrapped pollutant to microbes that might have previously been inaccessible (Parrish et al. 2005). In addition, the plant roots can provide natural niche to the degrader microbes; which in turn can stimulate plant based phytoremediation in conditions of stress (Huang et al. 2004a). These benefits from mutual action may have limited the overall efficiency of remediation process probably by effect on the transport of waste from roots to shoots, which is necessary because organic pollutants inhibit photosynthesis (Huang et al. 2004b).

Organic pollutants are generally categorized as recalcitrant xenobiotic pollutants mostly present in high residual concentrations in soils. These generate a significant environmental concern due to their hazardous nature, ability to exist as mutagen or carcinogen (Baek et al. 1991).Phytoremediation of organic pollutants have been attempted several times (Shann and Boyle 1994). However, the presence and survival of beneficial PGPR in organic pollutant rich environment is rarely observed. The success of microbial based bioremediation in such conditions entirely relies on the rhizosphere competence of microbes (Weller and Thomashow 1994). It reflects by the ability of the selected microbes to establish in the plant rhizosphere, sustain insufficient numbers, compete for exudate nutrients, survive the changing environment and keep colonizing the developing root system efficiently (Lugtenberg and Kamilova 2009).

It has been observed in a study that varying doses of TPH undergo successful reduction with the help of two PGPRs strains *Enterobacter cloacae* UW4 and *E. cloacae* CAL2. It was the enzyme aminocyclopropane-1-carboxylate (ACC) deaminase released by PGPR that played the key role in degradation process by reducing the ethylene levels of total petroleum hydrocarbons (TPHs) and making it degradable. Similarly, polycyclic aromatic hydrocarbons (PAHs) have been remediated by enzymes: dioxygenases (e.g., 1,2-dihydroxynaphthalene dioxygenase), dehydrogenases (e.g., 1,2-dihydroxy-l,2-dihydronaphthalenedehydrogenase) and aldolases (e.g., cis-2-hydroxybenzalpyruvate aldolase) released by *Pseudomonas paucimobilis*Q1. One of the most prevalent organic pollutants is polychlorinated biphenyls (PCBs); successfully remediated with enzyme biphenyl dioxygenases of microbial origin. Recombinant *Pseudomonas fluorescens* has been found effective in remediating trichloroethylene (TCE) by producing toluene o-monooxygenase. Microbial enzymes like lignin peroxidase (LiP) and Mn-dependent peroxidase (MnP) are able to degrade biopolymers such as kraft and lignin or trinitrotoluene (TNT).

14.13 Future Advancement

Once it is confirmed that soil is toxic and need for its remediation is recognized, then the next step is the selection of best technology for the soil remediation. The best available technology is dependent on many factors like the origin of the contaminant, nature and degree of toxicity, the conditions of soil containing pollutant (pH, moisture, temperature, organic matter, nutrients, microflora), the time available for remediation, the social acceptance and process economics. These different criteria vary widely among all the technologies. But the major need is the development of low-cost, low-input technologies that can tackle remediation of polluted soils.

Owing to ever-rising community concern for the harm posed by soil pollution, the development of more efficient, multi-action strategies in future is quite expected for human welfare. But at present, with emphasis on being cost effective, sustainable and environmental friendly technologies, PGPR are considered as the best method for the management of soil toxicity. Rapid advancements occurring in molecular biology will offer a better understanding of the microbial mechanisms involved in remediation of soil toxicity. This knowledge is of fundamental importance in order to optimize these processes.

14.14 Conclusion

Toxicity of soil is an important problem affecting soil properties, agriculture productivity and even human health. Remediation of soil toxicity with sustainable methods is gaining interest of researchers. Among all the approaches used for remediation of soil toxicity, biological systems using PGPR are getting popularity as they are eco-friendly and cost effective. But, a key element in use of PGPR in remediation methods is the understanding of the microbe–plant interaction. Despite many progress made in the soil toxicity remediation, the research is still at its infancy. Molecular engineering of degrader microbes and/or plants is an aspect still unexplored. It would provide opportunities to enhance efficiency or manipulate microbial metabolism for remediation of various soil pollutants. As a result, some PGPRs even have potential to increase plant tolerance to degraded soil and other extreme conditions.

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Earthworms, Plants, and GMO's Towards Natural Bioremediation

15

Rajalakshmi Sridharan and Veena Gayathri Krishnaswamy

Abstract

The development of urbanization and increase in population has lead to the production of synthetic compounds. These compounds are toxic if not treated properly. The process of treatment of these pollutants are widely studied and explored using various methods such as physical, chemical, and biological methods. The biological method of treatment was reported to be effective in treatment of pollutants by degrading into less toxic compounds. There are also some limits in this biological process as not all the biological living systems are used for the treatment of toxic compounds. The use of microorganisms has thrown light on the remediation and degradation of pollutants. But, the range of usage of the living systems is broadened even by using plants, invertebrates, and other classes of living forms. This might be a wider area for choosing the better method in biological treatment process. Each method has it pros and cons, instead turning it into an advantage for the sustainable environment requires the input of some biotechnological knowledge by developing a new strain or modifying the native strains for enhanced results. Hence, this chapter focuses on the upcoming and hardly explored methods of bioremediation involving earthworms (vermiremediation), plants (phytoremediation), and remediation using genetically modified organisms.

Keywords

Bioremediation · Earthworms · GMO's · Plants

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Table 15.1 Classification of earthworm (Goody 2018)

Phylum	*Annelida*
Class	*Clitellata*
Subclass	*Oligochaeta*
Order	*Haplotaxida or Lumbriculida*
Family	*Acanthodrilidae* *Ailoscolidae* *Alluroididae* *Almidae* *Criodrilidae* *Eudrilidae* *Exxidae* *Glossoscolecidae* *Hormogastridae* *Lumbricidae* *Lutodrilidae* *Megascolecidae* *Microchaetidae* *Ocnerodrilidae* *Octochaetidae* *Parganophilidae*

15.1 Introduction

Earthworms are Oligochaetes which are commonly referred to as soil engineer. Earthworms are involved in soil turning, mixing of soil zones, breaking down inorganic matters and they are collectively called pedogenesis (Carpenter et al. 2008; Coleman and Wall 2015). The classification of earthworms is given in Table 15.1.

15.2 Habitat

Earthworms are found widely in the aired and moisturized soil where the temperature is favorable. The earthworms are found abundance in temperate, tropical, and grassland regions (Curry et al. 1995). The habitats of earthworms are specified by the niche in which they live. The niche differs from family to family, species to species. The location of a niche by earthworm species indicates its physical characteristics. The niche of the earthworm can be identified by their color, size, and active movements (https://www.sciencelearn.org.nz/resources/7-niches-within-earthworms-habitat).

15.3 Classification of Earthworms Based on Niche

The earthworms, based on the niche in which they survive are classified into Epigeic (surface soil dwellers), Endogeic (topsoil dwellers), and Acenic (deep burrowing dwellers). The Fig. 15.1 shows the niches of earthworms and Table 15.2 explains the

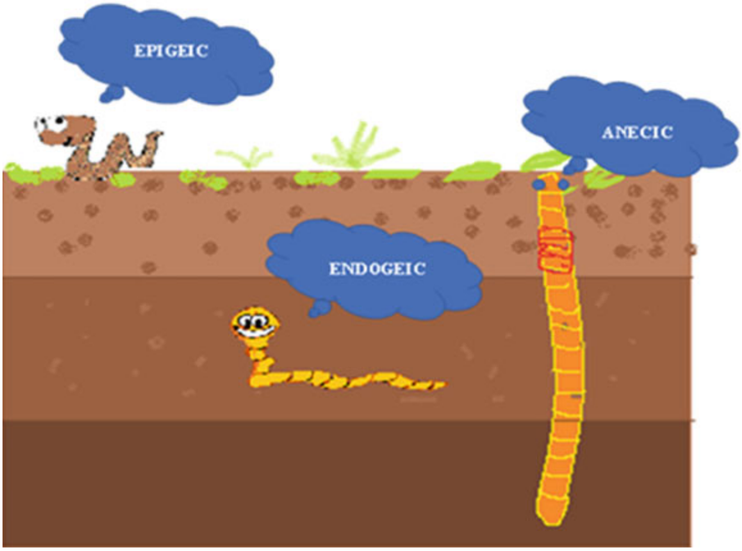

Fig. 15.1 The niches of earthworms (https://www.sciencelearn.org.nz/resources/7-niches-within-earthworms-habitat)

Table 15.2 Characteristics of earthworms based on niche (https://www.sciencelearn.org.nz/resources/7-niches-within-earthworms-habitat)

Niches	Size	Pigmentation	Movements	Channel	Soil depth
Epigeic	1–18 cm long	Dark	Quick	Not permanent	A top surface of the soil
Endogeic	2.5–30 cm long	Sparingly pigmented	Quick	Shallow semi-permanent burrows	Top 20 cm depth
Acenic	3 cm to 4 m long	Less pigmentation (mostly pale)	Sluggish	Extensive permanent burrows	3 m below the soil surface

characteristics of earthworms in each niche (https://www.sciencelearn.org.nz/resources/7-niches-within-earthworms-habitat).

15.4 Earthworms—Biomonitors of Soil Pollution

Earthworms are used as biomonitors as they accumulate the pollutants and break them with the help of microbiota and enzymes present in it or produced by it. The plants, snails, honey bees are also used as biomonitors but these organisms are not widely available and not easily cultivable (Harnly et al. 1997; Hirano et al. 2011). This explains the need for alternative biomonitors and earthworms fit the best. The earthworms are exclusively studied for its gut microbiota. Bioremediation by the microbiota and by the earthworm itself provides a new perspective. The toxicity and concentration of the pollutants have a direct effect on earthworm population. Thus, the processes of studying the toxicity of the pollutants are called as Ecotoxicology. *Eisenia fetida* are widely used as biomonitor for testing the toxicity as it is sensitive to pollutants (Brulle et al. 2006).

15.5 Earthworm—Home for Microbiota

The microorganisms in soil are enriched by the presence of earthworms. The earthworms have diverse gut microbiome as they feed on the various inorganic matters in the soil. Soil microorganisms ingested by the earthworm constitute a part of the diet. The elimination of irrelevant microbes and assimilation of nutrients by the symbiotic microorganisms present in the gut aides in enhancing the soil fertility (Edwards and Bohlen 1996). The mucus present in the earthworm gut provides an ideal environment for the growth of microorganisms (Barois et al. 1986). Hence, the digestive system of the earthworm is considered as "mutualistic digestive system" (Barois et al. 1986; Lavelle et al. 1995).

These microorganisms develop resistance against pollutants in the soil which in turn makes the earthworm resistance to the polluted environment and aids in the survival. Thus, earthworms and its microbiome have its importance not only in composting and maintaining soil fertility but also in degrading the pollutants either by the microorganisms in the gut of earthworm or in the niche in which they survive.

The microorganisms in the earthworm gut were observed to act as plant growth-promoting factors, nitrogen fixers, and phosphate solubilizers (Loreno-Osti et al. 2004; Romero and Martínez 2001). These microbes are known to exhibit mutualism (Brown et al. 2000; Barois and Lavelle 1986). The studies showed that there was an increase in the δ-*proteobacteria* and the *Cytophaga flavobacterium* post digestion and decrease in the α-, β-, and γ- proteobacteria (Horn et al. 2003). The genus *Acidovorax*, *Streptomyces*, and *Mycobacterium* were found in the earthworm gut (Thakuria et al. 2010). The number of actinomycete and bacterial isolates was found to be higher in number in the gut than in the soil. *Allolobophora caliginosa* contained more yeast, fungi, and bacteria in its gut. The number of microorganisms varies according to the feed of earthworm (Parle 1963). It was studied that the pH of the gut content is neutral as it contains 40% to 70% of the water in it. The pH of the midgut is slightly acidic compared to the anterior and posterior gut parts (Lee 1985). The carbon and nitrogen ratio in the gut of earthworm was observed to be seven which are due to high total carbon, organic carbon, and nitrogen in the gut (Horn et al. 2003).

15.6 Evolution and Resistivity for Survival in Pollution

The concept of earthworm resistivity rose during the years 1953 and 1979, the period where the Hudson River was contaminated by approximately 53 tons of cadmium and nickel hydride. The concentration of cadmium was more than 10,000 ppm in the river beds and the sediments. This, in turn, has to affect the survival of the earthworm population in the river sediments. Instead, the earthworm species *Limnodrilus hoffmeisteri* survived in the highly cadmium contaminated environment. Thus, it proved that the prolonged exposure of cadmium developed resistance in earthworms and this led to the survival of the earthworms. To study the concept of development of resistivity, researchers studied that the presence of the protein metallothionein (metal-binding protein) was the reason for the resistivity of cadmium/metal resistance in earthworm population. The major reason behind the resistivity was observed to be the gene that already existed in the earthworms and it was activated when the earthworms are exposed to cadmium. This reported that there is no role of evolution in the development of resistance in earthworms (Levinton et al. 2003; Blackman 2003). The heavy metals in the soil were reported to reduce the fertility, cocoon production, growth and cause earthworm mortality (Spurgeon et al. 1994; Siekierska and Urbanska-Jasik 2002; Nahmani et al. 2007; Usmani and Kumar 2015).

An outbreak in Italy by Seveso chemical plant explosion in the year 1976, in which the land was contaminated by chemical named TCDD (2, 3, 7, 8-tetrachlorodibenzo-p-dioxin). The earthworms survived by bio-accumulating the dioxin in their tissues up to 14.5-fold of its concentration (Satchell 2012). It is also reported that the earthworm can convert the fly-ash produced by coal plants into vermicompost. The heavy metals such as Cd, Cu, Ni, Pb, Zn are toxic to the earthworm species (Spurgeon and Hopkin 1995). The uptake and excretion of heavy metals by earthworms occurs either by biotransformation or biodegradation. The metals that enter the gut by ingestion get metabolized, immobilized, and excreted as non-toxic casts into the environment. The bioaccumulation of Pb occurs in the muscles, nerve chord, cerebral ganglion, seminal vesicles, and other parts which pass to the cocoon. This availability of Pb in the cocoons affects embryo development (Gupta et al. 2005). The earthworm's survival hacks are based on the process of bioaccumulation and biotransformation of heavy metals or other organic pollutants. The toxic heavy metals and pollutants get accumulated in the tissues and this cleanup process aids in the revival of the contaminated soil (Elliot 1997; Usmani and Kumar 2015). This made earthworm a potential bioindicator which helps to determine the concentration of the pollutant in the soil by assessing the quantity of pollutant accumulated in the soil (Butt 1999).

The earthworms are quoted as soil engineers as they contribute to soil structuring. This explains the importance of earthworms in agriculture as it plays a key role in the biogeochemical cycle. The application of pesticides/insecticides in the soil to prevent the loss of crops by pest invasion was developed. Thus, there is a need to test the toxicity of the pesticide on the living organisms. The toxicity of the pesticide or any other pollutant determination is achieved by performing Acute and Reproductive toxicity analysis. This includes monitoring the physical activities, growth, reproduction (cocoon formation and production), maturation, and mortality. The production of cocoons was reported to be inhibited by pesticides such as parathion, endosulfan, and fenamiphos (Yasmin and D'Souza 2010).

15.7 Vermiremediation

Vermiremediation is a process of remediation of contaminated soil using earthworms. This occurs either by absorption or bioaccumulation. The earthworm uptake the pollutants, break down to produce the non-toxic compound in the form of the cast which acts as a nutritional source to enhance fertility. The process of vermiremediation is an unexplored or flourishing technique. Vermiremediation of Poly Aromatic Hydrocarbons (PAH) (Zeb et al. 2020) and heavy metals are being widely studied. Earthworm species such as *Lumbricus rubellus*, *Eisenia fetida*, *Perionyx excavatus* are exclusively studied in the remediation of pollutants (Bhat et al. 2018).

15.8 Phytoremediation

The process of remediation which involves plants for removal of pollutants in soil or water is called the Phytoremediation. In this process, plants act as a trap or filter for removing or stabilizing or degrading the pollutants. The plants are grown in contaminated sites where the plants immobilize or degrade the inorganic pollutants. After a significant decrease in the concentration of the pollutant in the soil or water or after the plants meets its threshold, the plants are harvested and disposed of. The synergistic relationship exists between the plants, soil, and microorganisms. Plants act as a host system for aerobic and anaerobic microorganisms by providing a wide range of colonizable space. Phytoremediation has been used for the removal of pesticides, metals, PAH, solvents, explosives, and leachates (Ahalya and Ramachandra 2006). Table 15.3 explains the types of phytoremediation.

15.9 Merits and Demerits of Phytoremediation

The process includes minimum cost requirement compared to process like solidification, excavation, and leaching (Stehouwer 2014). The phytomining process includes the recovery of accumulated contaminants in the plants as it was

Table 15.3 Types of phytoremediation (http://www.cpeo.org/techtree/ttdescript/phytrem.html)

Rhizosphere biodegradation	Biodegradation by microorganisms in the root of the plants
Phyto-stabilization	Plants immobilize the compounds rather than degrading it
Phyto-accumulation/ phyto-extraction	Accumulation of pollutants in shoots and leaves of the plant
Rhizo-filtration	Ex-situ groundwater treatment by roots
Phyto-volatilization	The uptaken contaminants evaporate through the stomata in the leaves
Phyto-degradation	The contaminants are degraded with the plant tissues
Hydraulic control	The indirect remediation of contaminants by controlling the groundwater movement by the roots of trees

transformed into less toxic than the parent compound. This process is carried in many companies where the extracted contaminants were turned into a finished product. This is an eco-friendly approach which has minimal or no invasion of other species. It also structures the soil and enhances microbial growth (https://sites.google.com/site/thephytersphytoremediation/advantages-and-drawbacks). Planting trees in the contaminated sites makes the site pleasant and appealing (Sasi 2011).

The phytoremediation process also has its demerits. The major demerit that is considered is the duration of remediation. The phytoremediation is the slowest process of remediation of pollutants. This is because remediation is a dependent factor. The growth rate of the plants or trees, the ability of the plant to concentrate or accumulate or degrade the pollutant is considered as an important factor. The process may take even decades to reduce the concentration of the contaminants to half of its initial concentration (Mcgarth and Zhao 2003). The plants are known starters of the food chain. If they are applied in the remediation of pollutants, it should be monitored regularly or it might harm the living organisms at the high tropic level. There are also chances of biomagnification of the pollutants at high tropic level in the food pyramid. This can be avoided by regular monitoring and avoiding or reducing the usage of edible plants (https://sites.google.com/site/thephytersphytoremediation/advantages-and-drawbacks).

Figure 15.2 shows the process of bioaccumulation. The process of bioaccumulation, in turn, leads to the process called biomagnification. This involves the transfer of pollutants from one tropic level to another as shown in Fig. 15.3.

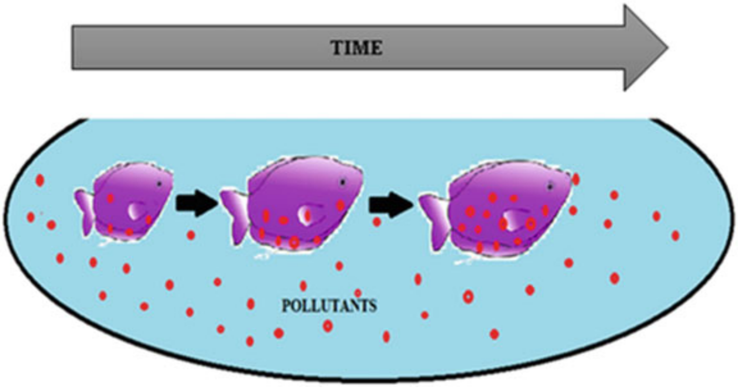

Fig. 15.2 Bioaccumulation of contaminants

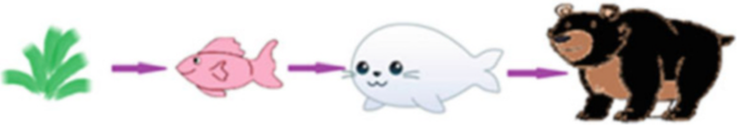

Fig. 15.3 Biomagnification of contaminants

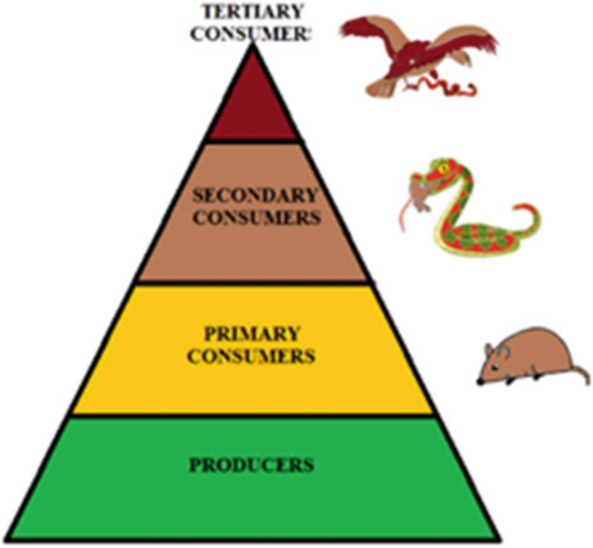

Fig. 15.4 Biomagnification in terrestrial habitats

Persistent Organic Pollutants (POPs) are the major cause of bioaccumulation and biomagnification. The POPs such as DDT, PCBs are not degraded, hence bioaccumulated. In the case of marine pollutants, the biomagnification has its base in phytoplankton. The phytoplankton accumulates the pollutants which passes to the zooplanktons and leads to the accumulation of the pollutants in higher tropic level. Figure 15.4 shows the biomagnification of pollutants in terrestrial environment. Microorganism (GEM), the factors such as target pollutant, the goal of the bioremediation process, the organism of interest and the molecular technique to be performed are to be planned and monitored. The selection of the molecular target depends on the target pollutant as shown in Fig. 15.5. The terrestrial plants that are commonly used in phytoremediation are *Brassica juncea* L (Indian mustard), *Salix* species (White willow), *Populus deltoides* (Poplor tree), *Sorghastrum nutans* (Indian Grass), and *Helianthus annus* (SunFlower) (Fig. 15.6) (Jai 2015). The plants such as alfalfa, corn, dates, and palm are also well-known plants for phytoremediation.

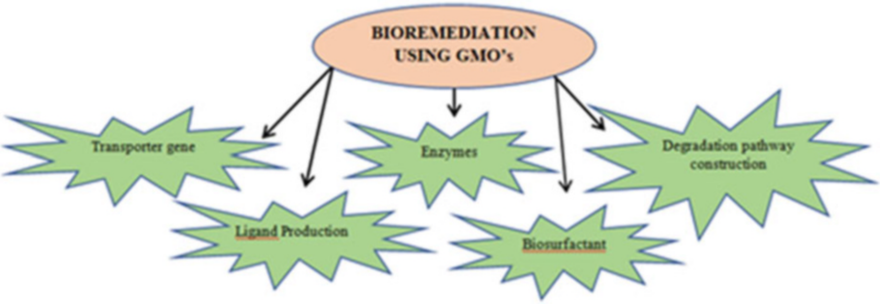

Fig. 15.5 Molecular targets for bioremediation using GEM

Fig. 15.6 *Helianthus annuus* (Sunflower) cultivated as oilseed crop and phytoremediation (https://land8.com/5-best-plants-for-phytoremediation/)

15.10 Biomagnification—A Major Disadvantage

The process of phytoremediation has a great impact on the organisms in higher trophic level. This is caused by the bioaccumulation of pollutants in plants. For this to occur, the pollutants must be lipid-soluble, biologically active, and have long half-life period (Carter 2018). These toxins enter the food web by increasing the concentration of the pollutants in an individual organism (https://cimioutdoored.org/bioaccumulation/). Figure 15.7 shows the process of bioaccumulation. The process of bioaccumulation, in turn, leads to the process called Biomagnification.

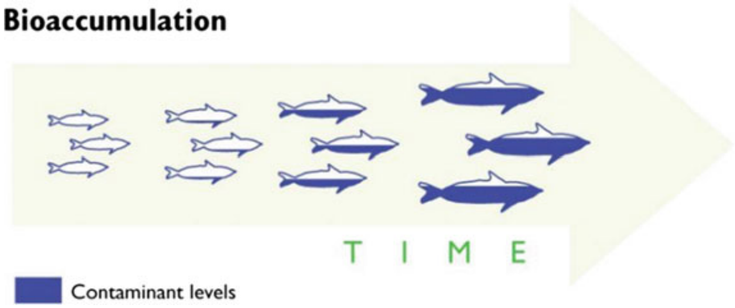

Fig. 15.7 Bioaccumulation of contaminants with increase in time (https://cimioutdoored.org/bioaccumulation/)

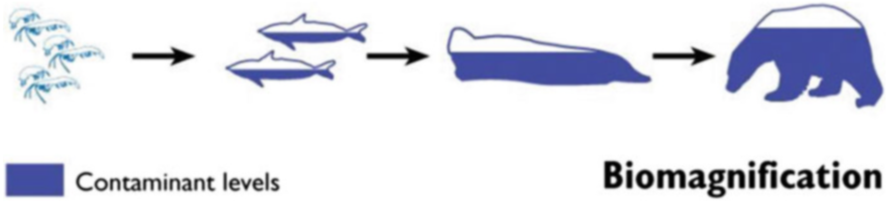

Fig. 15.8 Biomagnification of contaminants in animals (https://cimioutdoored.org/bioaccumulation/)

This involves the transfer of pollutants from one tropic level to another as shown in Fig. 15.8. Persistent Organic Pollutants or POPs are the major cause of bioaccumulation and biomagnification. The POPs such as DDT, PCBs are not degraded, hence bioaccumulated. In the case of marine pollutants, the biomagnification has its base in phytoplankton. The phytoplankton accumulates the pollutants which passes to the zooplanktons and leads to the accumulation of the pollutants in higher tropic level. Figure 15.9a and b shows the biomagnification of pollutants in aquatic and terrestrial environment.

15.11 Biomarkers in Plants

The accumulation of pollutants (mainly heavy metals) by the plants leads to the generation of reactive oxygen species (ROS). The ROS produced has an adverse effect on the plants causing cleavage of proteins, degradation of enzymes, uncoiling and breakage of DNA strands. To counteract the effects of ROS, plants possess defense mechanisms which are enzymatic and non-enzymatic. The plants synthesize enzymes such as catalase, superoxide dismutase, guaiacol peroxidase. Plants also produce compounds such as glutathione, ascorbate, proline, flavonoids, and tannins as the non-enzymatic process of defense (Emamverdian et al. 2015; Rastgoo et al. 2011). The availability of the pollutants in the plants is determined and analyzed using the biochemical markers in the plants. It helps us to compare the concentration of the pollutant in the environment and the plant cells.

There is a unique pathway for each chemical compound and is aided by the use of the specific biochemical markers. The flurocitrate is a specific biochemical marker for the fluoride incorporation in plants. This is aided by the synthesis of fluoroacetyl-CoA which converts the fluorides to flurocitrate via TCA cycle. The continuous monitoring of the plants is essential for the quantification of fluorides in plants (Meyer et al. 1992). Another specific biochemical marker in the plants is seleno proteins, proteins that are produced when plants are exposed to selenium. The plants uptake Se as they are homologous to sulfate in the soil. The plants that are sensitive to Se incorporate Se in the proteins which are not metabolized as Se–Se interaction is weak and this cause the deregulation in the metabolism of Se (Burnell 1981). In the case of Se resistant plants, seleno peptides or on-protein amino acids are produced

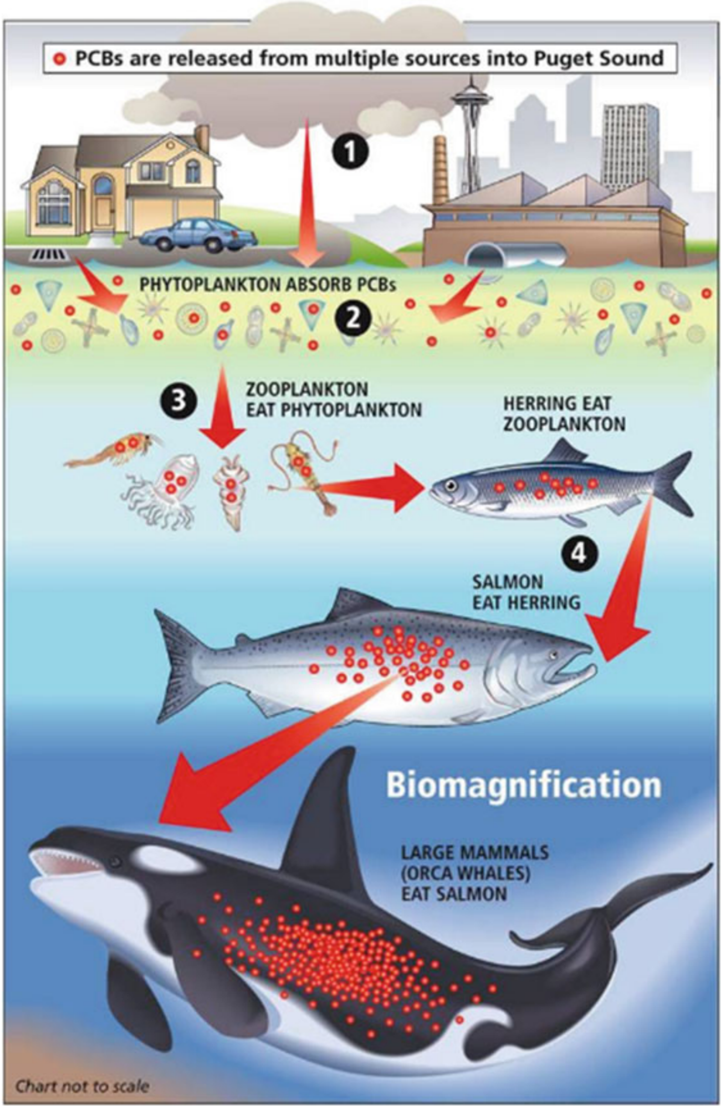

Fig. 15.9 (**a**) Biomagnification of pollutants in aquatic habitat (https://cimioutdoored.org/bioaccumulation/). (**b**) Biomagnification of pollutants in terrestrial habitats (https://cimioutdoored.org/bioaccumulation/)

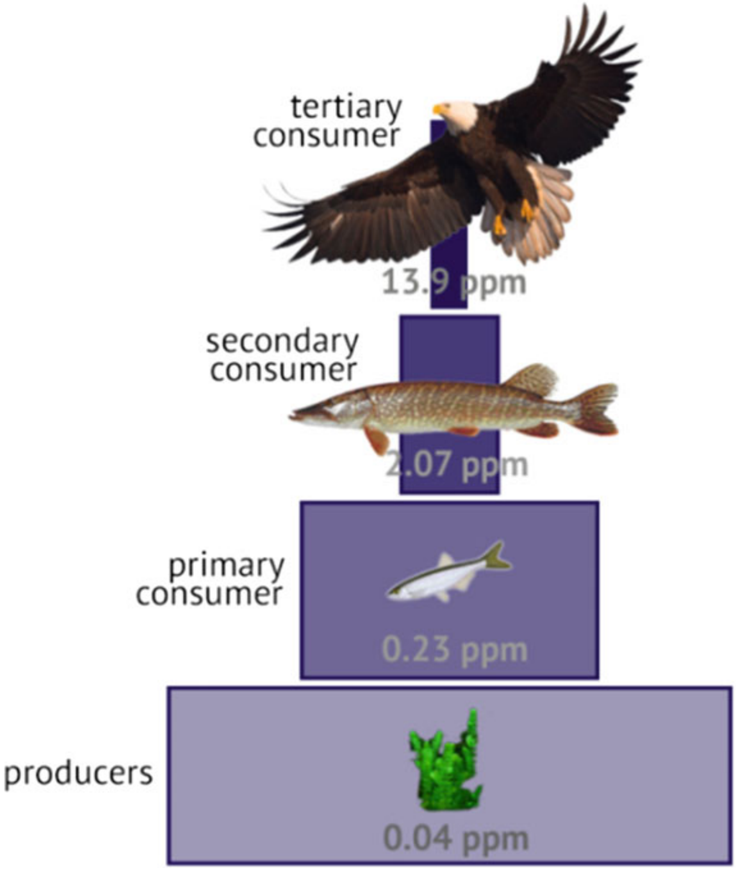

Fig. 15.9 (continued)

(Peterson and Butler 1967). Higher plants on exposure to free metal ions, produces phytochelatins (PCs) (with structure containing(gamma-Glu-Cys)nGly) in the cytoplasm of the plant cell for sulfur metabolism (Grill et al. 1985).

The effect of pollutants or the deficiency caused by the pollutants to the plants can be observed visually and hence the symptoms are the visual biomarkers. The physiological biomarkers are the change in the structure of the chloroplast, production of chlorophyll, color of the leaves, deficiency of minerals, and accumulation of heavy metals and necrosis of the plant (Ernst 1974). Jaskulak et al. (2018) studied the expression of the rbcL gene in *S. alba, R. pseudoacacia* and *I. luteus.* It inhibited growth of plants grown in the soil contaminated with heavy metals. This also showed a decrease in the Guaiacol peroxidase enzyme activity in the absence of the vermicompost. The chlorophyll content was also found to be reduced in the presence of Cd, Pb, and Zn but in contrast increase in the total phenolic compounds was observed in the plants grown in the contaminated soil than in the plants grown in the soil containing organic manure. The rbcL gene expression was enhanced in plants grown in organic manure than in contaminated soil.

15.12 GMOs in Bioremediation

There are microorganisms available in the environment that have developed resistance to survive in the contaminated environment by utilizing the contaminants as a sole carbon source. The remediation of pollutants by the naturally occurring microbes might be a little slower and also the microbes get to be accumulated in the environment. The complex structure of pollutants is quite difficult to cleave and degrade by the microorganisms. The development of the catabolic character by the microorganisms and the existing pathways are not efficient for complete degradation or removal of the complex contaminants (Chen et al. 1999). Thus, the removal of the pollutants is enhanced by introducing exogenous microbes into the contaminated site to increase the indigenous microorganisms. This process is named as bioaugmentation. This occurs by introducing the microbes possessing catabolic genes that are responsible for the degradative ability of the microorganism or microbes are genetically modified to degrade the pollutants (Genetically Modified Microorganisms GMOs). The GMOs are produced by the transfer of the target gene between the different groups of microorganisms. By doing so, the adaptation of specific catabolic pathway for a specific contaminant could be achieved. The carbon flux is redirected and this prevents the toxic intermediate compound formation. This also modifies the affinity and specificity of the enzyme, stable catabolic activity, and increased availability of pollutants for the remediation. The first release of the GMOs commenced in the year 1996 in the US Environmental Protection Agency (EPA). The GMOs in the environment are controlled by which the bacteria are killed by the controlled suicidal process (Garbisu and Alkorta 1999). The efficient genetically modified microbes are synthesized by incorporating various promoters and regulators. The stability of the mRNA was enhanced by ligating the cassettes of DNA at 5′ of the target gene. This forms the hairpin loop in mRNA by increasing the free energy for the formation of mRNA. This increases the stability of the mRNA. The cloning vectors used for modifying the microorganisms should contain broad host range. The vectors, namely RK2, TFK, and pPP8 are widely used. The vectors with a narrow host range are pDK1, pFME4, pKME5, pNK33, and pPS10 (Singh et al. 2018).

The pollutants present in the environment are mostly aromatic. The efficiency of the degradation or removal of these aromatic compounds is aided by combining the pathway of degradation of bacteria by conjugation in a single recombinant host to degrade a wide range of aromatic compounds (Reineke 1998). The *ohh* operon from *P. aeruginosa* and *fcb* operon from *Arthrobacter globiformis* were transferred into the bacterium *Comamonas testosteroni* strain VP44 for mineralization and degradation of monochlorobiphenyls by Hrywna et al. (1999). The toluene monooxygenase gene present in the *Burkholderia cepacia* was expressed in *Pseudomonas fluorescens*. This recombinant bacterium was coated in the wheat seeds, which

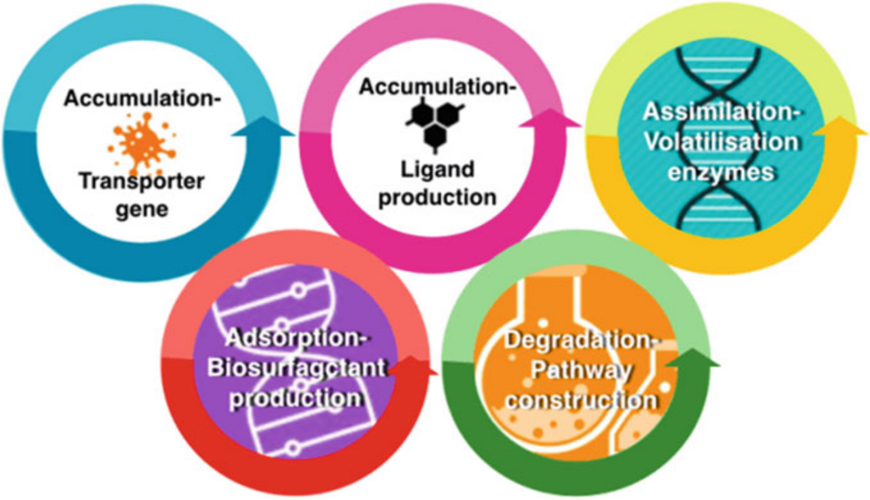

Fig. 15.10 Molecular targets for bioremediation using GEM

showed that the rhizosphere grown was more efficient in the degradation of trichloroethylene (TCE) within 4 days (Yee et al. 1998). Even though the microorganisms were able to degrade the complex pollutants, the microorganisms are sensitive to the radiations of the radioactive compounds. The bacterium *Deinococcus radiodurans* (Lange et al. 1998) and *Deinococcus geothermalis* (Brim et al. 2000) are radiation-resistant bacterium used as a host for genetic engineering.

The efficiency of the genetic engineering to enhance the bioremediation process is done either by the transformation of the new gene into the host organism or enhancing the expression of the genes existing in the microbe. To produce an efficient Genetically Engineered Microorganism (GEM), the factors such as target pollutant, the goal of the bioremediation process, the organism of interest, and the molecular technique to be performed are to be planned and monitored. The selection of the molecular target depends on the target pollutant as shown in Fig. 15.10 (Kapagunta 2017). To improve the bioremediation efficiency, the specificity of the enzymes to the pollutants should be broadened; development of effective bioprocess technology and monitoring the progression of the remediation should be performed (Joutey et al. 2013).

The phytoremediation of pollutants using genetically modified plants is performed to increase the absorption, transportation, and metabolism of pollutants. This process includes the transfer of a catabolic gene from microorganism into the plant genome (Jafari et al. 2013). Hassani et al. (2015) studied the phyto-extraction process of heavy metals by genetically engineering the *metallothionein* (*MT*) gene clones. Verbruggen et al. (2009) reported the transfer of MT-2 gene in tobacco for enhancing the Cd tolerance in plants. The genetic modification in plants modifies the metabolism, phenotypic and genotypic characters of the plants (Davison 2005). Tissue culture technique is used for the selection of genes and plants. The plants, namely *Populus angustifolia, Nicotiana tabacum*, or *Silene cucubalis* are genetically engineered for the overexpression of glutamylcysteine synthetase (Fulekar et al. 2009). The rate limiting factor of glutathione and phytochelatin is investigated using genetically engineered *Brassica juncea* (Ow 1996). The genes such as *AtNramps*, *AtPcrs, CAD1* from the plant *Arabidopsis thaliana* was isolated and incorporated into the plants for enhancing the heavy metal removal (Thomine et al. 2000; Song et al. 2004; Ha et al. 1999). The hyperaccumulation of pollutants in the plants follows a new metabolic pathway by the transfer of *MerA* and *MerB* genes to make plants Hg tolerant (Bizily et al. 2000).

15.13 GMOs—Scope in Bioremediation

The bioremediation of pollutants using native microorganisms, containing fauna or plants that symbiotically assist the survival of microorganisms in their rhizosphere has its advantages of an eco-friendly approach. Though the presence of the native organism aids in the bioremediation of a wide range of pollutants, these organisms do not have a specific degradative pathway for the various pollutants. The process of degradation is slower and the accumulation by the native microbes is difficult to monitor. The bioaugmentation of the pollutants can be performed using the wild microbes, but this might not be an effective alternative for a speed up eco-friendly process. Thus, genetically engineering the microbes and plants to remediate a wide range of pollutant using specific degradative pathway for a specific pollutant deciphers the pathway of degradation. This adds an advantage of cloning a specific microorganism with a genes coding for the catabolism of various pollutants irrespective of the environmental condition and the concentration of the pollutants. The GMOs produced should be monitored before releasing it to the environment. The transfer of genes from the GMOs to the native microbes can be monitored using the markers and this helps to track the spreading of the GMOs in the environment. This chapter helps to understand various aspects of degradation of pollutants using biological means which can be enhanced by the application of biotechnological approaches for the betterment of the environment towards a sustainable future.

15.14 Conclusion

The synthetic chemicals are a part of our life but the way of making it less toxic lies in the treatment process. Choosing an eco-friendly, cost effective, and efficient method is the only solution. This lead to the biological treatment processes which can be applied in multiple ways. The process utilizes all the available biological system to the fullest to remediate the pollutants. Exploring the unexplored process such as vermiremediation helps to get a better perspective. The application of GMOs requires consistent monitoring while the phytoremediation requires longer duration. The choice of biological method is based on the requirement and nature of the pollutants. Hence, this chapter provides an alternative biological treatment apart from the microbial and enzymatic process.

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Mitigation of Hazardous Contaminants: A Phyto-Microbiome Approach

16

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Abstract

The elimination of toxic waste in soils, water, and in general in all types of environmental scenarios has become a goal for scientists and environmental organizations, due to the devastating effects it causes on health, biodiversity, soils, and sources of water. The pollutants are divided for study according to their chemical composition in hydrocarbons and their derivatives, heavy metals and pesticides. Intensive, traditional techniques for eliminating or attenuating the effects of toxic waste on ecosystems are very expensive and consume a great deal of time. Instead, the interactions that occur naturally between plants and microbes are being exploited for this purpose, as it has been shown that numerous species of both types of organisms have the ability to act on various types of pollutants through various detoxification mechanisms, and that plants and microorganisms can act in this direction together. This chapter analyzes the applications of these interactions in reducing pollution by the three groups of toxic products, both through the use of plants and microbes in their natural state and through the use of genetically modified organisms.

Keywords

Heavy metals · Hydrocarbons · Pesticides · Plants · Microorganisms

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16.1 Introduction

Ecosystem contamination as a result of toxic waste dumping is a direct consequence of anthropic activity. Thousands of tons of waste are deposited in the soil and water every year, including hydrocarbons and their derivatives, heavy metals, pesticides, and many other products. The consequences of incorporating these substances into the environment are catastrophic, since their permanence in the soil or water is very long. For example, it is estimated that the decomposition time of plastic bottles should be about 1000 years, but of course this is no more than an estimate, since the time elapsed since its invention is much shorter and does not allow this assumption to be confirmed. In many cases, in addition to causing toxic effects on plants, animals, and humans, pollutants mix with other substances, forming new compounds; for example, excess aluminum tends to be associated with useful elements such as nitrogen and phosphorus, making it difficult for plants to absorb them.

Pollutants that can be detoxified from the soil by plants are divided into two large groups for study: inorganic (which includes heavy metals) and organic (including hydrocarbons, derivatives and pesticides) (Kuiper et al. 2004).

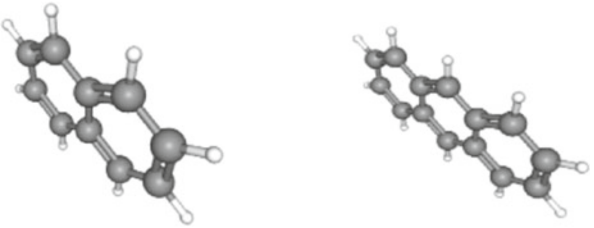
The main inorganic pollutants are heavy metals (lead, mercury, cadmium, arsenic, and chromium, among others) that come directly from industrial activity and mining. As they are not directly degraded by biological or chemical routes, once released into the environment they can remain in it for many years, which is why they have been the main subject of phytoremediation (Tangahu et al. 2011).

Polycyclic aromatic hydrocarbons (PAH) accumulate in soils as a result of some natural processes (such as forest fires and volcanic eruptions) and anthropogenic activity (partial combustion of organic substances, oil spills, and other industrial activities) (Chauhan et al. 2008). They are classified into two groups: low molecular weight compounds, such as naphthalene and anthracene, which have three or less rings, and high molecular weight, such as pyrene and benzo(a) pyrene, which contain four or more rings (Fig. 16.1). The hydrophobicity of these substances increases with their molecular mass, which increases their ability to be adsorbed by soil particles and makes their elimination difficult.

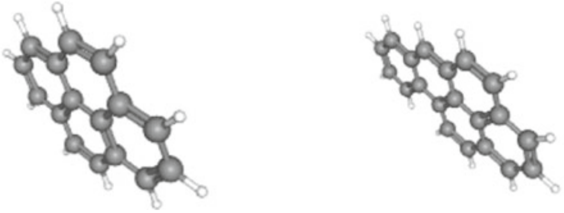
The term total petroleum hydrocarbons (TPH) (Divya and Kumar 2011) is used to name a mixture of different hydrocarbons that can be found in crude oil. In practice, due to the heterogeneity of the polluting sources and the degree of decomposition of these, it is very common to find mixtures of TPH and PAH in contaminated soils.

One of the strategies used to reduce the presence of toxic wastes in ecosystems is phytoremediation. Although the etymology of the term links it to the use of plants for that purpose, it actually includes not only plants, but also the microbial communities associated with them, the amendments and other agronomic practices tending to destroy, remove, or stabilize environmental pollutants (Yateem et al. 2000; Kumar et al. 2017).

Undoubtedly, plants are able to extract a wide range of contaminants from the soil. However, phytoremediation also suffers from limitations, which have been pointed out by Glick (2003): soil contamination causes stress that reduces the



Naphthalene Anthracene



Pyrene Benzo(a)pyrene

Fig. 16.1 Some polycyclic aromatic hydrocarbons (PAH) usually present in soils

germination of the plants used for this process, as well as reductions in growth and development, which leads to lower biomass and finally to low effectiveness in phytoremediation. On the other hand, most plants used in phytoremediation do not completely degrade contaminants, but accumulate them in vacuoles or apoplast (Eapen et al. 2007).

The presence of microorganisms in the rhizosphere allows plant–microbe interaction, whose usefulness has been demonstrated in the removal of toxic compounds, in particular insecticides and herbicides (Walton and Anderson 1990). For this reason, rhizoremediation is referred to the contribution that these rhizosphere microbes make to the degradation of pollutants (Schwab and Banks 1994). It is known that an important part of the degradation of pollutants is due to the action of microorganisms that live in the vicinity of plant roots.

The action of microorganisms in remediation can occur, according to Kuiper et al. (2004) through several mechanisms:

- Natural attenuation: The appearance of pollutants at a site leads to the microbes capable of using these compounds as a source of nutrients to prevail over other microorganisms, resulting in degradation of a part of pollutants.
- Bioaugmentation: It is based on the inoculation to the soil of microbes capable of degrading specific xenobiotic compounds. This allows to increase the degradation of the contaminants.
- PAH degradation: Polycyclic aromatic hydrocarbons (PAH) are a wide range of polluting compounds. Since the beginning of the twentieth century, the ability of

a variety of bacteria, fungi, and algae to degrade these compounds has been known.

This chapter analyzes the interaction between plants and microbes (rhizoremediation) in the degradation of hydrocarbons, heavy metals, and pesticides.

16.2 Plant–Microbe Interactions for the Remediation of Hydrocarbons as Environment Pollutants

The degradation of hydrocarbons and their derivatives by microorganisms can be carried out in two ways: aerobic or anaerobic (Chauhan et al. 2008). The degradation pathway depends on the conditions of the environment (generally in the soils the aerobic pathway and in the anaerobic aquifer spaces) and the bacterial genera present.

Numerous genera of bacteria capable of degrading PAH in interaction with various plant species have been identified. Kuiper et al. (2001) demonstrated the degradation of naphthalene by *Pseudomonas putida* in the rhizosphere of *Lolium perennial* L. Yateem et al. (2007) identified several PAH degrading microorganisms in the rhizosphere of *Paspalum vaginatum* Sw. and *Zoysia tenuifolia* Willd. Ex Thiele, among which the fungus *Fusarium solani* and the bacterium *Pseudomonas boreopolis* were the most effective. Several bacteria (*Alpha proteobacterium*, *Aspergillus versicolor*, *Bacillus licheniformis*, *Bacillus mojavensis*, *Rhodococcus equi*, *Arthrobacter globiformis*, *Mycobacterium fortuitum*) and a fungus (*Fusarium oxysporium*) degrade hydrocarbons in the rhizosphere of *Ficus infectious* Willd. and *Conocarpus lancifolius* Engl. trees (Yateem et al. 2008).

The association between microorganisms and plants plays an important role in the effectiveness of PAH degradation in soils. Degradation is usually more effective in the rhizosphere area (rhizoremediation). Plant roots exude substances that contribute to microbial survival, and the penetration of the radical system into the soil contributes to the spread of microbes (Gentry et al. 2004). On the other hand, the microorganisms that live in the rhizosphere provide the plant with various compounds, including vitamins, siderophores, and growth regulators (Kuiper et al. 2004; Kumar et al. 2018).

Legumes are plants that tend to form bacterial nodules, particularly with *Rhizobium* sp. Yateem et al. (2000) demonstrated the phytoremediation potential of *Vicia faba* L. and *Medicago sativa* L. in soils contaminated with 1% oil, observing that these species are capable of degrading oil by 36.6% and 35.8%, respectively, in contrast to the 24% reduction obtained in soils planted with *Lolium perenne* L. In addition, the presence of legumes increased the colonization of the rhizosphere by bacteria tenfold compared to that observed in the rhizosphere of the ryegrass. In contrast, Guo et al. (2017) found that the presence of *Lolium perenne* L. increased the degradation of PAH by *Mycobacterium* sp.

However, legumes are not the only plants with the capacity to participate in plant–microbial associations for the rhizoremediation of hydrocarbons and their derivatives in soils. In a study conducted by Sangabriel et al. (2006) in Colombia, it was observed that, although *Phaseolus coccineus* L. showed the highest tolerance to fuel oil and the largest microbial population in its rhizosphere, the greatest total degradation of fuel oil occurred in the rhizosphere of *Brachiaria brizantha* (Hochst. Ex A Rich) and *Panicum maximum* Jacq., two grass species. Ying et al. (2011) found that the species *Atriplex centralasiatica* Iljin (Amaranthaceae), *Scorzonera mongolica* Maxim. (Asteraceae), and *Limonium bicolor* (Bunge) Kuntze (Plumbaginaceae) were able to reduce between 5 and 8 times the concentration of TPH in their rhizosphere, while in the soil not close to the roots of the plant, the concentration of TPH was only reduced 1.6 times. Some plant species such as the poplar (*Populus* sp.) and the willow (*Salix* sp.) that have an aerenchyma in their roots—and are therefore capable of carrying oxygen to the soil at considerable depths—are frequently used in the rhizoremediation of contaminated soils (Zalesny et al. 2005).

In addition to the associated plant species, the degree of self-degradation of pollutants resulting from weathering apparently also influences the degradation activity of microbes (Prakash et al. 2014). Maldonado et al. (2010) investigated the degradation of TPH in soils contaminated with new and weathered oil for 25 years. Inoculation of a consortium formed by bacteria (*Pseudomonas* sp. and *Serratia marcescens*) and fungi (*Aspergillus* sp. and *Trichoderma* sp.) produced greater degradation in new oil when the plant species was the legume *Leucaena leucocephala* (Lam.) De Wit, but when the oil was weathered, the greatest results were obtained with the grass *Brachiaria mutica* (Forssk.).

Pantoea sp. is a genus of bacteria that includes about 20 species, among which some have proven to have beneficial effects on vegetables. Yousaf et al. (2010) showed that two strains of *Pantoea* sp. in combination with compost favor the growth of *Lolium multiflorum* Lam. and *Lotus corniculatus* L. These two bacterial lines, in addition to achieving degradation rates of hydrocarbons higher than *Pseudomonas* sp., a genus known to possess this property, managed to colonize both the rhizosphere and the endosphere of both plant species.

Bacteria and fungi such as *Pseudomonas* sp., *Agrobacterium* sp., *Trichoderma* sp., *Aspergillus* sp., and *Mucor* sp. are capable of degrading oil hydrocarbons. Hernández et al. (2003) managed to isolate these species from soils contaminated with petroleum; subsequently they were inoculated in soils contaminated with oil in which beans (*Phaseolus vulgaris* L.) and corn (*Zea mays* L.) plants were living. The greatest degradation of hydrocarbons was obtained in the combination bacteria + fungi + corn, possibly due to its extensive fibrous and radical system.

Siciliano et al. (2001) were the first to observe that the endophyte microbes of plants that grew in soils contaminated with hydrocarbons could degrade polluting organic compounds. Based on this result and the possibilities of microbial consortia in rhizoremediation, the path has been opened to a more efficient approach that includes plants, bacteria and soil fungi and endophytic bacteria (Juwarkar et al. 2010; Singh 2011; Abhilash et al. 2012). In this integral system, bacteria and soil fungi degrade part of the contaminants in the rhizosphere; other xenobiotics penetrate the inner space of plants, and there they are degraded by endophytic bacteria

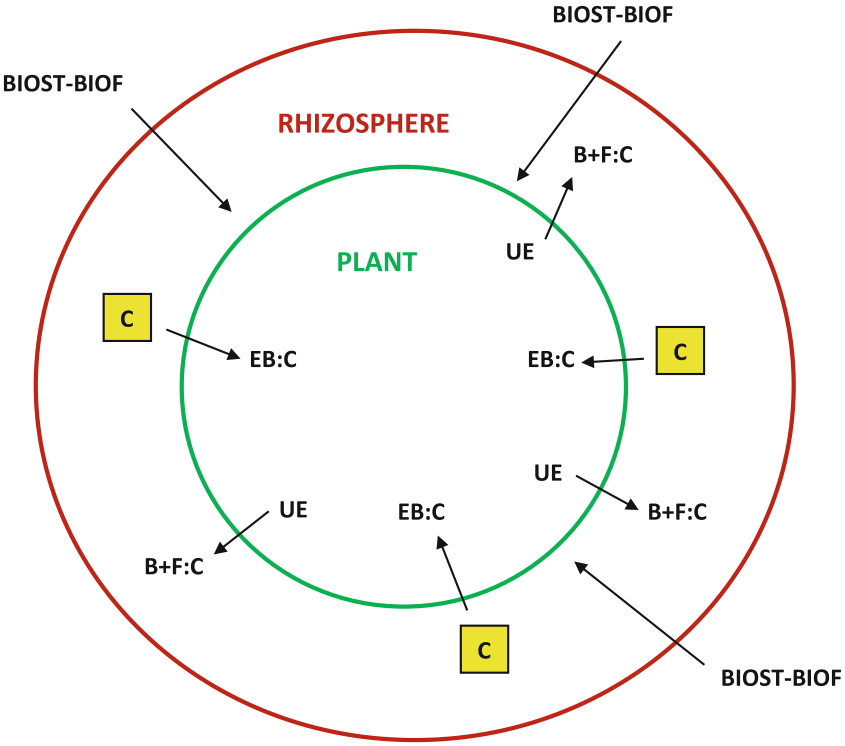


Fig. 16.2 Integrated strategy for rhizoremediation. B-bacteria; F-fungi; EB-endophytic bacteria. UE → B + F:C plant provides useful exudates to bacteria and fungi from rhizosphere which degrade contaminants. C → EB:C some contaminants enter the plant, where are degraded by endophytic bacteria. BIOST-BIOF → biostimulants and biofertilizers are provided in order to enhance plant growth and development

that have been selectively introduced. The system could be complemented with the addition of biofertilizers and biostimulants (Fig. 16.2). Additionally, it has been found that good tillage practices, such as proper cultivation and good soil drainage, favor the degradation of PAH by microorganisms (Mmom and Deekor 2010).

In general, the increase in the efficiency of rhizoremediation involves the acquisition of deeper knowledge about the signals emitted in the plant–microbe association that regulate the process. The clarification of these signals and their role in the activation of degrading mechanisms is essential, since it is known that the presence of a certain bacterial strain in the rhizosphere does not imply that it is metabolically active (Kiely et al. 2006).

Once the presence of a microorganism with PAH degrading activity is confirmed, a possible task would be to use it as a source of genes to enhance the activity of other microbes, through genetic engineering. The search for genes encoding the degradation of PAH is directly related to the activity of the catalytic enzymes involved, which are mainly oxygenases, dehydrogenases, phosphatases, and lignolytic enzymes (Bisht et al. 2015).

An important advance in the understanding of plant–microbe interactions for survival in environments contaminated by hydrocarbons has been achieved from the work of Oliveira et al. (2014a, b) made in saline estuaries. In these sites, the presence of certain plant species (*Halimione portulacoides* L. and *Sarcocornia perennis* Mill.) is associated with the colonization of the rhizosphere by certain microbial genera (among which *Pseudomonas* sp. predominates). These genera, which appear particularly in areas where pollution is most severe, carry PAH-dioxygenase genes involved in the degradation of PAHs, which allow them to survive in these harsh conditions. In turn, the plants with which they are associated favor them by the vital space that their roots and radical exudates give them (Oliveira et al. 2012). In parallel, Fatima et al. (2016) revealed that the activity of a consortium of two degrading bacteria of crude oil (*Acinetobacter* sp. strain BRSI56 and *Pseudomonas aeruginosa* strain BRRI54) works better in *Brachiaria mutica* (Forrsk.) than *in Leptochloa fusca* L.

From the identification of the genes involved, it is possible to undertake genetic engineering projects to improve the efficiency of rhizoremediation. The two main lines of work would be the transformation of plants to stimulate population growth and the activity of microorganisms, and the transformation of microorganisms to increase their ability to live in contaminated environments and degrade xenobiotics.

A variant to increase the effectiveness of rhizoremediation would be to obtain transgenic plants in which the absorption of pollutants or their transport is increased (Doty 2008). Although numerous transgenic plants have been designed for almost two decades to fulfill these purposes in the detoxification of heavy metals, pesticides, and other organic compounds (Cherian and Oliveira 2005) there are no reports on obtaining transgenic plants for PAH remediation.

Genetic engineering can be useful in harnessing the natural potential of bacteria to build genetically modified lines capable of acting in rhizoremediation; however, the main results have been applicable mainly in laboratories (Wasilkowski et al. 2012). There are no abundant results in the genetic engineering of bacteria useful in the rhizoremediation of hydrocarbons and their derivatives, but some progress has been made in obtaining genetically engineered bacteria capable of degrading naphthalene (Sayler and Ripp 2000; Filonov et al. 2005) and oil (Jussila et al. 2007).

Not always the bacterial strains that carry genes for the degradation of hydrocarbons also have genes that stimulate plant growth, and vice versa. The genetic transformation to obtain bacteria that carry both types of genes would give them an additional advantage over other microorganisms (Iqbal et al. 2018) and would make them ideal candidates for use in rhizoremediation. An example of this type of gene construction is to obtain a recombinant bacterium capable of stimulating the growth of *Zea mays* L. and degrading phenol, from *Pseudomonas aeruginosa* SZH16 (phenol degrader) and *Pseudomonas fluorescens* (growth promoter) (Yang et al. 2011).

The difficulties in obtaining genetically modified organisms and achieving character expression are joined by legal restrictions for the introduction of transgenic organisms (Ghosal et al. 2016), and the low survival of individuals introduced in areas where levels of contamination are truly problematic (Kuppusamy et al. 2016; Ite and Ibok 2019). However, the increase in the use of these technologies in the immediate future can be taken for granted.

16.3 Plant–Microbe Interactions for the Remediation of Heavy Metals as Environment Pollutants

Heavy metals are pollutants that cannot be biodegraded; they accumulate in soils and in living organisms causing several damage because of their toxicity (Singh et al. 2011). Numerous methods are used such as biological, chemical, and physical but they are expensive, long time is needed, and they can damage the environment (Jadia and Fulekar 2009; Danh et al. 2009; Ahmadpour et al. 2012; Kumar et al. 2017). Phytoremediation is a method that use green plants to degrade, stabilize pollutants such as heavy metals from soils, waters, etc. (Paz-Ferreiro et al. 2014; Elekes 2014) and bioremediation use plants and microbes for decontamination (Rayu et al. 2012). Both processes are most effective and less cost.

Green plant for phytoremediation is used according to the development of their root system, the contaminant to be treated, the soil and the temperature of the region (U.S. EPA 2001). Different types of plants are used for this purpose depending on the soils structure, contaminant nature (which is the principal factor for plant selection), soil fertility, and so on (Pivetz 2001). On this regard, for example, grasses can clean approximately <3 ft, shrubs <10 ft, and <20 ft for deep rooting trees (Sharma and Reddy 2004).

Grasses are the most recommended plants for phytoremediation because they grow rapidly, have a lot of biomass, are very resistant to biotic and abiotic stresses, and they have the capacity to remediate different types of soils (Elekes 2014).

16.4 Where Heavy Metals Come From?

Heavy metals are elements with metallic characteristics, natural components of the earth crust, with a density superior to 5 g cm^{-3}, atomic number >20, and natural constituents in soil (Alloway and Ayres 1997; Lasat 2000; Adriano 2001; Jadia and Fulekar 2008; Ismail et al. 2013). Some of them are necessary for plant growth [zinc (Zn), copper (Cu), manganese (Mn), nickel (Ni), and cobalt (Co)] and the most dangerous do not have a biological function [(cadmium (Cd), lead (Pb), and mercury (Hg)] (Gaur and Adholeya 2004).

The contamination of water, soil, sediments, and some living organisms by heavy metals comes mainly from industries and mining activities, and began between nineteenth and twentieth centuries (Benavides et al. 2005). According to Zhen-Guo et al. (2002), some other sources of heavy metals are fuel production, smelting processes, military operations, agricultural chemicals (fertilizers, pesticides), small-scale industries (including battery production, metal products, metal smelting, and cable coating industries), brick kilns, and coal combustion.

Mining activities produce some particles named tailings that are discharged mainly in wetlands, resulting in higher concentrations of heavy metals (DeVolder et al. 2003). These activities also produce elevate quantities of Pb and Zn that contaminate soils resulting in risk to humans and ecological health.

The disposal of municipal wastage in some countries is an important source of soil contamination because they can be accumulated in landfills and the leachates usually are incorporated to soils or water for irrigation; most of these wastes contain carcinogens. Another cause of heavy metals increases in soils is the indiscriminate use of pesticides, fungicides, and fertilizers in agricultural activities (Zhen-Guo et al. 2002).

The use of wastewater dates back 400 years ago and at present has become a common practice in many countries (Reed et al. 1995). In 2007 approximately 20 million hectares of agricultural soil were irrigated with wastewater and in many Asian and African cities the vegetables supply for urban areas depends in a 50% of wastewater (Bjuhr 2007).

Fertilizers are necessary for the growth of plants as macro (N, P, K, S, Ca, and Mg) and micronutrients (Zn, Cu, Mn, and others) (Lasat 2000). Several fertilizers are used intensively to apply NPK to the soil so that plants can take them, but usually fertilizers contain small amounts of heavy metals such as Cd and Pb whose concentrations increase considerably (Jones and Jarvis 1981).

According to Atafar et al. (2010) concentrations of Cd, Pb, and As (arsenic) have increased in the soils cultivated with wheat (*Triticum sp.*) and the statistical analysis indicates that Pb and As concentrations increased dramatically compared to Cd concentration. The high concentrations of Pb, As, and Cd found were because an over application of fertilizers as well as the pesticides that are used to control plant pests, herbs, and rats. Another research in China showed that after the analysis of 177 organic fertilizers the concentrations of trace metals varied widely and the standard limits were exceeded by 0.85% for Cr (chrome), 5.98% for As, 1.71% for Cd, and 4.27% for Pb (Gong et al. 2019).

In India, not only fertilizers and pesticides applications increased heavy metals concentrations in soils, also industrial waste, wastewater irrigation, and corrosion of sewerage pipes (Mapanda et al. 2005; Sharma et al. 2007).

Ikem et al. (2008) reported in southeastern Missouri (USA), that the concentration of heavy metals, increased by 2–31%, where the lowest concentrations was for Mn and the highest for Pb, mostly produced by the use of chemical fertilizers and sewage sludge.

According to Raven et al. (1998), some fertilizers with phosphorus (phosphatic) indirectly add certain heavy metals such as Cd, Hg, and Pb. Also, Fan et al. (2012) found that the high concentration of heavy metals in the finer fractions of soil aggregates is because of fertilization.

The increase of Zn and Cd in soils is also because of the excessive application of low-quality fertilizers, pesticides, and sewage irrigation, among several causes (Tang et al. 2010; Wei and Yang 2010).

The contamination of soils by heavy metals is an important topic because a lot of land extension has become dangerous and non-useful for animals and humans. Today it is uncommon to find soils without traces of these elements, and they become more toxic with the time because the anthropogenic or natural activities are still increasing (Turan and Esringu 2007).

16.5 Bioremediation as Technologies to Clean up the Environment of Heavy Metals

The conventional methods used for the remediation of heavy metals in soil and water are expensive, need a lot of time and exhaustive work that induces the mobilization of contaminants and damages the soil by destroying the biotic and structure, so they are not recommended for large contaminated areas (Baccio et al. 2003). Examples of those methods are ex situ excavation, landfill of the top contaminated soils (Zhou and Song 2004), detoxification (Ghosh and Singh 2005), and physico-chemical remediation (Danh et al. 2009).

Bioremediation is a heavy metal remediation technique that uses microorganisms to degrade them into a low toxic level (Vidali 2001) and they use some mechanism such as (Jan et al. 2014):

1. Proteins such as metallothioneins (MT), phytochelatins, and compounds like siderophores produced by bacteria and fungi (hydroxamate siderophores) which can sequestrate toxic metals;
2. Change or variation of some biochemical pathways with the aim of block metal uptake;
3. Enzymes that can transform toxic metals into harmless forms;
4. Concentration of metals that can be dangerous can be reduced by the use of precise efflux systems.

Several microorganisms are related to heavy metal remediation, and in this cases bacteria that live in plant rhizosphere are important, because they can change metal bioavailability by the alteration of soil pH, generation of chelators (organic acids, siderophores), and oxidation/reduction reactions (Khan et al. 2009; Wenzel 2009; Ma et al. 2011). Also, mycorrhizal fungi have been reported in metals remediation (Zarei et al. 2010; Miransari 2011).

Isolation of 15 strains of Pb-solubilizing bacteria from mine soils contaminated with heavy metals was done and they were proved in a solid medium containing PbO or $PbCO_3$ where they solubilized Pb and dissolved the Pb minerals in a liquid medium. The molecular study (16S rRNA gene) showed that the strains are from the genera *Bacillus*, *Paenibacillus*, *Brevibacterium*, and *Staphylococcus* (Yahaghi et al. 2018).

A research was done by testing *Pseudomonas fluorescens* and *P. aeruginosa* for the remediation of heavy metals where the concentrations of Fe^{2+}, Zn^{2+}, Pb^{2+}, Mn^{2+}, and Cu^{2} were near to 100 mg L^{-1} and the elimination percentage was 86 and 74 after using them. The examination of metal percentage was realized in an atomic adsorption spectrophotometer (Perkin-Elmer) at 0.01 ppm sensitivity level after dilution of the samples (Paranthaman and Karthikeyan 2015).

Two bacterial strains (PB-5 and RSA-4) were identified from mangrove sediments by Priyalaxmi et al. (2014) and they were described as Cd resistant, but only the strain RSA-4 was useful for remediation purpose. The study was done under several pH levels (pH 5, 6, 7, 8, and 9) and two concentrations of Cd (40 and 60 ppm); percentages of Cd reduction and absorption were 83.5, 39% and 98.10, 92% for 40 and 60 ppm of cadmium, respectively, at pH 7. The strain was identified as *Bacillus safensis* accession JX126862.

Several Pb resistant bacterial isolates (*Salmonella choleraesuis* strain 4A, *Proteus penneri* strain GM10, *Bacillus subtilis* strain GM02, *Pseudomonas aeruginosa* strain 4EA, *Proteus penneri* strain GM03, and *Providencia rettgeri* strain GM04) from soil polluted with car battery waste in India were quarantined to be used for remediation. By PCR (Polymerase Chain Reaction) analysis (amplification of smtAB genes encoding bacterial metallothionein) was demonstrated that *Salmonella choleraesuis* strain 4A and *Proteus penneri* strain GM10 express the smtA gene for occurrence of metal-binding metallothionein (SmtA), responsible for the resistance towards Pb (Naik et al. 2012).

According to Machuca et al. (2007) some ectomycorrhizal fungi (EMF) (*Scleroderma verrucosum*, *Suillus luteus*, and *Rhizopogon luteolus*) isolated from *Pinus radiata* (tree species belonging to the family of the Pinaceae) can produce siderophores (catecholates and hydroxamates) in a soil with iron deficient condition.

Cellular toxicity induced by Cd can be reduced by *Pseudomonas putida* expressing EC20 (metal-binding peptide) which was demonstrated in sunflower (*Helianthus annuus* L.). When the plant roots were inoculated with the bacteria the Cd phytotoxicity was reduced and the accumulation of this metal increased in the roots (40%) (Wu et al. (2006).

In the case of fungi, several examples illustrate the application in bioremediation. Oladipo et al. (2018) studied several filamentous fungi isolated from gold and gemstone mine site according to their tolerance to several toxic metals like Cd, Cu, Pb, As, and Fe. Using PCR technique (internal transcribed spacer 1 and 2 (ITS 1 and ITS 2) regions) the strains were identified as *Fomitopsis meliae*, *Trichoderma ghanense* and *Rhizopus microspores* and they were grown in malt extract agar with 0-100 mg kg^{-1} of Cd, 0-1000 mg kg^{-1} of Cu, 0-400 mg kg^{-1} of Pb, 0–500 mg kg^{-1} of As, and 0-800 mg kg^{-1} of Fe. The results showed that all tested fungi had tolerance to Cu, Pb, and Fe in all the concentrations and specifically *T. ghanense* and *R. microspores* had a great capacity for Cd and As concentrations.

Gohre and Paszkowski (2006) pointed out the importance of arbuscular mycorrhizal fungi (AMF) to reduce the metals uptake in plants so the effect of these fungi were study on wheat plants (*Triticum aestivum* L.) cultivated with Zn concentrations of 0, 100, 300, and 900 mg kg^{-1}. Results showed that plants with AMF association had a better growth and Zn content on those plants was lower in the aerial part than in the roots, also the phosphorous (P) content was higher in plants with AMF association that in the control (Kanwal et al. 2016).

Massaccesi et al. (2002) isolated several fungi (*Aspergillus terreus*, *Cladosporium cladosporioides*, *Fusarium oxysporum*, *Gliocladium roseum*, *Penicillium* spp., *Talaromyces helicus*, and *Trichoderma* koningii) from industrial contaminated soils in La Plata, Argentina, and after that they were cultivated in cadmium-basal medium where they developed 5–53% of biomass.

16.6 Phytoremediation as Technologies to Clean Up the Environment of Heavy Metals

Plants can be used to clean up contaminated sites through a technology called phytoremediation. This technology does not need a lot of money, is environmentally friendly, immobilized/stabilized metals pesticides, hydrocarbons, and chlorinated solvents (Zhao et al. 2003; Jadia and Fulekar 2008). Phytoremediation can be used not only to decontaminate soils but also water (U.S. EPA 2001).

This technology emerged more than 300 years ago and is based on natural processes ago (Lasat 2000). The plants used for decontamination process can accumulate great quantities of toxic heavy metals ($\geq$100 times) (Ghosh and Singh 2005) and they are classified as hyperaccumulator plants (Barceló and Poschenrieder 2002).

16.7 Phytoremediation Can Be Classified into Different Applications (Jadia and Fulekar 2009) Such as

16.7.1 Phytofiltration or Rhizofiltration

This process is similar to phytoextraction with the difference that plant roots are used to absorb or adsorb pollutants (metals) from liquid environment (groundwater and aqueous waste streams) (Garbisu and Alkorta 2001). Metals are either adsorbed on the root surface or are absorbed by the plant roots. These plants are first adapted to a polluted water (they are hydroponically cultivated with clean water until the roots are well developed and later the clean water is changed by polluted one) and then they are planted in situ (Scragg 2006).

16.7.2 Phytostabilization

Through this process soil sediment and sludge are immobilized by plants that are capable to decrease water infiltrating, avoid direct contact with the contaminate soil by acting as a barrier and prevent soil erosion (Raskin and Ensley 2000). This technique is valuable for the cleaning of several heavy metals such as Pb, As, Cd, Cr, Cu, and Zn (Jadia and Fulekar 2009).

16.7.3 Phytovolatilization

Through this process plants absorb contaminants and then these contaminants are volatilized to the atmosphere (complex organic molecules are degraded into simple ones) so heavy metals are present in groundwater, soils, sediments, and sludges medium (Prasad and De Oliveira 2003).

16.7.4 Phytodegradation

In this process contaminants that were absorbed by plants are degraded through metabolic process inside the plant, or external contaminants decomposition is achieved through the effect of several compounds produced by the plant (Prasad and De Oliveira 2003).

16.7.5 Phytoextraction

In this process the plant roots take the heavy metals from the soil and they are translocated to the upper tissues. The plants that realize this process should be tolerant to heavy metals concentration, grow rapidly with a lot of biomass per hectare to be able to accumulate these metals in the foliar part, and they also need a well-developed root system with a high bioaccumulation factor (Ghosh and Singh 2005; Scragg 2006; Jadia and Fulekar 2008).

Some examples of phytoremediation are soil improvement with organic compounds; thermophilic compost, vermicompost, and coconut coir were tested for the bioavailability of trace heavy metals of Zn, Cd, Pb, Co, and Ni under laboratory conditions, and results showed that the organic compounds used decreased the amount of bioavailable metals in the soils and increased soil pH, electrical conductivity (EC), and soil nutrient content. The conditions of switchgrass were also evaluated and shoot and biomass were higher in the soils where the organic compounds were used (Shrestha et al. 2019). Another example is the use of *Brassica juncea* L. to remove heavy metals from urban soil amended with cow dung: Pb uptake by this plant was better than for other heavy metals; finally, this plant was classified as hyperaccumulator according to the Translocation Factor (Gayatri et al. 2019).

Some species (*Macrotyloma uniflorum* (Lam.) Verdc., *Vigna radiata* (L.) R. Wilczek, and *H. annuus*) were used to evaluate their potential for metal extraction in contaminated soil. The higher remediation potential for three metals (Cr 74%, Cd 42.2%, and Pb 62%) was displayed by *H. annuus*, while the other two species remediated chromium more than the other two metals (Reddy et al. 2019).

H. annuus was used for the phytoextraction of Cd and Pb from contaminated soil in pots and the decrease in fresh and dry weights of the plants was clear when heavy metals concentrations increased (up to 200 mg kg^{-1} of both metals). The roots of the plant showed higher accumulation of Cd (Alaboudi 2018).

Some plants species are classified as they accumulate metals mainly in roots because they have a translocation factor (TF) <1 and a bioconcentration factor (BCF) >1; these plants are *Cyperus involucratus* Rottb. (accumulates Cu in roots), *Ipomoea pescaprae* (L.) R. Br. (accumulates Zn in roots), *Typha angustifolia* L. (accumulates Mn in roots), and *Phragmites karka* (Retz.) Trin. ex Steud (accumulates Pb in roots) (Kaewtubtim et al. 2016). According to Prapagdee and Khonsue (2015) plants of *Ocimum gratissimum* L. growing for 2 months in soil contaminated with Cd can accumulate this metal in association with a bacterium (*Arthrobacter* sp.) in roots, above-ground tissues, and whole plant.

An hyperaccumulator plant (*Micranthemum umbrosum* (J.F. Gmel.) S.F. Blake) was reported than can remove 79.3–89.5% of As compared to Cd (60–73.1%) (Islam et al. 2013).

16.8 Plant–Microbe Interactions for the Remediation of Pesticides as Environment Pollutants

Pesticides can be defined as different types of chemicals such as insecticides, fungicides, herbicides, and rodenticides (Singhvi et al. 1994). The uses of pesticides varied over time (according to Singhvi et al. 1994; U.S. EPA 2000):

- In the middle of 1940s the production and application of synthetic organic pesticides increased;
- Until 1991 the US Environmental Protection Agency (EPA) registered about 23,400 pesticides;
- In 1997, 1.2 billion pounds of pesticides were used;
- The distribution of this product use is: in the agriculture sector 77% of pesticides are used, while 12% are used by industrial, commercial, and government organizations and the other 11% is used by private houses.

There are organizations that regulate the production and application of pesticides such as The Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA), and Environmental Protection Agency (EPA) which regulate the registration of the product taking into an account the risk to human health and the environment. The persistence of the compounds is determined in the soil according to aerobic and anaerobic soil metabolism and photolysis, for example, the re-registration fact sheet for metolachlor estimates a half-life between 7 and 292 days in soil surface (U.S. EPA 1995).

Due to biological stability of pesticides and higher degree of lipophilicity in food they have a great effect on human and animal health (Tayade et al. 2013). It is also important to know that the continuous use of them induces their accumulation in soils and water. The reason why they are widely used is because of the necessity of increasing the yield of crops (Bag 2000).

Bag (2000) also points out that the continuous use of pesticides causes several health and environmental problems such as poisoning of farmers, miscarriages, cardiopulmonary diseases, fetal deformities, neurological and skin disorders, low sperm count of applicators—as human health problems—and soil and water contamination, damage to insects and microorganisms, as environmental problems (Singh et al. 2014). One of the most dangerous and problematic pesticides used are organochlorines (Odukkathil and Vasudevan 2013). Chlororganic compounds (aldrin, heptachlor, endosulfan, DDT) are of deep concern, due to these pesticides can accumulate in living tissues inducing several diseases in humans (Das and Chandran 2011).

According to Ahmad and Ahmad (2015) pesticides can be classified by their chemical nature in the following major groups:

- *Organochlorines*: These synthetic organic pesticides are chlorinated hydrocarbons used extensively from the 1940s through the 1960s in agriculture and mosquito control. They have low toxicity level and long residual effects with stable chemical structure; thus, these pesticides are difficult to breakdown in nature and this leads to environmental pollution. Examples of these pesticides are DDT, methoxychlor, dieldrin, chlordane, toxaphene, mirex, kepone, lindane, and benzene hexachloride.
- *Organophosphates*: These pesticides can control a wide variety of pests and they are potent nerve agents, functioning by inhibiting the action of acetylcholinesterase (AChE) in nerve cells. They are one of the most common causes of poisoning worldwide, and are frequently intentionally used in suicides in agricultural areas. In the environment they are biodegradable, so the pollution caused by their use is minimum. Examples of these pesticides are:
  - Insecticides: malathion, parathion, diazinon, fenthion, dichlorvos, chlorpyrifos, ethion;
  - Ophthalmic agents: echothiophate, isoflurophate;
  - Antihelmintics: erichlorfon;
  - Herbicides: tribufos (DEF), merphos.
- *Carbamates*: The principle of the action of these pesticides is the same of organophosphates, that means they affect signals transmitted by nerves so the pest die by poisoning. These pesticides are also fumigants, stomach and contact poisons. In the environment they are biodegradable so the pollution caused by their use is minimum. Examples of these pesticides are: aldicarb, carbofuran, carbaryl, ethienocarb, fenobucarb, oxamyl, methomyl.
- *Synthetic pyrethroids*: These are pesticides derived from naturally occurring pyrethrins, taken from pyrethrum of dried Chrysanthemum flowers. They are very toxic with the property of lower break down times and are formulated with synergists increasing potency and compromising the body’s ability to detoxify the pesticide. The extensive use of pyrethroids is a main problem because they pollute the agricultural soils and water resources and affect non-target organisms and humans. Examples of these pesticides are allethrin, permethrin, cypermethrin, deltamethrin, bifenthrin, cyfluthrin.

16.9 Bioremediation as Technologies to Clean Up the Environment of Pesticides

Microorganism like bacteria, fungi, and algae can be used to clean up the environment. In 1973 was isolated the first microorganism that degraded organophosphorus compounds identified as *Flavobacterium sp*. Some strains of Pseudomonas have been informed to mineralize organophosphorous pesticides and fungicides (*Pseudomonas sp.*) and *Pseudomonas fluorescens* SM1 strain was reported as a bacterium that could remediate sites polluted with pesticides in India. Table 16.1 summarizes published results on these topics in the last 10 years.

The mechanism that fungi use to bioremediate soils contaminated with pesticides is through introducing minor structural changes, making the pesticide nontoxic and susceptible to additional biodegradation by bacteria (Gianfreda and Rao 2004). Several pesticide groups such as phenylurea, phenylamide, chlorinated and organophosphorus compounds can be degraded by fungi like *Hypholoma fasciculare,*

Table 16.1 Recent studies on some pesticides degrading and/or detoxifying microbes published during 2010–2019

Pesticides	Microorganisms	References
Organochlorine		
Aldrin	Bacteria: *Pseudomonas fluorescens* and *Bacillus polymyxa*	Doolotkeldieva et al. (2018)
Lidane, hexachlorocyclohexane, DDT, pentachlorophenol	Bacterium: *Pseudomonas sp.*	Kurashvili et al. (2016)
Endosulfan	Bacteria genera: Klebsiella, Acinetobacter, Alcaligenes, Flavobacterium, and Bacillus; and fungi *Pleurotus ostreatus*	Kadilzadeh et al. (2015), Sadiq et al. (2019)
Lindane	Fungus: *Fusarium verticillioides*	Guillen-Jimenez et al. (2012)
Tetrachlorvinphos (TCV)	Consortium of bacteria: *Stenotrophomonas maltophilia, Proteus vulgaris, Vibrio metschnikovii, Serratia ficaria, Serratia* spp. and *Yersinia enterocolitica*	Ortiz-Hernández and Sánchez-Salinas (2010)
Organophosphate		
Monocrotophos	Bacteria: *Enterobacter sp* and *Pseudomonas aeruginosa*	Jaramillo et al. (2016)
Methamidophos	Fungus: *Penicillium oxalicum*	Zhao et al. (2010)
Herbicide		
Linuron, metribuzin, and chlorpyrifos	Fungi: *Pleurotus ostreatus, Pycnoporus coccineus, Phlebiopsis gigantea* and *Trametes versicolor*	Gouma et al. (2019)
Chlorsulfuron	Fungi: *Alternaria alternata*, *Metacordyceps chlamydosporia*, *Stachybotrys chartarum*, *Penicillium simplicissimum*	Ergüven (2017)

Pleurotus ostreatus, *Coriolus versicolor*, *Avatha discolor*, and some others (Bending et al. 2002).

Ectomycorrhizal fungi have been used for degradation of DDT pesticide using a media with 5 mg L^{-1} of the DDT and the fungi used (*Laccaria bicolor*, *Boletus edulis*, *Leccinum scabrum*, and *Gomphidius viscidus*) degraded all the pesticide in 15 days of exposition (Huang et al. 2007).

Several white rot fungi from basidiomycete orders were investigated by Boyle et al. (1998) with the aim to analyze the degradation of mono-aromatic pesticides (diuron, atrazine, terbuthylazine, metalaxyl). Authors found that *Coriolus versicolor*, *Hypholoma fasciculare*, and *Stereum hirsutum* at 42 days degraded diuron, atrazine, and terbuthylazine until 86% and for metalaxyl not more than 44%. Proteases are enzymes involved in ligninolytic activities regulation in cultures of *T. versicolor* under nutrient limitation (Staszczak et al. 2000) and naphthalene (aromatic hydrocarbon) has a positive influence on protease (Margesin et al. 2000).

In the case of bacteria, they use hydrolytic enzymes as degrading mechanism breaking down some herbicides such as atrazine; examples are *Pseudomonas sp.* and *Klebsiella pneumoniae*. Other enzymes like oxygenases, hydroxylases, hydrolases, and isomerases that can degrade herbicide 2, 4-D; bacteria having these enzymes are *Pseudomonas* and *Alcaligenes* sp. The mainly reported genera of bacteria than can degrade pesticides are *Flavobacterium, Arthrobacter, Azotobacter, Burkholderia, and Pseudomonas* (Mulbry and Kearney 1991).

In Kyrgyzstan, a research to study the microorganisms that can live in soils from dumping zones contaminated with pesticides identified bacteria from *Micrococcus* genus in some of these soils, also authors identified bacteria from the genus *Pseudomonas* and *Bacillus* species. *Pseudomonas fluorescens* and *Bacillus polymyxa* population were selected for Aldrin (organochlorine insecticide) (Doolotkeldieva et al. 2018).

Kurashvili et al. (2016) investigated growth of several strains of Pseudomonas with organochlorine pesticides. The pesticides used were lindane (hexachlorocyclohexane), DDT and PCP in concentrations of 0.01, 0.1, and 1 mM and they found that after bacteria cultivation with DDT, several strains from genera Pseudomonas (35) grow better with glucose, while 15 strains had a superior growth with DDT. Respect to lindane 14 strains had a better growth with glucose and 13 strains with lindane than with glucose. About PCP, 14 strains from genera Pseudomonas revealed best growth with glucose and 4 strains were grown better with PCP. Finally, respect to DDT 11 strains of Pseudomonas that showed best grown with glucose were selected; for lindane and PCP, 11 and 10 strains, respectively, of Pseudomonas that revealed best grown with glucose were selected (Kurashvili et al. 2016).

16.10 Phytoremediation as a Technology to Clean Up the Environment of Pesticides

Plants can use different mechanisms to eliminate or degrade contaminants from the environment; some of the mechanisms are via root uptake, detoxification or conjugation, and some others (Van Eerd et al. 2003; Wilson et al. 2000).

Trees can be used also for phytoremediation because they have a lot of biomass (stems and branches, 95%). In this sense polychlorinated biphenyls (PCBs) can accumulate in bark of black walnut and white oak (*Quercus alba*) and poplar trees (Meredith and Hites 1987).

The degradation of atrazine (herbicide of the triazine class) was studied by Anderson and Coats (1995). The research was made in the rhizosphere of 15 plant species and they found higher mineralization in rhizopshere soil from several of the species under study, such as kochia (*Kochia scoparia*), common lambsquarters (*Chenopodium album*), witchgrass (*Panicum capillare*), and some others. Another study of atrazine was done with poplar (*Populus deltoides x nigra)*; this plant can transform the herbicide into dealkylates (Burken and Schnoor 1996; Burken and Schnoor 1997).

Another research was made with atrazine, metolachlor, and cyanazine where bromegrass strip (*Bromus inermis* L.) retained atrazine (11–100%) and the three herbicides were retained by the grass because of infiltration process (Arora et al. 1996).

Wilson et al. (2000) reported use of *Typha latifolia* to remove simazine (herbicide of the triazine class) from contaminated water.

Schnabel and White (2001) reported that balsam poplar (*Populus balsamifera*) is tolerant to aldrin because of uptake and metabolism, and Baz and Fernandez (2002) reported several plants that can be tolerant or sensitive to some pesticides like: Virginia sweetspire (*Itea virginica* L.), white willow (*Salix alba* L.), black pussywillow (*S. gracilistyla*).

After harvest of crops in a field, phytoremediation technology can stop leaching of contaminants to groundwater (field without crops) (Wilson et al. 2000; Coleman et al. 2002).

Several grasses (*Andropogon gerardii* Vitman; *Sorghastrum nutans* L., and *Panicum virgatum* L.) were studied referred to atrazine and metolachlor degradation by Zhao et al. (2003). The grasses mentioned were grown in soil with atrazine (100 μg g^{-1} of dry soil) and metolachlor (25 μg g^{-1} of dry soil); the use of mixed grasses increased the degradation of atrazine in soil without microorganism, also metolachlor concentration was reduced with the mixture.

Soils cultivated with *Pennisetum clandestinum* can be cleaned up of atrazine and simazine due to the high rates of removal of this plant (Singh et al. 2004).

Lunney et al. (2004) investigated the ability of five plant varieties (zucchini, tall fescue, alfalfa, rye grass, and pumpkin) for the mobilization and translocation of DDT used in soil at concentrations of 3700 ng g^{-1} (high concentration) and 150 ng g^{-1} (low concentration). Results showed that *Cucurbita pepo* species (pumpkin and zucchini) had the highest translocation and bioaccumulation factors.

Xia and Ma (2006) studied the phytoremediation capacity of *Eichhornia crassipes*, an aquatic plant known as water hyacinth with long pendant roots, rhizomes, and stolons. This plant was used with the aim to decontaminate polluted water of malathion and ethion and as results *E. crassipes* degraded about 56% of 10 ppm of malathion in 250 mL and the accumulated ethion in this plant decreased in different parts of the plants like in shoots (55–91%) and roots (74–81%) after the plant growing for 1 week in ethion free culture solutions.

At present there are several examples of genetically modified plants for pesticide degradation: *A. thaliana*, *Solanum lycopersicum* L., *Nicotiana tabacum* L. and *Glycine max* L. plants can express glyphosate oxidase, cytochrome P450 enzymes, a Rieske non-heme monooxygenase that converts dicamba to 3,6-dichlorosalicyclic acid (Behrens et al. 2007); corn can express aryloxyalkanoate dioxygenase enzymes (TfdA) useful for the degradation of 2,4-D and pyridyloxyacetate herbicides (Scott et al. 2008).

Ricinus communis L. was used for the degradation of several persistent organic pollutants (POPs), in a 66-day period. The results showed that hydrophobicity of the organic compound and its molecular constitution interacted with soil or root matrix and increased its tendency to concentrate in root tissues hexachlorocyclohexane (HCHs) < diclofop-methyl < chlorpyrifos < methoxychlor < heptachlor epoxide < endrin < o,p′-DDE < heptachlor < dieldrin < aldrin < o,p′-DDT < p,p′-DDT. The plant removed 25–70% of pollutant, proving that *R. communis* can be used for the phytoremediation of such compounds. The greatest results were found for the remediation of HCHs (65.07–68.33%), chlorpyrifos (46.34–69.01%), diclofop-methyl (53.66–54.98%), and trans-chlordane (44.17–49%) (Rissato et al. 2015).

Five plants (alfalfa, oat, ryegrass, Indian mustard, sunflower, tall fescue, and switch grass) were grown under greenhouse conditions to phytoremediate soil contaminated with mixed metal-PAH-pesticide (DDT as model). The results revealed that sunflower and Indian mustard were the most tolerant plants to the studied mixed contaminants; also, sunflower removed metals and PAH at the same time. In the case of oat, it was inappropriate for phytoremediation of metal-PAH contaminated soil (Ndubueze 2018).

Aioub et al. (2019) used *Plantago major* (perennial herb) and some surfactants [liquid silicon dioxide (SiO_2, 750 mg L^{-1}), 2-hydroxypropyl-beta-cyclodextrin (HPßCD, 1%), humic acid (HA, 10 mg L^{-1}) and Tween 80 (Tw80, 9.2 mg L^{-1})] for reducing soil contamination with cypermethrin (CYP, 10 μg g^{-1}) (pyrethroid insecticides). Soil improvement with *P. major* together with SiO_2 significantly decreased the quantity of CYP and increased the concentration of the insecticide in *P. major* roots and leaves.

16.11 Conclusions

Interactions between plants and microorganisms begin to bear fruit in the elimination of toxic waste from the environment. In contrast to the indiscriminate dumping of waste, which is increasing every day due to the increase in population and anthropic activities, solutions have begun to appear that contribute to the reduction of the impact of these actions. In reducing pollutants, the combined possibilities of plants, bacteria, and fungi are used, which, through different mechanisms, hydrolyze the pollutants or a part of them, transform them into nontoxic substances or accumulate them in the plant organs, removing them from the soil and the water.

Plant–microbe interactions have been useful in the detoxification of hydrocarbons and their derivatives, heavy metals, and pesticides. The genetic engineering of plants and microbes is also providing results in this regard (mainly in the remediation of heavy metals and herbicides) although it stumbles upon the laws that in many countries regulate the introduction of genetically modified organisms. However, due to the demonstrated ability to enhance the capacities of natural organisms, genetically modified plants and microorganisms are expected to participate in environmental detoxification in a much larger proportion in the future.

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Microbes: A Potential Tool for Bioremediation

17

Nilesh Sonune

Abstract

Environmental pollution has become a universal problem because of the fast growth of population, civilization and industrialization. It leads to the accumulation of contaminants in the environment that has an adverse effect on human health and ecosystem. Bioremediation is a most efficient, eco-friendly and cost effective technology for the transformation of contaminates. Culturable microorganisms have been exploited efficiently in biodegradation of contaminants but, inefficient in exploitation of unculturable microorganisms. The successful implementation of technology needs a detailed knowledge of microbial metabolism, growth and function of native microbial population at polluted site. This could be overcome by exploitation of recent innovative tools such as nanobioremediation, biosurfactant, cell immobilization, genetically modified organism, chemotaxis, metagenomics and proteomics. These tools have provided crucial insights of microbial communities and their mechanisms in bioremediation of environmental contaminants. These tools provide important information of microorganism along with their mechanisms for restoration of contaminants. This chapter focuses on the overview of important techniques of bioremediation as well as recent advances used for the bioremediation of environment.

Keywords

Bioaugmentation · Bioremediation · Chemotaxis · Genomics · Nanoremediation

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17.1 Introduction

In the last couple of decades, due to explosive rise in industrialization, urbanization and human population, the utilization of the natural resources has increased enormously. This has led to high stress on agricultural and industrial production. However, it reults in the production of huge quantity of different organic and inorganic products such as chemicals, pesticides, fertilizers and industrial waste. The release of such waste into the environment, leads to the pollution of the habitats like soil, water and air (Bharagava et al. 2019; Sonune and Garode 2015).

The release of these contaminants can occur either accidentally or because of anthropogenic activities into the environment that ultimately results in environmental pollution, leading to many health hazards. These pollutants or chemicals come into the different food chains from the atmosphere. The chemicals flow occurs from one tropical level to others resulting in bioaccumulation that imparts risks to the ecosystem (Das et al. 2014). Because of these, nature is constantly evolving, posing new difficulties and making consistent requirement to develop new and more suitable technology (Juwarkar et al. 2014).

There is a need of efficient, cheap, long lasting and effective treatment for waste generated in the environment. To meet the challenges, there are several conventional techniques available such as physico-chemical methods to treat these chemicals or waste. Although these methods are not cost effective, unsuccessful to eliminate contaminants completely and the final product is also again lethal. Therefore, development of eco-friendly and cost effective techniques is necessary. Hence, currently, microbial treatment process has become popular and accepted globally which overcome the problems associated with traditional techniques (Sonune and Garode 2018; Kumar et al. 2018).

Nowadays, biotechnology is being considered as emerging science and has tremendous potential of protection and management of the environment. It involves the exploitation of microbes for biological treatment of environmental pollutants (Azadi and Ho 2010; Pandey and Fulekar 2012). Bioremediation is a green technology for the treatment of the harmful chemicals and a popular alternative to traditional methods for degradation of contaminants because it uses natural activities of different types of microbial consortia (Juwarkar et al. 2014).

17.2 Bioremediation

Bioremediation is a process by which living organisms are stimulated to rapidly degrade harmful organic contaminants to environmentally safe levels in the environment (Sasikumar and Papinazath 2003), which may be aquatic, terrestrial or both. In bioremediation mainly microorganisms have been exploited because of their miscellaneous metabolic capacities to transform toxic pollutants to non-toxic compounds through mineralization, carbon dioxide and water production (Singh et al. 2017).

The efficiency of bioremediation needs the presence of precise types of microbes, their proper quantity, combination and suitable environmental conditions.

Microorganisms that are already present at polluted environments are frequently well adapted to live in the presence of existing pollutants, pH, temperature and oxidation/reduction potential of the site (Pandey and Fulekar 2012).

17.3 Microbial Bioremediation

Microbes are extensively scattered in nature because of their diverse metabolism, thrive in a broad range of environmental conditions and versatility in nutrients. Therefore, they can be utilized for bioremediation of contaminants. The basis of the bioremediation is capability of certain microbes to transform and utilize contaminates to acquire energy for their growth (Prakash et al. 2014; Abatenh et al. 2017). Microorganisms are well-known to be the most important agents for bioremediation, which transform and clean up the complex lipophilic organic molecules, to the simple water soluble molecules. The biological agents used for bioremediation are mainly microorganisms includes bacteria, fungi and algae for removal of contaminants from polluted areas (Strong and Burgess 2008; Kumar et al. 2018). When selective microbial population are exposed to the specific or structurally related contaminants, they first attack on this by enzymatic process. These contaminants if present in the environment may act as inducer or repressor for the enzymatic function of microorganisms. Primary or secondary groups of microorganisms typically attacked on these water soluble intermediates and convert them into the inorganic end product by complete degradation. The microorganisms involved in this process may be indigenous or exogenous to polluted location. Polluted substances are altered by metabolic processes of the microorganisms. Generally, multiple microorganisms are involved in biodegradation of a compound (Gupta and Mahapatra 2003).

17.4 Bioremediation Organisms

Bioremediation is the method of eco-friendly waste management that utilizes the inherent ability of microorganisms which includes bacteria, algae and fungi to eliminate or transform the contaminants from the environment (Saxena and Bharagava 2015; Bharagava et al. 2017). Such microbes have potential to obtain energy from almost all compounds by using different electron acceptors in aerobic or anaerobic environment.

17.4.1 Bacteria

Numerous types of bacteria are reported that involved in the transformations or degradation of pollutants includes genera of *Achromobacter, Alcaligenes, Arthrobacter, Acinetobacter, Flavobacterium, Micrococcus, Bacillus, Escherichia, Pseudomonas, Gordonia, Moraxella, Pandoraea, Streptomyces, Rhodococcus,* *Nocardia, Sphingobium, Desulfotomaculum, Azoarcus, Clostridium, Methanospirillum, Sphingomonas, Desulfovibrio, Methanococcus, Geobacter, Methanosaeta, Syntrophobacter, Pelotomaculum, Syntrophus, Xanthomonas, Thauera,* etc. (Lopez et al. 2002; Kim et al. 2007; Hasin et al. 2010; Weelink et al. 2010; Liu et al. 2011; Jayashree et al. 2012; Garode and Sonune 2014; Sonune and Garode 2018).

17.4.2 Fungi

Many fungal genera have been isolated and identified for bioremediation of contaminates. These fungal genera include: *Aspergillus, Cladosporium, Mucor, Fusarium, Phanerochaete, Trichoderma, Rhizopus, Penicillium, Agaricus, Pleurotus, Hansenula, Rhodotorula, Coprinellus, Gloeophyllum, Candida, Saccharomyces,* etc. (Tigini et al. 2010; Aranda et al. 2010; Karigar and Rao 2011; Pereira et al. 2014; Safiyanu et al. 2015; Burghal et al. 2016).

17.4.3 Algae

Phycoremediation is application of algae for bioremediation and is effective for removal of contaminants (Wang et al. 2016). Many algal species are involved in bioremediation that includes genera of *Spirulina, Selenastrum, Portieria, Chlorella, Agmenellum, Monoraphidium, Chlorococcum, Scenedesmus, Oscillatoria, Caepidium, Chlamydomonas*, *Monoraphidium, Anabaena,* etc. (Terry and Stone 2002; Boshoff et al. 2004; Wang et al. 2011; Newete and Byrne 2016; Bwapwa et al. 2017).

17.5 Methods for Bioremediation

On the basis of transport and removal of contaminants, bioremediation has been categorized into two types- ex situ and in situ bioremediation (Fig. 17.1). Both methods are essentially depending on the metabolism of microorganisms. Among them, in situ method is preferred than ex situ method for bioremediation of polluted site. However, the selection of particular technology is based on many factors such as native microbial population, conditions of site, and quantity, type and toxicity of contaminants present (Jorgensen 2007).

17.5.1 In Situ Bioremediation

In this technique, the treatment of polluted substances is done at the site of pollution. This technique does not require excavation of contaminated materials such as soil and water to achieve the remediation process. In this process, aqueous solution

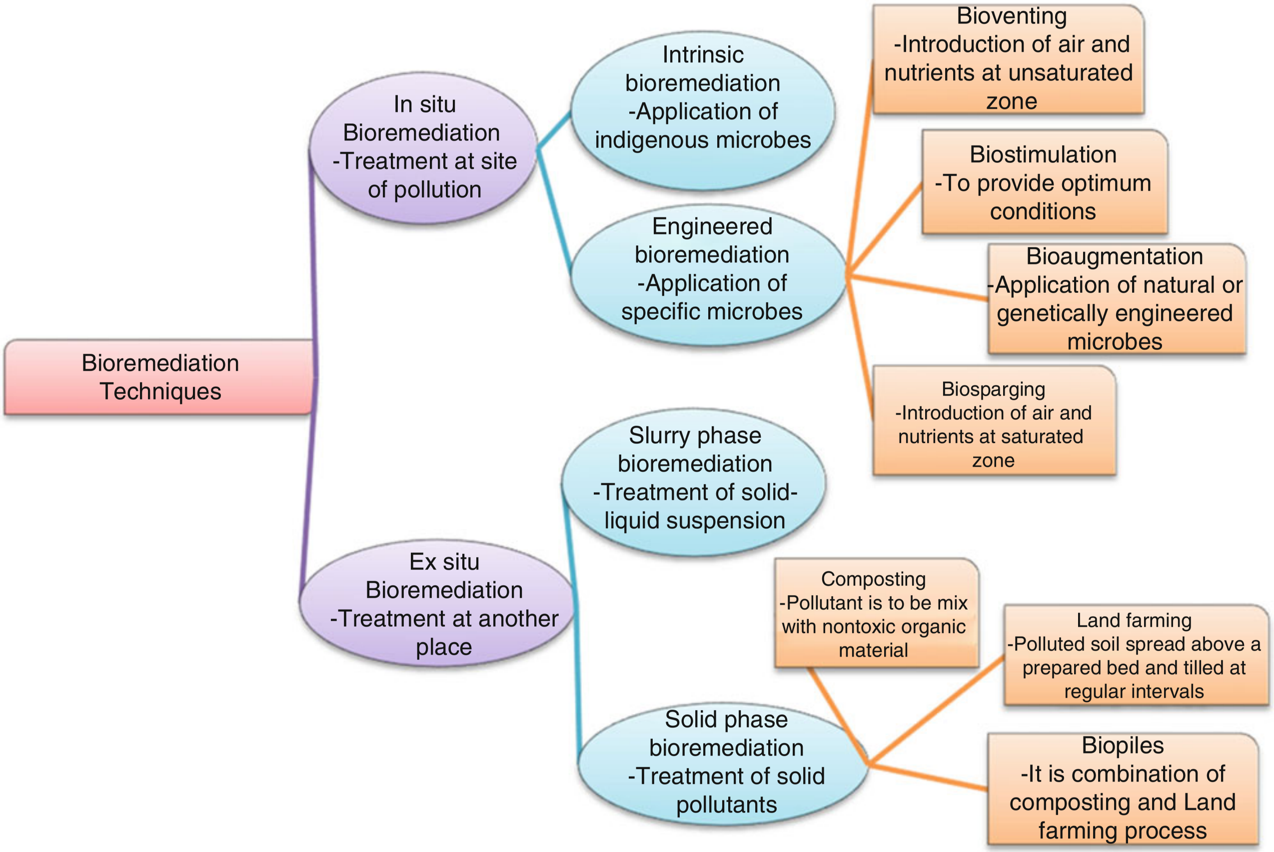

Fig. 17.1 Various bioremediation techniques

containing nutrients and oxygen is circulated through contaminated soil to increase the activity of the indigenous microbial community to degrade toxic organic pollutants (Folch et al. 2013; Frascari et al. 2015). These techniques are less costly compared to the ex situ techniques because extra costs are not needed for the excavation processes. Similarly, it uses native harmless microbial organisms for degradation of pollutants, and has potential to treat large amount of contaminant. Based upon the origin of microorganisms applied, there are two types of in situ bioremediation, i.e. Intrinsic and Engineered bioremediation (Kim et al. 2014; Roy et al. 2015).

17.5.2 Intrinsic In Situ Bioremediation

It is also referred as natural attenuation or bioattenuation. In this method, natural processes are employed to degrade contaminants or to decrease the quantity of contaminants at polluted sites by stimulating the activity of indigenous microorganisms by providing stimulants such as oxygen and nutrients (Philp and Atlas 2005). For the success, intrinsic remediation depends on various factors such as adequate biodegradable microbial population, sufficient nutrients availability and suitable environment at the contaminated site (i.e., pH, oxygen, temperature) and appropriate time for degradation (NRC 2000).

17.5.3 Engineered In Situ Bioremediation

With this approach, bioremediation achieved through the introduction of specific microbes to a polluted site. This approach speed up the degradation of contaminants by providing proper physic-chemical conditions to supports the microbial growth. For this purpose, sufficient quantity of oxygen and nutrients is to be provided to promote microbial growth and enhance the remediation process. Some methods of this approach include biostimulation, bioventing, bioaugmentation and biosparging (Sardrood et al. 2013).

17.5.3.1 Bioventing

This method is one of the most widely recognized *in situ* methods for the bioremediation. In this, air and nutrients are delivered to the unsaturated zone of contaminated soil through wells to stimulate the indigenous microorganisms. This approach provides optimum quantity of oxygen required for the degradation with minimize the volatilization that discharges it into the environment. Bioventing works for hydrocarbon as well as those contaminants which are deep beneath the surface (Vidali 2001; Philp and Atlas 2005).

17.5.3.2 Biostimulation

Biostimulation is another strategy for bioremediation in which native microbial activity in ground water and/or soil is enhanced by adjusting pH, optimum nutrient and oxygen in order to speed up the bioremediation. This technology is designed mainly for the treatment of groundwater and soil contaminated by fuels, herbicides and pesticides. It needs the presence of native microorganisms which are capable of degradation of particular pollutants (Li and Li 2011; Azad et al. 2014).

17.5.3.3 Bioaugmentation

Bioaugmentation is a process where the natural or genetically engineered microbial culture with potential of transformation or degradation of contaminants is to be added at contaminated environment (Azad et al. 2014). Two factors that limit the use of addition of microbial cultures in a land treatment unit, i.e. competition of non-indigenous microbes with an indigenous microbial population for their survival and the soil which have long-term exposure to the contaminants has native microbes which are highly efficient for degradation (Vidali 2001).

17.5.3.4 Biosparging

Biosparging method is very much related to bioventing where in both air is to be introduced into the soil subsurface for enhancement of microbial activities for remediation of contaminants from sites. However, in bioventing approach, air is introduced at unsaturated zone that causes movement of volatile compounds at upward direction in to the saturated zone to help biodegradation. However, the efficacy of this method depends on pollutant biodegradability and the permeability of the soil. Biosparging has been extensively exploited for the treatment of aquifers polluted with petroleum products (Philp and Atlas 2005; Azubuike et al. 2016).

17.6 Ex Situ Bioremediation

Ex situ method have need to dig polluted materials to assist degradation process. This method has many drawbacks than the advantages. Here, cost can be high as it required for the excavation process of the contaminated samples and its transportation for remediation treatment. Based on the state of the pollutant to be removed for bioremediation, ex situ bioremediation methods are classified into two systems, i.e. slurry phase and solid phase bioremediation (Hashmi et al. 2017).

17.6.1 Slurry Phase Bioremediation

This method includes treatment of the solid-liquid suspensions. It is comparatively fast treatment compared to the other methods. In this method, degradation is accomplished in bioreactor in which polluted soil is combines with the water, native microbes, appropriate nutrients and oxygen to provide optimal condition. After completion of the treatment, the liquid part is separated from the solid and is properly disposed of. The remaining solid wastes material is disposed of or subjected to other processes for further decontamination (Sardrood et al. 2013).

17.6.2 Solid Phase Bioremediation

This method involves treatments of various solid pollutants includes agricultural wastes, industrial wastes, municipal solid wastes and sewage sludge. This process is simple to manage; however, requires more space and time for degradation compare to the slurry phase process. Principle of this process is based on the mechanical breakdown of contaminated soil by abrasion and intensive mixing in an enclosed vessel. This treatment process includes composting, land farming and biopiles techniques (Sardrood et al. 2013).

17.6.2.1 Composting

Composting is an aerobic and the thermophilic surface treatment process used to transform contaminants. In composting, polluted is to be mixed with non-toxic organic amendments, i.e. agricultural waste or manure (Kumar and Singh 2001). This process enhances the development of robust microbial communities that speed up the composting. A composting process occurs at elevated temperatures ranging from 55 to 65 °C. This temperature range achieved as a result of heat production by microbial activity during organic material degradation present in the waste (Vidali 2001).

17.6.2.2 Land Farming

In land farming process, polluted soil is excavated, spread above a prepared bed and tilled at regular intervals up to contaminants are degraded. The main objective of this process is to stimulate indigenous microorganisms that are capable of biodegradation. However, this treatment process limited for uppermost surface of soil generally up to 10–35 cm. This approach received much attention as a disposal option of waste material because of low monitoring and maintenance cost (Margesin and Schinner 1999; Vidali 2001).

17.6.2.3 Biopiles

Biopiles techniques are the combination of composting and land farming bioremediation methods. This method reduces physical losses of the pollutants which take place due to volatilization and leaching (Kastner and Mahro 1996). Biopiles give a favourable environment for native microbes involved in degradation. Generally, this method is a refined version of land farming and applied for treatment of the surface contaminated with petroleum hydrocarbons (Whelan et al. 2015).

17.7 Emerging Approaches in Bioremediation

In recent year, a number of new tools and techniques are developed that overcome some of the limitations of traditional processes and helps to speed up the process, improve reliability, cost efficiency of bioremediation (Fig. 17.2). A brief overview of such important processes involved is discussed as follow:

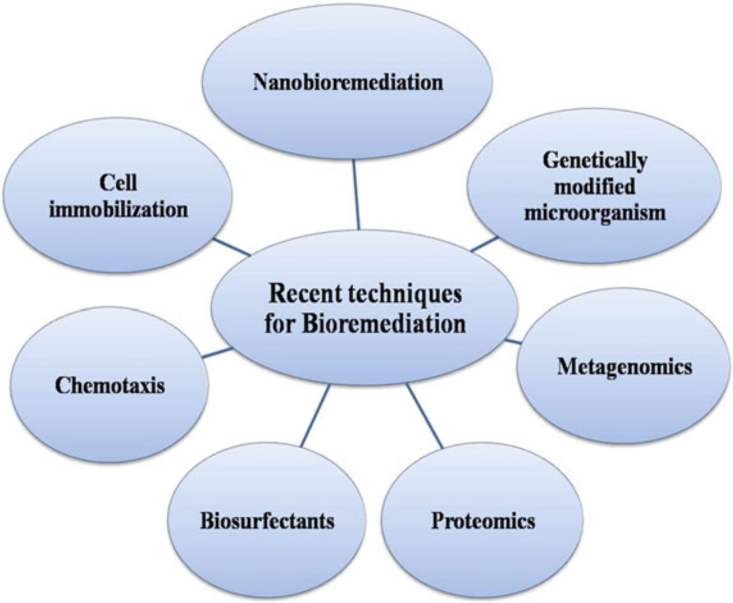

Fig. 17.2 Recent bioremediation techniques

17.7.1 Biosurfactants

Biosurfactants are surface active molecules produced by living cells particularly microorganisms. Application of biosurfactants is an excellent option to enhance the bioremediation of contaminated site that would enhance the effectiveness of efficient microorganisms for bioremediation potential. The availability of targeted pollutants to degradative microbes is one of the major problems in the bioremediation process because of the hydrophobic nature of the contaminants. This problem can be overcome with the help of biosurfactants that facilitate direct contact between contaminants and the microbes (Banat et al. 2000). Biosurfactants reduce the hydrophobic nature of pollutants and make it readily accessible to the microorganism for their degradation. Microbial surfactants are non-toxic, biodegradable, non-hazardous and cheap, and cost effective, hence they have been using for bioremediation (Ron and Rosenberg 2002). The most common biosurfactants are glycolipids, lipoproteins, lipopeptides and heteropolysaccharides (Dua et al. 2002). The application of biosurfactants has been progressively rising in recent year because of their environment friendly nature, selectivity, diversity, production in large scale and performance under extreme conditions (Banat et al. 2000). Use of the biosufactants is mainly involved in the bioremediation of hydrocarbons and heavy metals contaminated sites, to enhance oil recovery, management of oil spill and oil recovery from the sludge (Dua et al. 2002). Considerable studies were done on the biosurfactant production by a variety of microbial strains (Chen et al. 2011; Imura et al. 2014; Anaukwu et al. 2015; Kuyukina et al. 2015).

17.7.2 Cell Immobilization

In recent times, applications of cell immobilization methods in bioremediation of contaminants are increased significantly. Immobilization means restricting the movement of microorganisms or their enzymes without disturbing their catalytic functions and viability (Guzik et al. 2014; Kourkoutas et al. 2004; Dzionek et al. 2016). Immobilization process has many benefits in bioremediation process like multiple use of biocatalysts, reduced costs as reuse of cells, higher efficiency of pollutant degradation, resistance to the shear forces in bioreactors and other adverse environmental conditions, reduced risk of genetic mutations and increased tolerance to high pollutant concentrations (Rivelli et al. 2013; Bayat et al. 2015). For microbial cells immobilization, carriers are essential for surface binding. The carriers used may be rather organic or inorganic in nature. Carrier selection is important aspects in bioremediation as on its surface microbes is to be attached. In immobilization, total five techniques are there. However, adsorption is the most frequent method employed in bioremediation because of the simplicity. Considerable work has been done on microbial cell immobilization (Angelim et al. 2013; Bhatnagar et al. 2015; Dzionek et al. 2016).

17.7.3 Nanobioremediation

Application of nanoparticle for bioremediation of contaminated sites is also known as nanobioremediation. Nanotechnology is a recent and promising branch of science that attracted the attention of researchers interested in different subjects because of its small size and efficient outcomes towards issues such as environmental pollution. Nanobioremediation involves the use of nanomaterials for the treatment of contaminants either by using in situ or ex situ method. In the recent year, nanotechnology has significantly contributed in bioremediation of the pollutants from soil, water and air into non-toxic and eco-friendly compounds. Along with bioremediation, it also plays important role in pollution monitoring, detection and prevention (Rajan 2011; Carata et al. 2017). Various types of microorganisms such as bacteria, actinomycetes, fungi and algae are used for biological synthesis of metal nanoparticles. Various types of metals have been used for the preparation of biological nanoparticles for bioremediation includes nickel, iron, silver, gold and palladium (Thome et al. 2015). The role of nanoparticles in bioremediation is to sequester or degrade pollutants like the herbicides, pesticides, insecticides and heavy metals from contaminated atmosphere (Sakulchaicharoen et al. 2010). It is cost effective and potential technique for bioremediation. It facilitates chemical reduction as well as catalysis to mitigate the contaminants of the concern. Because of their innovative surface coatings and tiny size, they are capable to permeate the subsurface in very small spaces and stay suspended in the groundwater. This allows them to move fast than large sized particles and achieve wider distribution (Kanatzidis and Poeppelmeier 2007).

17.7.4 Genetic Engineered Microorganisms

Degradation of xenobiotic compounds remains a serious issue of environmental pollution. In recent years, the interests have been increased on bioremediation of such compounds. The common use and lack of biodegradation of xenobiotic compounds leads to their widespread occurrence and persistence in the environment. Investigations on the microbial biodegradation pathways on these compounds shown that recalcitrance is a factor that causes biochemical blockage which result in dysfunctional catabolic routes. This factor has raised interest to construct genetically engineered microorganisms with superior catabolic activities (Janssen and Stucki 2020). Genetic engineering technologies have been used on many occasions to improve the rate of biodegradation of particularly recalcitrant organic pollutants. The exploitation of genetically engineered microorganisms for restoration purpose is cost effective and eco-friendly method for removal of pollutants in contaminated sites (Panz and Miksch 2012). To remediate heavy metals from polluted sites is difficult by natural bacteria, however, this can be overcome by the use of genetically engineered bacteria. For the remediation of different types of heavy metals like Ni, Hg, Cd, Cu, Fe and As, genetically engineered microbes have been used (Bruschi and Goulhen 2006). Several kinds of genetically engineered microorganisms have been developed through recombinant technologies and applied for remediation of sites polluted with heavy metals and other toxic materials (Azad et al. 2014). Some studies reported remediation of metals and recalcitrant chlorinated chemicals from different polluted sites by different microorganisms (Murtaza et al. 2002; Furukawa 2003; Cases and de Lorenzo 2005; Bondarenko et al. 2008; Gong et al. 2017).

17.7.5 Chemotaxis

Chemotaxis is an important feature of some motile microorganisms. It is a movement of microbes under the influence of the chemical. This movement helps them to search the most favourable environment for their survival and growth (Ford and Harvey 2007). It has been observed that chemotaxis is a selective advantage for bacteria to sense and locate the environmental contaminants. Chemotaxis has the ability to significantly improve in situ bioremediation processes (Paul et al. 2006). Though, this feature has not received much attention, even though certain microorganisms have capability of chemotatic movement towards various xenobiotic compounds (Bhushan et al. 2000). Some reports are available on the isolation and characterization of chemotactic microorganisms towards various xenobiotic compounds (Parales and Harwood 2002). In several cases, chemoattractant is a compound that serves as a source of carbon and energy, whereas chemorepellent is toxic to bacteria. Recently, number of microbes with chemotactic activity towards diverse environmental contaminants have been reported (Pandey and Jain 2002; Parales and Harwood 2002; Ford and Harvey 2007). The several studies reported direct or indirect correlation between chemotaxis and bioremediation of contaminated ground water and soil (Samanta et al. 2000; Parales and Harwood 2002; Bhushan et al. 2000).

17.7.6 Metagenomics

Metagenomics is the study of metagenome which recovered directly from the environmental samples. It is an emerging approach which can be used for the characterization of microbial population, gives detail information of the genomes of uncultured microorganisms and degradation of contaminants at the contaminated site (Uhlik et al. 2013; Bharagava et al. 2019). This approach is helpful to find out the efficient microbes for degradation of a particular contaminants or catabolic gene that is responsible for degradation or detoxification of the particular contaminants. The accessibility of entire genome sequences from many environmental microbes is an important step for bioremediation. This technique is valuable in assessing the gene pool of the enzymes which involved in pollutants the degradation (Galvao et al. 2005; Desai et al. 2010). In recent years, methods focused on metagenomics have been useful in evaluating novel gene families as well as microorganisms involved in remediation of xenobiotic compounds. Nowadays, DNA microarray has been used to track microbial communities, to characterize contaminants, biodegrading microorganisms and to identify novel pathway for biodegradation (Bae and Park 2006). The construction and screening of metagenomic libraries for identification of genes involved in bioremediation has been documented in several studies (Jennings et al. 2009; Wang et al. 2012; Ma et al. 2015; Sul et al. 2016; Hong et al. 2017).

17.7.7 Proteomics

Investigation of proteins, termed as proteomics, is recently being used as a technique in bioremediation. It involved identification and quantification of proteins of the microorganisms (Aslam et al. 2017). Expression of proteins in the microorganisms depends on the various environmental conditions which are responsible for their adaption as well as physiological changes. Proteomics approach is helpful for the examination of protein components and detection of key proteins that are involved in the physiological state of the microorganism in the presence of particular contaminants. Because of the proteomics approach, novel pathway for biodegradation of contaminants are uncovered that provides an idea for detection of novel proteins (Santos et al. 2004; Kim et al. 2006).

17.8 Conclusion

Bioremediation is one of the green, eco-friendly and inexpensive technology for degradation or removal of toxic contaminates from the environment. Various approaches of bioremediation efficiently involved in the removal of contaminants, however, certain factors such as recalcitrant and high toxicity of contaminates remain a challenge for this approaches. This can be overcome by implementing the recent tools and techniques. Recent tools help for bioremediation by many ways such as selection of microorganism with suitable traits for degradation of particular compound, provide detail information of the genomes of uncultured microbes, type of condition at contaminated sites and uncovered new pathway for biodegradation of toxic wastes.

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18

Physical, Chemical, and Biological Remediation Techniques for Textile Effluents in Context with Developed and Developing Countries

Anum Mahmood, Barira Bilal, Zainab Naeem, and Shazia Iram

Abstract

There is an immense increase in the demand of colorful, sophisticated, and versatile garments produced by textile industry. Previously dyes were obtained from the natural sources but the quantity generated was very low and the color produced was not steady. In the present world natural dyes are widely replaced by synthetic dyes because of their stability, brightness, and cost effectiveness. Like every man-made product, synthetic dyes have their own set of disadvantages. Most prominently the dyes having chromophore groups are persistent, carcinogenic, and toxic to the aquatic environment in which they are released. This chapter focusses on the techniques adopted by developing and developed nations for the remediation of textile dyes. In a broader perspective these practices are divided into physical, chemical, and biological remediation techniques. Pros and cons of each method are discussed along with the recent developments in each method. To overcome the harsh effects of textile dyes effluent on the ecosystem,it is highly recommended to develop a combined approach that has benefit from all the remediation techniques.

Keywords

Biological remediation · Microbes · Mechanism · Textile effluents

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18.1 Introduction

Natural dyes are harnessed from the plants, insects, and shells of fish but provide a very short range of colors. The extract from all the natural sources was very limited thus making it highly expensive and short lived. The hard work for the development of such a dye that is long lasting and cost effective results in the formation of highly stable and inert organic structures now commonly known as textile dyes (Ziarani et al. 2018). The excessive usage of synthetic colors was noticed in the mid of the previous century. These dyes were designed to be resistant to color fading, UV radiations, chemical and biological degradation (Shahid et al. 2013). Synthetic dyes are not only toxic but if released as it is in the aquatic environment are potent to produce such by-products that can lead to the eutrophication and decrease sunlight penetration (Ahmed et al. 2018). The fabric industry is responsible for the most toxic effluent discharge as compared to rest of the production sectors due to high chemical oxygen demand, resistant dyes, raised pH, and low biodegradability (O'Neill et al. 1999; Vilaseca et al. 2010). The textile effluent poses serious threat to environment due to their complex mixture of various organic, inorganic, elemental, and polymeric pollutant substances (Choi et al. 2004). They have major environmental implication because 50% of initial dye used for coloring process remain in consumed bath as hydrolyzed entity which cannot be used again for dyeing the fabric (Laszlo 1995). Excessive employment of chemicals with in the textile processes leads to the release of huge amount of toxic effluents in fresh water resources. The major fraction of textile wastewater encompasses cancer causing dyes, noxious heavy metals, bleaching agents, and other such chemicals with sediments dissolved solids (Correia et al. 1994). The improper disposal of highly colored and toxic effluent when discharged into freshwater bodies stops re-oxygenation capacity and blocks sunlight that causes disturbance in the aquatic ecosystem (Nassar and Magdy 1997). Dyes having aromatic rings are known carcinogen. The presence of toxic aromatic compounds and their degraded forms in aqueous medium leads to severe ailments in humans' that resulted into irreversible impairment of various vital organs such as kidneys, liver, and all body systems (Ramachandran et al. 2013).

As the need of the hour many techniques have been developed and practiced by both developing and developed nations. These techniques can broadly be distinguished into physical, chemical, and biological remediation techniques. Physical as name suggests deals with the removal of pollutants without any permanent change, chemical involves use of chemical moieties that can undergo certain reactions for detoxification, whereas biological includes employment of living organisms (both plants and microorganisms) for the pollutant's removal from waste water.

18.2 Types of Textile Dyes

Dyes retain pigment because they absorb light in the range of 400–700 nm. All of them holds at minimum one chromophore group (Uday et al. 2016). Many dyes along with chromophores possess *auxochromes*. These are color helpers and can be

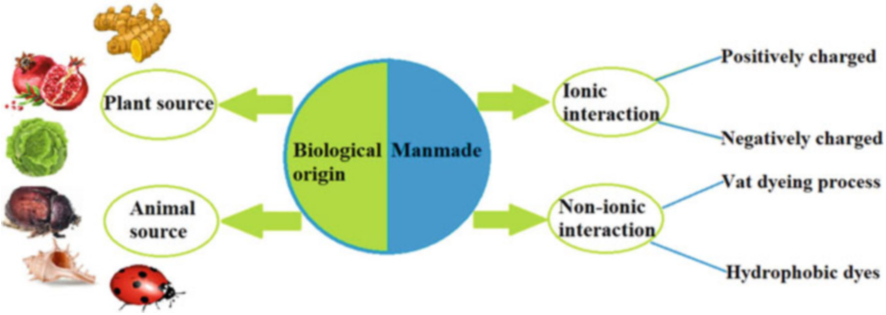

Fig. 18.1 General classification of dyes

composed of various acids (carboxylic, sulfonic) and polar groups (amino, hydroxyl) (IARC Working Group on the Evaluation of Carcinogenic Risk to Humans 2010). They do not impart any color but crucial for the dye solubility (Abrahart 1977).

There are two main categories of dyes, i.e. ionic and nonionic dyes (Ahmed et al. 2018). The ionic dyes can be alienated into cationic (positively charged) and anionic (negatively charged) dyes. The cationic dyes can further be classified as basic dyes (e.g. Basic Brown 1). Basic dyes form a cationic salt in water and are powerful coloring agents for acrylic fibers (Gupta and Suhas 2009). Anionic dyes can be classified into acidic (e.g. Acid yellow 36), reactive (e.g. reactive blue 5), and direct (e.g. Direct orange 26) dyes (Fig. 18.1). Dyes that are acidic have greater water solubility and are employed for dying the natural and synthetic fabric (Axelsson et al. 2006). Reactive dyes are most preferable in fabric business as they own high color intensity and reactivity towards cellulose (Khataee et al. 2013). Direct dyes are not readily dried up fast and are more specifically required for the dying of protein fibers (Royer and Cardoso 2009). Nonionic dyes are segregated into vat (e.g. Vat Blue 4) are insoluble in water used for coloring cellulosic fibers (Gutowska et al. 2006). Disperse dyes such as Red 4 is used for dyeing the polyster, nylon, cellulose and acrylic fibers (Tan et al. 2008).

18.3 Physical Remediation Techniques for Textile Effluents

Textile industry is a complex and labor intensive sector which is also a backbone of South Asian economies. This sector is a source of profit but at the cost of environmental degradation. Following section discuss some of the physical remediation methods which are being practiced by major textile producers of South Asia.

18.3.1 China

In South Asia, China is the principal exporter of yard goods and dyes and also the Chinese silk is in high demand globally. Moreover, China's textile sector share in

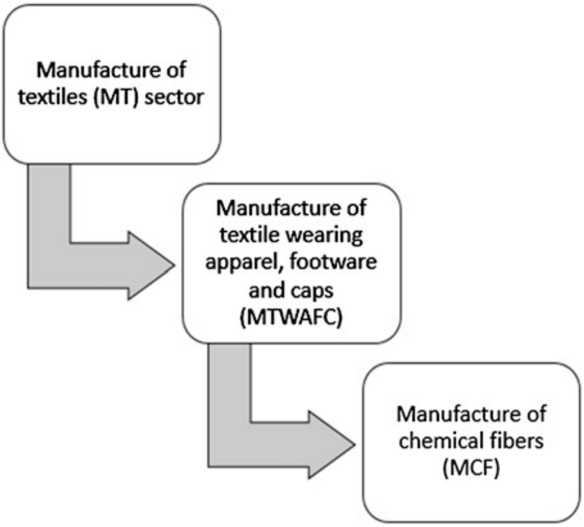

Fig. 18.2 Textile sector division as per China industrial classification for national economic activities (GB/T 4754–2011)

global economy is 34% and Fig. 18.2 shows division of Chinese textile sector (Jichao 2010). The main products from textile sector in China include cotton, silk, and man-made fibers produced via wet processing, spinning, and weaving including other processes. The major pollution is caused by waste water in China which is produced as a result of different processes involved in textile sector such as bleaching, scouring, salt bath, dyeing, desizing, and mercerizing (Peng et al. 2015). There are certain physical processes which are being used in Chinese textile industry for pre-treatment of sludge and waste water. One of the common physical methods is using screens and bars for treating waste water to remove suspended solids, fibers, and yarns. After screening, mechanical scrapper is used to scrap the floating particles and the remaining sludge is transferred to the equalization tank. This tank mixes the sludge to improve the flow and clear it from other impurities. Later, floatation ensures the separation of oil particles and fibers from the treated water through buoyancy caused by air introduced within the tank (Yang et al. 2019). Then this water is mixed slowly with paddles so that the smaller particles coagulate with heavier particles which can settle and can be removed as sludge. This method known as clariflocculation separates the colloids and adsorbs them into flocks which are easily removed (Wang et al. 2011). Then for secondary treatment, trickling filters are used which contain circular beds coated with either PVC or coal which curtail the microorganisms present in the sludge (Fig. 18.3). For tertiary treatment, electrolytic precipitation is practiced in China which uses an electric pulse which passes through the electrodes. This result in the combination of disbanded metallic ions with disseminated particulates thus developing heftier metallic ions that can be expelled via precipitation. In addition, some textile sectors in China also use reverse osmosis and electrodialysis techniques for the remediation of textile wastewater (Mostafa 2015).

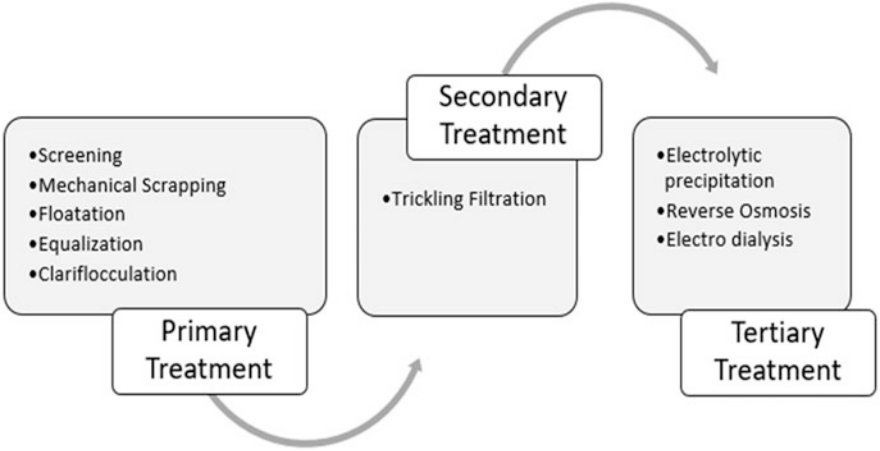

Fig. 18.3 Physical remediation methods used for treating effluents in textile industry of China

18.3.2 India

Globally, India is the subsequent major manufacturer of textile and is the third largest producer of cotton and like China; textile sector incorporates small and medium scale industry because of linkage with heritage and culture. India also produces 18% of the global silk making it second largest silk producing country (Sharma and Dhiman 2016). Though this sector is unorganized yet its diversity and products are globally competitive. It is the traditional industry of India and a backbone to the economy and is scattered in Mumbai, Chennai, Ahmedabad, Bangalore, and other parts of India (Jain 2010). However, this sector is also a major contributor to water pollution in India because 10–15% of untreated synthetic dyes are released in the water bodies (Hasanbeigi and Price 2012; Rani et al. 2014). For removal on synthetic dyes from effluents, adsorption method using bagasse is commonly applied (Desai and Kore 2011). Moreover, coagulation is also practiced in some parts of India for removing contaminants from industrial waste water. Another technique known as gamma radiation (by controlling radiation dose and oxygen supply) is also practiced by major textile finishing sector (Zahid et al. 2017).

In some cities of India, there are common effluent treatment plants established which can be used by textile based SMEs to treat the effluents before releasing in water bodies. Moreover, maximum pollution is produced from cotton weaving and polyester fiber production in the country (Raichurkar and Ramachandran 2015). Also, because of the diverse dye industry, gray fabric is purchased and even imported sometime to convert it into dyed finished fabric. So this is how value addition is practiced. Also, like Pakistan, Indian textile sector is based on fossil fuels. Commonly used methods of physical remediation of industrial waste water are described in Fig. 18.4.

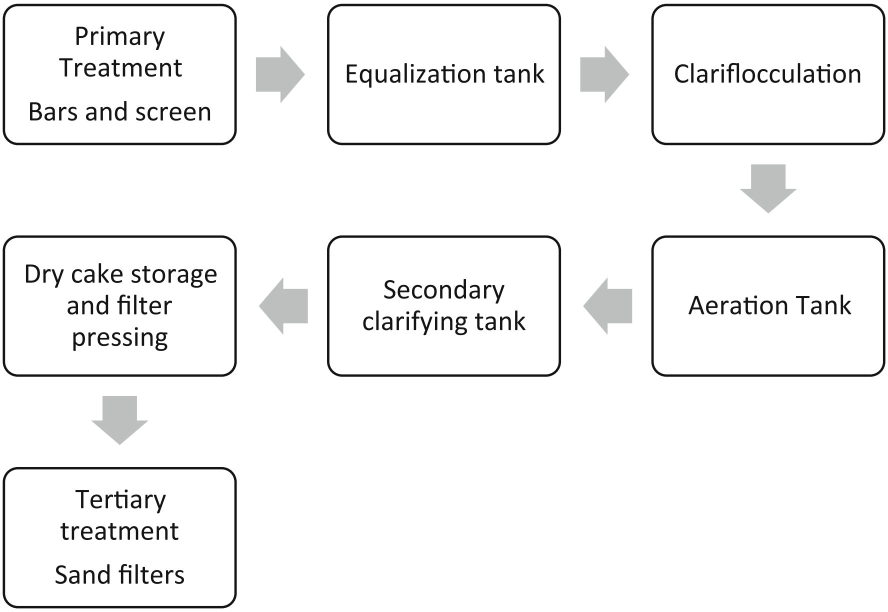

Fig. 18.4 Steps of physical remediation method of textile industrial waste water in India

18.3.3 Pakistan

Pakistan's share of textile exports to the world is accounted to be 65% as per the year 2011–12 (WB) and it is the 8th largest exporter of textile in Asia. Moreover, cotton fabric is the most widely produced and exported from Pakistan to the international market (Chequer et al. 2013). Currently, 700 textile industry units are operational in the country, however; the city of Faisalabad in Punjab is considered a hub of textile sector which produces maximum export quality textiles. The industry has suffered huge losses owing to the issues of electricity shortage and also the global recession (Khan and Khan 2010). Furthermore, this sector is contaminating the environment by discharging effluents without proper pre-treatment to the fresh water bodies. The main fresh water rivers like Ravi and Chenab are getting polluted due to the discharge from textile sector. Usually, azo and synthetic dyes are used and bleaching is also performed extensively. Hence waste water and effluents pose a serious threat owing to the textile industry because this sector generates waste water which is high in Biological Oxygen Demand (BOD), pH, temperature, Chemical Oxygen Demand (COD), color, and turbidity (Malik et al. 2010). Furthermore, dye fixing agents and retarders are cancer causing and pose a serious threat to the environment. Another cause of concern is the dust generated during fabric production and is released directly into the air, thus furthering air pollution (Ismail et al. 2019). Hence, one of the reasons why Faisalabad is considered to be one of the most polluted cities in the world (Asghar et al. 2018).

Some of the conventional pre-treatments are carried out in by some textile industrial units after regulations and check and balance by the Pakistan Environmental Protection Agency. This involves primary, secondary, and tertiary physical treatments for removal of contaminants. Such as in primary treatment, screens are used to separate fiber and yarn from the sludge which is then further treated chemically. Secondary treatment involves aerobic and anaerobic processes to treat sludge and in tertiary system, another physical remediation method of reverse osmosis is used commonly to treat the sludge. Only a few textile units practice electrolysis because it is costly (Kiran et al. 2019). Also, water heating is commonly used for dyeing process in Pakistan and since textile sector is run on fossil fuels, there is a need to consider solar heating for this purpose. The reason is because Pakistan has great potential for solar energy (Muneer et al. 2006). Although there is a demand for eco-friendly practices and there are certain cost effective methods which are being tested at pilot phase, still physical practices for removing contaminants needs to be encouraged.

18.4 Chemical Remediation Techniques for Dye Removal

Chemical methods involve the addition of certain chemicals including solvents for the removal of pollutants from any desired entity such as polluted water and soil. The aim of the chemical remediation techniques can either be to stabilize the pollutants or convert them into less toxic forms and making them safe for the consumption of all the living organisms including plants, animals, and human beings. The complete waste water remediation is hard to be achieved using physical and biological methods alone, so in many situations certain chemical reactions and entities are required for the restoration purposes (Choudhury et al. 2018). The materials generally employed for chemical degradation are carbon based, metallic oxides, clays, and sometimes of biological origin (Tara et al. 2020). Chemical methods are usually faster than the physical and biological processes but can be expensive or generate more toxic by-products (De Castro et al. 2018). So selection of appropriate method regarding the nature of pollutant is crucial in remediation process. The ongoing and recent research has revealed the potential of discussed below techniques for the remediation of coloring compounds from waste water (Fig. 18.5).

18.4.1 Adsorption of Dyes

Many processes and methods employing basic principles, i.e. physical interactions and permanent reactions have been practiced for the removal of natural/manmade dyes from effluents. Few of these processes involve removal via activated sludge, membrane separation and coagulation, etc. All of these techniques have their own certain advantages and disadvantages. The adsorption technique has a cutting edge over the rest of the methods because of its simple design, cost effectiveness, consistent results, and recovery of adsorbing material. These properties have made

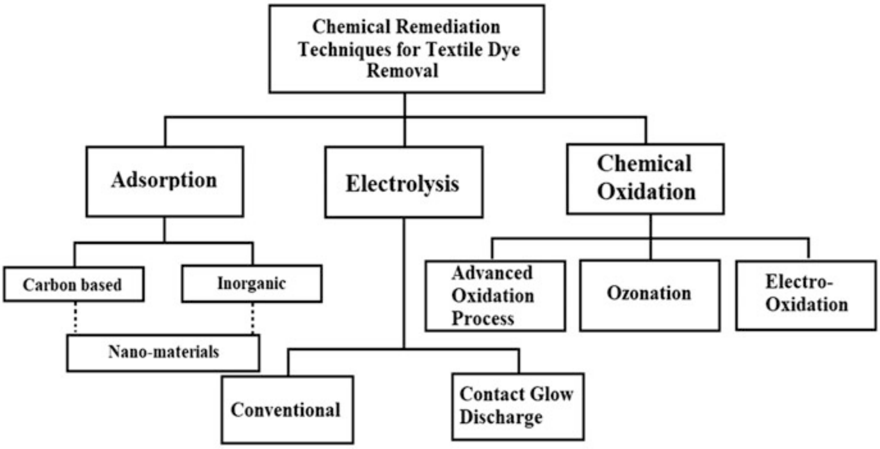

Fig. 18.5 Chemical remediation techniques for the removal of textile dyes

many researchers to discover the potential of various materials as adsorbents for the extraction of dying compounds from the textile waste effluents (Kausar et al. 2018). In process of adsorption the solute molecule gets attached to a solid substrate's surface either by physical or chemical bonding, sometimes both phenomena's can occur. The solute that gets adsorbed is known as adsorbate whereas the solid surface on which it gets attached is called adsorbent. The dyes have a chromogenic moiety that imparts a characteristic color to the dye (Nassar et al. 2017). In terms of adsorption these groups act as a suitable site for attachment on adsorbent. In the process of adsorption many factors are involved such as nature of bonding between the adsorbate-adsorbent, pH, contact time, and particulate size of the adsorbent. In order to prepare a good adsorbent optimization of all the parameters is important.

In literature many studies have been reported that had examined the adsorption potential of various adsorbents in terms of dye removal from textile effluents. In terms of adsorption two types of processes occur "chemisorption and physisorption." Chemisorption is considered to be irreversible because of the exchange of electrons between adsorbate and adsorbent molecules that results in the strong bond formation. In contrast physisorption is reversible because of the formation of weak van der Waals interactions among the molecules of adsorbent and adsorbate. Adsorbents such as activated carbon owned the properties such as high porosity, surface area, and restoration that makes it a very desirable adsorbent for variety of dyes. Many textile industries have been reported to use the saleable grade activated carbon for remediation of dye wastewater but it is not a cost effective option. Some studies have reported to employ coconut husk to synthesize activated carbon to generate a cost effective solution (Aljeboree et al. 2017).

Now a days among the class of carbon based adsorbents graphene oxide is the most well studied nano-material. Graphene owned superior adsorption properties because of the two factors; one it has a planar structure and secondly has a very high surface area per layer. The graphene oxide is derived from the graphene that is basically a single sheet of graphite. The oxygen containing functional groups, i.e. hydroxyl, epoxy, and carboxylic group imparts hydrophilic character to the graphene oxide. Many researchers have reported adsorption of anionic and cationic dye using the nanosheets of graphene oxide. The ability of adsorption of graphene oxide can be attributed to the electrostatic interaction of oppositely charged adsorbate and adsorbent species (Xiao et al. 2016). In current scenario, immense work has been completed on synthesizing and employing nano-particles as adsorbents for the elimination of dyes from textile waste effluents because of their exceptional great surface area (Tara et al. 2020). Among carbon based nano-materials carbon nanotubes possess large surface area, hollow and layered structures. These properties make them efficient adsorbents and have shown the potential to be used as a potent dye removal from the textile effluents. Nano-materials have been vastly studied and employed in a variety of applications such as nanocoatings and electronic devices. The inorganic nano materials such as metal oxides owned the capability to decontaminate wastewaters due to high surface area, greater availability of active sites, and high stability. Among various inorganic nano materials, nano magnesium oxide (MgO) is cost effective, more chemically stable, non-toxic and easily producible having greater surface area. All these properties make MgO nano-particles an auspicious material for the exclusion of anionic dyes. MgO nano-particles can be produced via various methods, e.g. laser vaporization, chemical vapor deposition, and laser vaporization technique (Nassar et al. 2017). Recently it was discovered that simultaneous adsorption of two dyes “Reactive red 195” and “Reactive yellow 145” can be done using the nano-composite cobalt ferrite-alginate within 60 min and pH range of 3–6 and could be prepared via *polymerization*. The exceptional adsorption of this nano-composite can be attributed to the presence of various polar functional groups (amine, hydroxyl and carbonate) at the superficial side of the particles. This new composite material proposes a sustainable and cost effective adsorbent for the actual elimination of chromophore moiety from effluents. More interestingly, this adsorbent can be separated because of having magnetic properties and hence it is reusable (Jayalakshmi and Jeyanthi 2019).

18.4.2 Chemical Oxidation of Dyes

Remediation of textile dye effluent is a difficult task due to complex chemical structure of dyes, low biodegradability, strong color and greater organic and salt content in wastewater. Chemical oxidation derived techniques most notably “Advanced Oxidative Processes” (AOP) have expected to be potentially the most appropriate technique for the remediation of persistent and recalcitrant chemical moieties known as dyes (Baeissa 2016). AOP technique is a clean solution for the remediation of contaminated water either by mineralizing or decreasing the resistance of conjugated organic compounds. They possess the potential to decompose persistent compounds into inert substances such as carbon dioxide, water, and inorganic compounds (da Rocha Santana et al. 2019). AOP is centered on the creation of highly reactive and strong oxidizing chemical moieties such as hydroxyl radicals ($^{\bullet}OH$). These radicals have the capability to oxidize any organic molecules up to the complete mineralization (Saeed et al. 2018). Out of many methods of AOP the photochemical one has the advantage over the rest because it is non-toxic, quick, and effective. In this process the hydroxyl ions (OH) are produced during the reaction and non-selectively attack the organic contaminants either by generation of atomic hydrogen or electrophilic addition via transfer of electrons (Mousset et al. 2018). The photochemical-assisted Fenton reaction is found to be very effective for oxidation of pollutant in an aqueous solution with a pH around 3. In this process the principal ferric iron species $Fe(OH)^{2+}$ appreciably absorbs the light in ultraviolet region that afterwards lead to the reduction of this species resulting in the creation of Fe^{2+} along with OH^{-} (depicted in Eq. 18.1). Fe^{2+} then reacts with H_2O_2 for the further generation of OH^{-} (as depicted in Eq. 18.2). The photolysis of H_2O_2 acts as a supporting source for the production of $\cdot$ OH (as depicted in Eq. 18.3). Whereas, the impact of photolysis of H_2O_2 is less significant as compared to reactions (18.1) and (18.2) as its absorption coefficient is low (Tarkwa et al. 2019)

$$\mathrm{Fe(OH)}^{2+} + hv \rightarrow \mathrm{Fe}^{2+} + \mathrm{OH} \tag{18.1}$$

$$\mathrm{Fe}^{2+} + \mathrm{H_2O_2} \rightarrow \mathrm{Fe(OH)}^{2+} + \mathrm{OH} \tag{18.2}$$

$$\mathrm{H_2O_2} + hv \rightarrow 2^{\cdot}\mathrm{OH} \tag{18.3}$$

The conditions required to achieve the optimal dissociation of chromophore is hinged on the acidity of solution (optimal at around 3), the quantity of H_2O_2 and ferric iron (as catalyst) along with wavelength of subjected light ($\lambda = 240–300$ nm) (Ameta et al. 2013). Many researches have achieved the Fenton-related successful degradation of chemical dyes in wastewater. One such study depicted the degradation mechanism of an Orange G dye via oxidation done through photo-Fenton (homogeneous photo catalysis) process (Fig.18.6).

The intermediate products that originate during the Photo-Fenton degradation of Orange G dye involved aromatic hydroxyl amines, nitroso and phenolic substituted compound. In the reaction high electron density azo bonds were the primary cites targeted by the OH radical as proposed in the literature (Brillas and Martínez-Huitle 2015). Afterwards the sulfonate groups were triggered and attacked to be released as sulfates. The major intermediates were subjected to oxidation that further leads to subsequent hydroxylation and results in the formation of hydroxylated aromatic intermediates. The aromatic's hydroxylation finally lead to the opening of ring and production of short-chain carboxylic acids. These acids further lead to the formation of inorganic species and complete mineralization of the dye (Tarkwa et al. 2019).

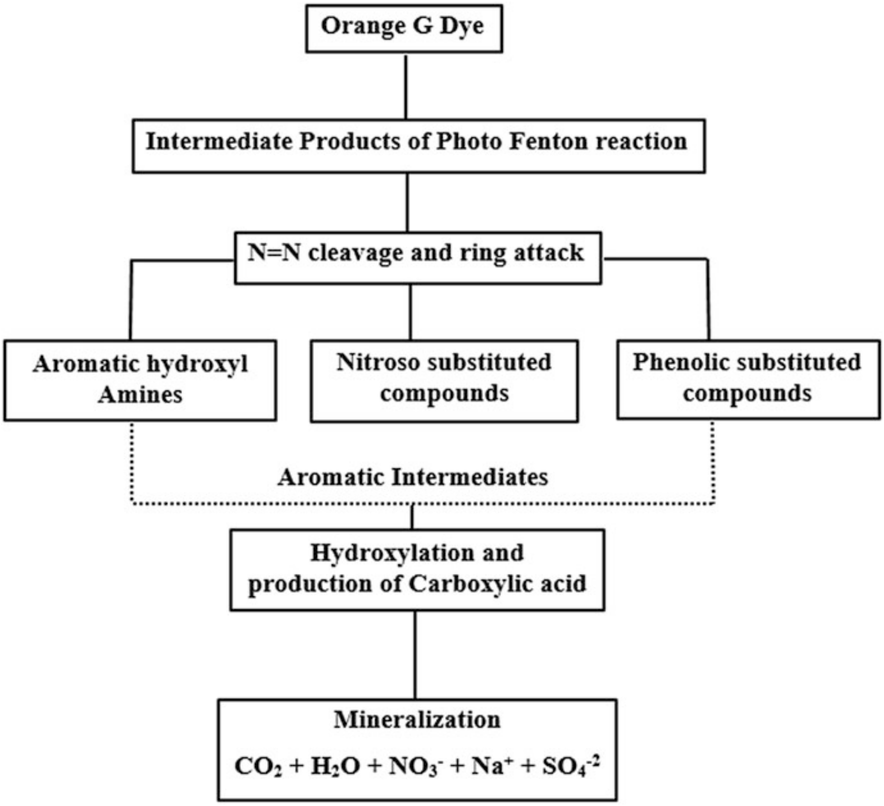

Fig. 18.6 Schematic representation of degradation of Orange G Dye by Photo-Fenton reaction

18.4.3 Ozonation

Ozone (O_3) is an extremely reactive gas which comprises of three oxygen atoms. It can be produced both naturally and by anthropogenic activities. Ozone is considered to be a very strong oxidizing agent in the presence of water and displays a rapid reactivity with more or less all of the organic moieties. This capability of ozone has made it a well-known and established technique for the removal of color imparting organics present in waste water especially dyes. The oxidation carried out by ozone mainly occurs either by a direct electrophilic reaction or through an indirect route that comprises of the generation of another powerful radical that in most cases is a hydroxyl radical (.OH) (El Hassani et al. 2019).

Studies have revealed that if only ozone is used for the waste water remediation, then an effective discoloration could occur but a complete mineralization would not be possible. This would lead to the buildup of biodegradable organic matter or inorganic compounds along with water. In order to overcome this issue ozonation technique can be coupled with a solid catalyst thus naming the process as catalytic ozonation process (COP). It is an advanced oxidation process that makes the degradation process much better while enhancing the efficacy. To be precise in COP, the oxidation via ozone is increased because of the addition of a solid substance that acts as a catalyst and produce more reactive radicals. In comparison to the conventional ozonation, the radicals generated here enhance the mineralization rate thus reducing the reaction time that afterwards make the process cost effective. More over solid catalysts enhance the surface area that plays a vital role in the process of adsorption (El Hassani et al. 2019). Multiple solid catalysts have been investigated up to this date that involves metal oxides, zeolites, clay minerals, and activated carbon (Faria et al. 2008). According to the type of catalyst used, the COP can be distinguished into heterogeneous and homogeneous processes. Among all the types of solid catalysts the most notable are the (LDHs) layered double hydroxides. LDHs comprise of the synthetic clays that are anionic in nature having general formula $[M_{1\text{-}x}{}^{2+}M_x{}^{3+}(OH)_2]A_{x/m}{}^{m-}.nH_2O$, here M^{2+} depicts divalent metal, M^{3+} = trivalent metal, and A^{m-} represents an anion. The extensive selection of metal cations and the profusion of hydroxyl groups within the layered structure of LDH, makes it an outstanding material with superior catalytic abilities. LDH come under the heading of nano-materials and are used in heterogeneous catalysis systems speeding the various reactions such as electro catalysis, photo degradation, and decomposition reactions.

The LDHs compounds in a heterogeneous nano-catalyst system can be employed for the decomposition of Azo dye via the process of ozonation. Methyl orange (MO) is a type of an Azo dye regarded as a toxic entity. A variety of reaction mechanisms are possible to be going on during the breakdown of methyl orange under the effect of Ni-LDH catalyst assisted Ozonation. According to the literature adsorption of ozone molecules occurs on Ni-LDH catalyst via getting weakly bonded with hydroxyl groups oriented outside the layered structure of catalyst. The Ni with in the catalyst acts as an initiator site for the ozone decomposition and is oxidized to $Ni^{(II)}$ forming a reactive complex of $Ni^{(IV)}O(OH)_2$. This reaction is depicted as follows:

$$Ni^{(II)}(OH)_2 + O_3 \rightarrow Ni^{(IV)}\,O(OH)_2 + O_2$$

As the $Ni^{(IV)}$ is the peak oxidation state of Nickel so the complex will disintegrate and oxygen is released that results in the availability of active sites throughout the reaction (Stoyanova et al. 2006). Moreover, the $Ni^{(II)}$ and $Ni^{(III)}$ will be available on the surface of catalyst followed by ozone disintegration as depicted in the following reactions:

$$2Ni^{(IV)}\,O(OH)_2 \rightarrow 2Ni^{(II)}\,(OH)_2 + O_2$$

$$3Ni^{(IV)}O(OH)_2 \rightarrow Ni^{(II)}\,(OH)_2 + 2Ni^{(III)}\,O(OH)_2 + H_2O + O_2$$

Along with all the reactions going on, the molecules of methyl orange quite possibly get chemically or physically attached on the surface. Overall organic molecules and active complexes established by the catalyst will efficiently undergo the oxidation of the methyl orange dye at the boundary between solid and liquid phase. Along with the going on reactions, the disintegration of dye at pH $\sim$ 9 can also be associated to an indirect reaction carried by the active **.**OH radical formation which causes degradation of ozone. In that case the dye molecule is attacked at the azo group site which leads to the cleavage of chromophore group (N=N) that connects two aromatic rings of methyl orange molecule. This will result in the breakage of N-N bond. The literature suggests that at the termination of this remediation process, these molecules can further be decomposed into organic acids and inorganic species. The nitrogen in the parent dye moiety will be transformed to NO^{3-} ions whereas the sulfonyl group becomes harmless SO_4^{2-} ions (Devi et al. 2009).

18.4.4 Electro-Oxidation

Electro-oxidation (EO) methods employ electrons as the basic tool for the remediation of the waste water having synthetic dyes as impurities. As in this technique electrons are used so it is considered to be the most clean and green process of remediation. This method is divided into two main catagories, namely direct electro-oxidation and indirect electro-oxidation. In case of direct EO, hydroxyl radicals are generated on the anode surface, as **.**OH is a powerful oxidant it disintegrates dye structure (Fig. 18.7). In indirect EO, oxidizing agents (either oxygen or chlorine-based) are electrochemically generated in the solution. This process involves the generation of hydrogen peroxide (oxidizing agent) at the cathode and the generation of active chlorine species at the anode. In case of electro-fenton process the generated H_2O_2 in the availability of iron metal (Fe^{2+}) can produce the hydroxyl radicals (Ghanbari and Moradi 2016).

18.4.5 Electrolysis of Dyes

In early 90’s electrolysis was opted for the remediation of textile effluents. Since then it have been proved to be an effective method for the elimination of undesired material from discharged water. This technique has many good aspects as compared to conventional methods such as it does not require any other chemical, no sludge is generated and complete conversion of toxic dyes into non-toxic is achievable. The remediation of dye is influenced by optimization of some parameters in order to achieve the maximum removal of certain pollutants. These parameters involve chemical nature of electrode, separation between the electrodes, density of applied current, concentration of dye, pH, and time given for the electrolysis (Fig. 18.8). A huge versatility is available in terms of material that is used to make electrodes. Mostly anode is easily corroded or dissolved while remediation. Due to this reason

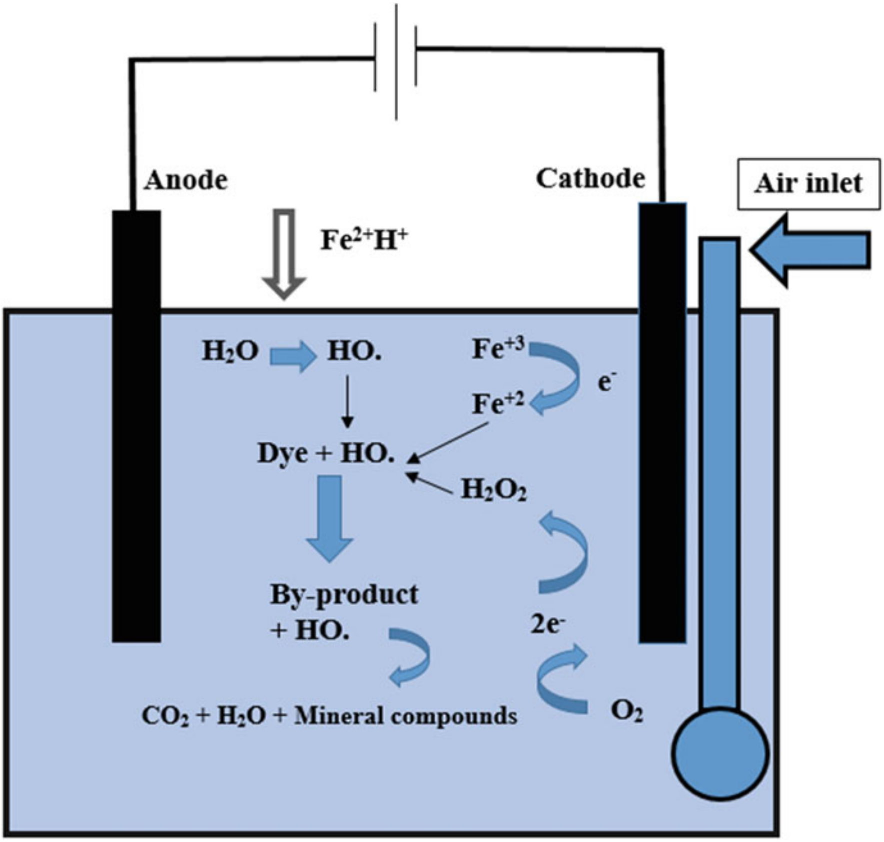

Fig. 18.7 A general representation of electro-oxidation

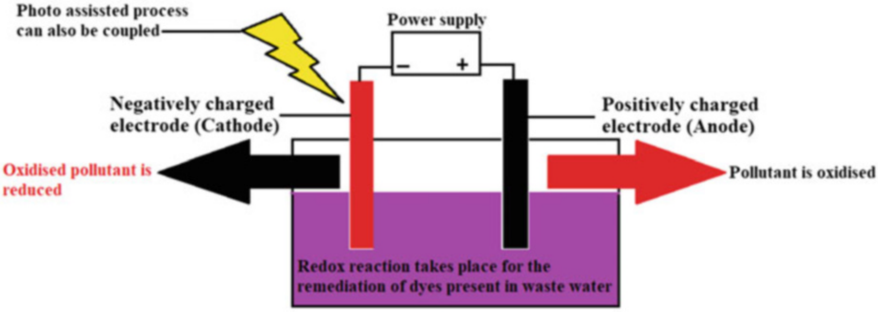

Fig. 18.8 General setup of electrolysis

such type of material should be selected for anode that can withstand corrosion. Among such materials carbon is one of the best, easily available and cost effective option. The corrosion tendency of carbon is almost negligible (Arif and Malik 2017).

Along with conventional electrolysis methods one of the most recent and promising techniques is the contact glow discharge electrolysis (CGDE) method for the removal of color from the water contaminated with dyes. CGDE is a type of electrochemical process, here development of plasma occurs by the glow discharge of direct-current between an electrode and electrolyte (Gao et al. 2003) CGDE is comparable to conventional electrolysis, the only difference is the requirement of high-voltage conditions that are necessary to originate plasma emission (Saksono et al. 2014). The enormous potential gradient accelerates the gaseous H_2O^+ ions of the plasma towards the plasma–liquid interface. As of the massive energy carried by these ions they ionize various water molecules releasing an immense amount of hydroxyl radicals ($.OH$). As prescribed earlier the hydroxyl radicals are very reactive and possess great oxidizing capability which makes them very short lived that can affect the rate of decolorization. In order to overcome this issue various types of catalyst can be added such as the addition of Fe^{2+} ions. These ions are capable to catalyze the decomposition of H_2O_2 and increase the productivity of $.OH$, overall enhancing the capability of decolorization of dyes. Using 40 mg/L of Fe^{2+} ion for 30 min can lead to the removal of Remazol Brilliant Blue up to 99.63% (Saksono et al. 2018).

According to the literature the air injection in CGDE is very important for the overall process efficiency. The air injection can simplify the generation of high energy electrons thus increasing the OH radical's production. In the presence of air the hydroxyl radicals react with the oxygen and generate other reactive fractions. The available oxygen has the tendency to synthesize O_3 and H_2O_2 after reacting with H_2O molecules. This phenomenon can be explained with the help of the following reactions (Zainah and Saksono 2017):

$$e + O_2 \rightarrow O. + O. + e \tag{18.4}$$

$$O. + O_2 \rightarrow O_3 \tag{18.5}$$

$$.O + H_2O \rightarrow .OH + .OH \tag{18.6}$$

$$e + H_2O \rightarrow H. + .OH + e \tag{18.7}$$

$$.OH + O_2 \rightarrow HO_2. + O. \tag{18.8}$$

Eqs. (18.4), (18.5), (18.6), (18.7) depict in what way air injection harvests a large amount of reactive species ($HO_2.$ and $.O$ radicals) along with $.OH$. The reduction potential of $HO_2.$ and $.O$ active species (Augusto and Miyamoto 2011) is associated with these supplementary reactive species involved in the dye degradation (Budikania et al. 2019).

Above described methods are few of the recently discovered methods some are being employed by different textile industries whereas other require more in-depth study. The poisonous organic dye remediation from the textile effluents is of vital importance for creating the harmony within the aquatic ecosystem. It is a very tedious task to opt any single treatment option for the complete removal of dyes. Each technique is accompanied with certain positive sides and down sides. The basic disadvantage of the chemical remediation methods is the requirement of special equipment and expertise. The chemical techniques are proved to be quite effective in terms of dye removal but in some cases toxic sludge can also be produced. This issue is being answered by the development of emerging techniques among which the most notable one is advanced oxidation processes. This process is highly effective for the complete mineralization of the organic dyes but there cost is very high which makes them suitable only for the developed nations. China is the world's largest trader of textile products. In 2017 China started first radiation waste water plant in Jinhua city. In that plant electron beam is employed for the treatment of textile waste water (He 2018). The establishment of effective, fiscal, and eco-friendly techniques to reduce the percentage of dye in wastewater up to an acceptable limit in a cost effective way is of paramount importance (Couto 2009). According to International Atomic Energy Agency (IAEA) this is the only technique that can remediate any kind of organic dye completely and safely without the release of any toxic by-product. This technique has the same problem like use of AOP that is it is quite expensive. Today, textile dyeing is responsible for a fifth of all global industrial wastewater pollution. Although some industrial nations use radiation to treat contaminated water from textile dyeing plants, some developing countries in Asia do not have the resources to minimize wastewater pollution. The IAEA plans to incorporate more radiation wastewater plants in China and other Asian countries in coming years. Other textile manufacturing countries, like Bangladesh, Sri Lanka and India, have also expressed interest in working with the IAEA to improve wastewater treatment sustainability at their factories.

18.5 Biological Remediation of Textile Effluents

The huge demand for environmentally friendly methods for industrial processes and wastewater treatment shifted focus on the biological treatments and techniques. Biological treatments are much cheaper and easily operable at various stages of textile effluent treatment and remediation. Among biological materials bacterial and fungal cultures and their enzymes are most commonly used methods to treat textile effluent (Rather et al. 2018). There are many advantages to use biological methods for textile industry effluent treatment;

- eco-friendly,
- cost effective,
- less sludge production,
- non-toxic metabolites,
- full mineralization (Hayat et al. 2015).

Bioremediation is the green technology which employs use of biological material and sources for the degradation and discoloration of textile dyes in wastewater. Microorganisms such as bacteria, fungi, yeast, and algae are used to disintegrate and absorb synthetic dyes. Many plant species are also quite efficient for the treatment of textile wastewater (Ekambaram et al. 2016). Bioremediation involves the process of degradation of toxic synthetic dyes by breaking bonds into less toxic inorganic compounds (Babu et al. 2015). Biological methods are broadly classified into aerobic and anaerobic, a combination of both and on the basis of oxygen requirements (Xu et al. 2018). The azo dyes degradation occurs in two steps, firstly under anaerobic conditions azo bonds breaks and forms aromatic amines that are toxic for bacterial culture and secondly the aromatic amines are further catabolized into less toxic metabolites under aerobic environment (Ajaz et al. 2019). The dye degradation and discoloration depends on many factors and it is influenced by the type and concentration of dyes in effluent, the culture load, pH, temperature and oxygen concentration (Holkar et al. 2016).

18.5.1 Bacterial Degradation

Bacteria are generally preferable for the remediation of textile wastewater because they grow quickly, easy to culture and amenable to genetic manipulations. In literature many bacterial species, i.e.; *Acinetobacter*, *Bacillus subtilis*, *Bacillus cereus*, *Corynebacterium* specie, *Clostridium* specie, *Dermacoccus*, *Enterococcus* species, *Streptococcus, faecalis*, *Pseudomonas, Staphylococcus* species, *Lactobacillus* sp., *Micrococcus* sp., *Rhizobium* sp., *Morganella* sp., *Klebsiellla* sp., and *Shewanella* specie have been reportedly degraded the textile dyes (Imran et al. 2016; Haghshenas et al. 2016). Azo dye degradation using the pure bacterial culture is effective but dye specific. Because of this using a single bacterial specie culture for large industrial unit with complex mixture of dyes in effluent is unfeasible (Kumar et al. 2018). Moreover, some bacterial species end up producing carcinogenic secondary products that require further detoxification. To avoid this, remediation processes involves using mixed or multispecies culture for complete mineralization of complex mixture of dyes (Ghosh et al. 2016).

The dye degradation may cause change in the composition of mixed bacterial culture which may change the efficacy of the process. The biodegradation process strongly dependent on pH, temperature, concentration of dye, capacity of microbial consortium to degrade a particular dye. Bacteria require optimum pH for the degradation of textile dyes and adaptability to varying pH enhances the treatment process. Bacterial cultures prefer the pH that is between the ranges of neutral to somewhat alkaline (7–9.5). Strongly acidic or basic pH conditions reduce the degradation efficacy of bacteria. Bacterial cell require optimum temperature condition (35–45 °C) for degradation of dyes in textile effluent and high temperatures usually cause cells to denature effecting removal efficiency. While high temperature causes the denaturation of enzymes in bacterial cells (Garg and Tripathi 2017).

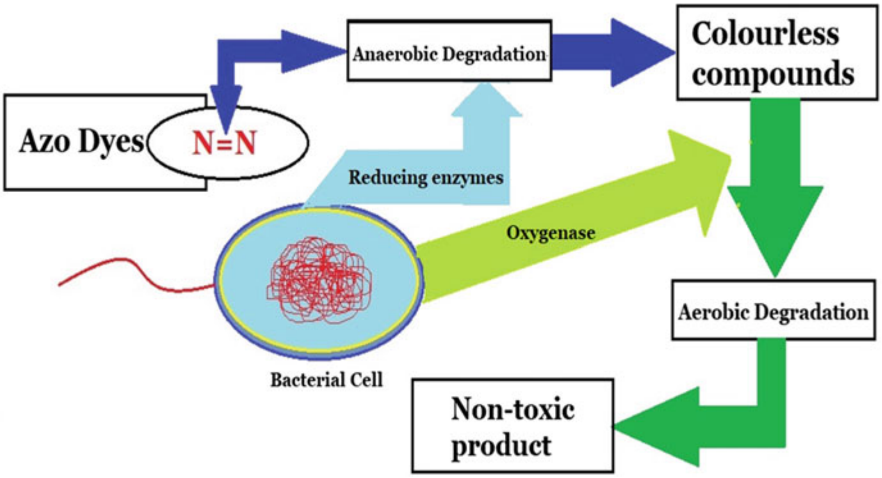

Fig. 18.9 Bacterial decolorization of azo dyes in the textile effluent

18.5.2 Degradation Mechanism

A combination of both anaerobic and aerobic conditions are a reasonable biological treatment strategy for degradation of dyes in textile effluent. The azo dyes are degraded with the help of azoreductase enzyme in anaerobic conditions with four electron transference (Fig. 18.9**).** The primary pathway is the reductive cleavage of azo bonds. Azoreductase enzyme reduces the dye into colorless amines that are very resistant and mineralized only in aerobic conditions (Misal and Gawai 2018; Singh et al. 2017). There are two types of azoreductase enzyme one is Flavin dependent azoreductases which requires NADH (nicotinamide adenine dinucleotide hydrogen), NADPH (nicotinamide adenine dinucleotide phosphate hydrogen), or FADH (flavin adenine dinucleotide) cofactor as an electron donor for reducing azo bond (Pande 2019). These were isolated from *Enterococcus faecalis* (AzoA) (Punj and John 2009) and *S. aureus* (Azo1) (Chen et al. 2005).

Other type is flavin-independent azoreductases does not contain flavin molecule in the structure nor they require any exogenous flavin for catalysis (Suzuki 2019). It was isolated and characterized from alkaliphilic and neutrophilic bacterial strains (Misal et al. 2015). The functional group present near the azo bond also influences the substrate specificity of azoreductases enzyme. Azoreductases enzyme can use some unstable electron donors such as 1-benzyl-1,4-dihydronicotinamide (Qi et al. 2017). To speed up the biodegradation process of azoreductase enzymes various redox mediator are used, such as riboflavin, Anthraquinone 2–6 disulphonate, sodium 1,2-naphthoquinone-4-sulfonate, and 2-hydroxy-1,4-naphthoquinone are notable examples (Santos et al. 2016; Dai et al. 2018).

Another enzyme NADH-DCIP reductase belongs to the bacterial mixed function oxidase system and takes part in the detoxification of xenobiotic compounds and especially decolorization of textile dyes (Song et al. 2018; Salokhe and Govindwar

1999). It reduces the DCIP (Dichlorophenolindophenol) using NADH as an electron donor. DCIP is blue in its oxidized form and becomes colorless after reduction (Parshetti et al. 2014). The intermediate products synthesized during dye decolorization can also be reduced by other enzymes such as hydroxylase and oxygenase produced by bacteria (Elisangela et al. 2009).

18.5.3 Degradation by Fungi

Fungi secrete many extracellular and intracellular enzymes to mineralize toxic chemical compounds (Sweety et al. 2017; Baltazar et al. 2018). The fungal mycelia due to increased cell to surface ratio is well equipped to solubilize substrates by secreting extracellular enzymes (Shahid et al. 2014b). Among fungal specie the white rot fungi is considered to be crucial for global carbon cycle because of their ability to mineralize the lignin in woody plants (Bruner et al. 2016). The enzymes from white rot fungi have high oxidative potential which is capable of decolorizing wide variety of textile dyes (Yesilada et al. 2018). Many fungal species such as *Pleurotus ostreatus, Pichia sp., Penicillium sp.,* and *Candida tropicalis* are capable of degrading azo dyes (Gou et al. 2009; Tan et al. 2013). The mechanism of dye decolorization by white rot fungi is depicted in (Fig. 18.10).

There two main enzymes which play central role in the biodegradation of textile dyes. The first is extracellular enzyme lignin peroxidases which is required to depolymerize lignin and attack the non-phenolic methoxy subunits. Second enzyme is manganese peroxidase belong to the class of oxidoreductases enzymes. It attacks the phenolic compounds through redox reactions facilitated by Mn^{2+}/Mn^{3+} ions (Abadulla et al. 2000). Another strong enzyme, Laccases, abundantly found in fungi is multicopper extracellular enzyme which use molecular oxygen to oxidize phenolic compounds (Karnwal et al. 2019). Laccases enzyme from white rot fungi can be produced by different methods of fermentation such as submerged, semisolid state or solid state with carbon and nitrogen sources as inducers (Vantamuri and Kaliwal 2016). Biosorption is reported to be the primary dye removal process in wood rotting basidiomycetes which involves moving the dye from the water phase to the solid phase (the bioadsorbent) while in biodegradation enzymes break bonds of dye and transformed into other chemical compounds (Holkar et al. 2016).

Biodegradation of metal complex dyes occurs in three steps. The first is dye is adsorbed to the fungus; second step leads to the splitting of metal complex bond and finally degradation of dyes takes place with release of transformed products in culture medium (Blanquez et al. 2004). Bioreactors are used for culturing fungi. There are many examples which include bioreactors that can degrade and decolorize the textile effluent at the same time which include processes based on immobilized fungi in fixed-bed reactors, rotating drum, packed bed, fluidized bed, and membrane bioreactors (Sen et al. 2016). In rotating reactor the microbial biofilm is formed on the surface of vertical disks suspended in liquid and in trickling reactors, biofilm is humidified by liquid (Kapdan and Kargi 2002). In membrane biofilm reactors stable gas supply is ensured for microbial biofilm by attaching it to porous gas permeable

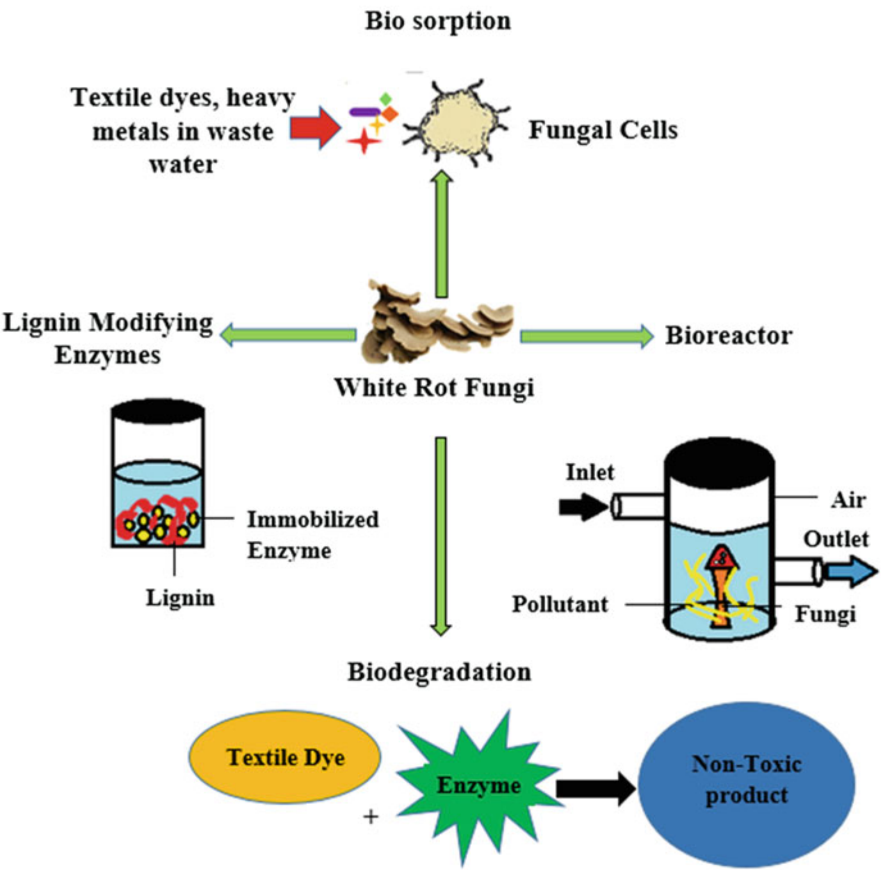

Fig. 18.10 Different methods of dye decolorization and degradation by white rot fungi

membrane (Lema and Omil 2001). These bioreactors are often disadvantageous due to mycelia aggregation, clogging, and electrode fouling (Hossain et al. 2016). Table 18.1 shows the dyes degraded by white rot fungi.

18.6 Phytoremediation of Textile Dyes Effluent

Phytoremediation of textile effluent treatment is based on using plant species that have ability and adaptability to remove toxic dyes from wastewater. Phytoremediation approach is holistic and eco-friendly technology with aesthetic value as well as cost effective method that can treat large volume of effluent (Malik et al. 2017). Plants large surface area due to root hairs accumulates nutrients necessary for growth (Ng et al. 2018). Phytoremediation is subdivided into rhizofiltration, phytoextraction, phytodegradation, phytostabilisation, and

Table 18.1 White Rot fungi potential for degrading different textile dyes

White rot fungal species	Type of dye	Reference
Bjerkandera adusta	Amaranth Reactive violet 5 Reactive blue 72	Gomi et al. 2011; Baratto et al. 2015
Dichomitus squalens	Remazol brilliant blue R Heterocyclic methylene blue	Novotný et al. 2012
Irpex lacteus	Malachite green	Yang et al. 2016
Phanerochaete chrysosporium	Reactive black 5 Reactive yellow MERL Reactive red ME4BL Congo red	Enayatizamir et al. 2011; Koyani et al. 2013; Bosco et al. 2017
Phlebia brevispora	Remazol brilliant blue R	Lee et al. 2017
Pleurotus ostreatus	Synazol red HF6BN	Ilyas et al. 2012
Trametes versicolor	Grey Lanaset G Acid orange 7 Acid blue 74 Reactive red 2	Gabarrell et al. 2012; Ramírez-Montoya et al. 2015

phytovolatilization according to the method and nature of contaminant as illustrated in (Fig. 18.11).

According to Pilon-Smits (2005) various physio chemical factors determine the efficiency of particular plant species to remove the textile dye from industrial wastewater such as pH of contaminant, temperature, humidity, nutrients, organic matter present in water, sediment or soil, availability of oxygen, microbial diversity, and biomass of plants used for phytoremediation.

Many plants in nature have remediation potential because of enzymes secreted by plant cells and some are genetically manipulated to do so. Plant enzymes (dehalogenase, nitroreductase, nitrilases, peroxidase, and laccase) found mostly on the external root surfaces of plants. Degradation activities of these enzymes depend on production, release rate, nature and concentration of the contaminant present in soil, sludge or water matrix (Dwivedi and Tomar 2018). Usually plant species with quick growth rate and fibrous deep roots such as grasses, herbs and creepers are favorable for phytoremediation of textile effluent (Ekambaram et al. 2018). Many species of wild plants such as *Typhonium flagelliforme, Phragmites australis, Rheum rabarbarum, Rumex hydrolapathum, and Blumea malcolmii* are also used in treating the textile effluent (Chandanshive et al. 2018). Plant species and aquatic macrophytes with degradation potential for textile dyes is given in (Table 18.2).

It has been speculated that dye decolorization induce an enzymatic stress response of a plant. The X-ray diffraction showed that *T. angustifolia* precipitate metal ion in root and leaf area (Nilratnisakorn et al. 2008). Due to protein molecules induction and enzymatic activity protons are released by plant cell membrane and cell wall so the dye-metal complex is translocated to semipermeable membrane without comprising photosynthesis process.

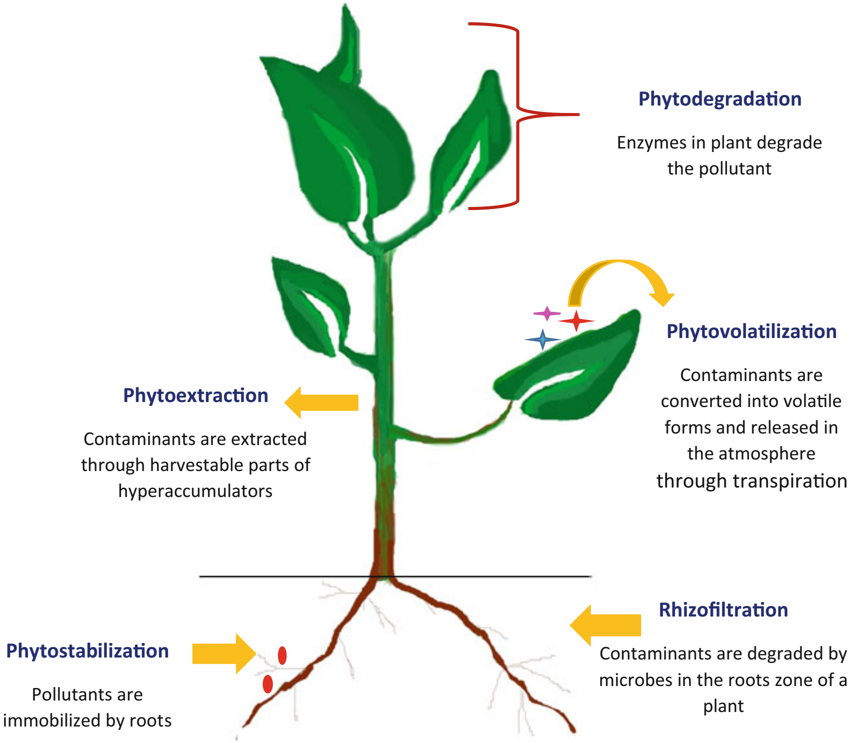

Fig. 18.11 Various methods of Phytoremediation

These molecules are then released into surrounding rhizosphere to maintain soil pH, gas composition through phytochemical reactions and relieving plants from toxic effects (Bassindale et al. 2003). Plant enzymes are pivotal for the degradation and decolorization of textile effluent. In a study *B. malcomii* enzymes decolorized the dye *Red 5B* with lignin peroxidase, tyrosinase, DCIP, reductase, azoreductase, and riboflavin reductase (Kagalkar et al. 2009). Peroxidases enzyme from *P. australis* was effective in degrading *acidic Orange 7* (Movafeghi et al. 2013) while peroxidases from *Cucurbita pepo* was more efficient for *Direct Yellow* degradation (Boucherit et al. 2013).

There are different methods of phytoremediation of textile effluent such as artificially created wetlands, vertical flow beds, hybrid systems, Fenton's oxidation and hydroponic (Muthusamy et al. 2018). The artificial or constructed wetlands were first used by Max Planck Institute in Germany by Dr. Seidel in 1950's. The novel experiment involved the use of plants for the compensation for the over fertilization, sewage pollution treatment, and siltation of inland water bodies. Experiments revealed that some giant reed species were able to remove reactive dyes form the textile effluent behaved differently than those grown in unpolluted environments (Alwared et al. 2020). Aquatic macrophytic treatment system (AMATS) using

Table 18.2 Phytoremediation potential of various plants

Serial #	Plant specie	Type of dye	Decolorization conc. %	Reference
1	*Tagetes patula*	Reactive blue 160	90%	Patil and Jadhav 2013
2	*Hydrocotyle vulgaris*	Basic red 46 (BR46)	95%	Vafaei et al. 2013
3	*Typha angustifolia*	Reactive blue 19	70%	Mahmood et al. 2014
4	*Alternanthera philoxeroides*	Remazol red (RR)	100%	Rane et al. 2015
5	*Azolla pinnata*	Malachite green	75%	Kooh et al. 2016
6	*Typha angustifolia* *Paspalum scrobiculatum*	Congo red	80% 73%	Chandanshive et al. 2017
7	*Azolla pinnata*	Methylene blue	85%	Al-Baldawi et al. 2018
8	*Asparagus densiflorus*	Rubin GFL	90.50%	Watharkar et al. 2018
9	*Pistia stratiotes*	Azul Marino Negro	90% 23%	Ferdes et al. 2019
10	*Lemna minor*	Methylene blue	80%	Imron et al. 2019

aquatic macrophytic plant species is well established method for removing textile dyes in effluent (Rane et al. 2015). The roots of floating plants are main route of heavy metal uptake while in case of submerging plants both roots and leaves remove heavy metals and uptake the nutrients. The submerged plant species provide remediation potential for both water and sediments and rootless plants are more efficient in extracting heavy metals from water (Schück and Greger 2020).

Despite being most eco-friendly technique, phytoremediation has some drawbacks. Phytoremediation is a time intensive technique which requires a several growth season for plant to clean up the effluent, but also the metabolites can be cytotoxic to plants. Moreover, phytoextraction and disposal of incarnated biomass can take several months. Bioremediation techniques for dye removal are convenient, cheap and have universal application due to ubiquitous nature of microbes involved for textile effluent treatment. But conventional methods are sometimes not very effective for treating effluent containing mixture of complex synthetic dyes. That leads to use of combination of physical, biological, and chemical methods for dyes degradation in effluent. Recently, research has been focused on making the biological methods more precise and target oriented. It is necessary to understand the dye degradation pathways by enzymes and factors that influences efficacy of certain enzymes produced by microbes to be more potent for complex mixture of textiles wastewater.

Bioinformatics plays a pivotal role in the advancement of biological treatment options for wastewater. The “in silico” molecular modelling and docking studies are useful tool for the screening of potential microbial consortium for textile dye degradation and decolorization. Molecular docking predicts the binding of macromolecules (receptor) and a small molecule (ligand) efficiently. Another technique, Response surface methodology, a mathematical modelling tool for the analysis of degradation process is quite useful for predicting the most viable output of remediation process. The RSM approach is used to determine the optimal levels variable like temperature, pH, and dose to establish relationship between variables in degradation process. This modelling technique is helpful in optimizing the resource use and evaluates the relationship between various variables in the system (Khamparia and Jaspal 2017).

18.7 Conclusion

Untreated wastewater discharge from textile industries affects the aquatic ecosystem and aesthetics quality. It inhibits the plant growth, impairs photosynthetic functions, increases the biological and chemical oxygen demand and is detrimental for aquatic life. Moreover, recalcitrant chemicals enter the food chain to bio accumulate which lead to mutagenicity and carcinogenicity. Textile industry effluent is treated with various techniques based on biological, physical, and chemical methods. Every technique has its own set of advantages and disadvantages. In case of physical methods complete removal of pollutants is not possible. In terms of chemical methods, some provide 100% dye removal but they are not cost effective thus can only be employed by the developed nations. The bioremediation or mineralization of harmful textile dyes in effluent by the action of plants, bacteria, and fungal biomass is eco-friendly, inexpensive, readily available technology with significant potential for textile effluent treatment but like other methods it also has some drawbacks. The phytoremediation technology is rather slow and complex effluent might limit the efficiency if a particular plant species is not able to process the toxicity of effluent. Similarly, bacteria, fungi yeast could be utilized with much higher potential with modern outlook towards bioremediation equipped with molecular biology, genetic engineering, and nanotechnology. Biotechnology can be a great tool to promote sustainable practices in waste water treatment and textile dye degradation in near future. In order to promote complete removal of textile effluents developed nations are required to cooperate with developing nations. Development of such dyes are required that can degrade on their own after some specific time. Textile industry has progressed so fast throughout this era but it is the need of the hour to develop sustainable, cost effective, and robust remediation techniques accordingly.

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Remediation of Toxic Environmental Pollutants Using Nanoparticles and Integrated Nano-Bio Systems

19

Amrita Kharangate-Lad and Nezlyn Cressida D'Souza

Abstract

Rapid industrialization and urbanization have led to the release of many toxic contaminants in the environment. Environmental pollution is a major concern as it affects health and well-being of all organisms. The toxicity and health hazards associated with the environmental pollutants requires clean-up from the soil and water. Remediation using nanotechnology is an effective alternative to conventional physicochemical methods as it is eco-friendly and economical. In this chapter we emphasize the use of nanoparticles in the remediation of toxic environmental pollutants such as heavy metals, hydrocarbons, antibiotics, hormones, dyes, and recalcitrant agro-based and organohalide compounds. Nanoparticles are synthesized biogenically which involves its synthesis using plants and microorganisms. Nanobioremediation is a technology that integrates microbial bioremediation and nanoremediation. This chapter provides a brief outlook on applications of nanobioremediation through integrated nano-bio systems in removal of organic or inorganic toxic pollutants and discusses the implications of using these integrated systems on a larger scale. The benefit of this collaboration is the development of more efficient, cost-effective, environmentally friendly solutions in remediation of toxic environmental pollutants.

Keywords

Nanoparticles · Microbes · Synthesis · Toxic pollutants · Remediation

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19.1 Introduction

Environmental pollution is undeniably a major issue that the society faces. The environment gets polluted with toxic compounds released due to industrialization and unplanned urbanization. Toxic pollutants like heavy metals, particulate matter, industrial effluents, sewage, pesticides, fertilizers, oil spills, and other organic compounds are a few examples of environmental pollutants. The use of conventional physical and chemical technologies in the treatment of contaminated soils and water is expensive as they have high energy requirements and usually leave behind hazardous waste residues. Therefore, cost-effective bioremediation technologies that use microorganisms to detoxify and transform pollutants have been developed for the treatment of polluted soils and water (Abatenh et al. 2017; Kumar et al. 2018; Tomei and Daugulis 2013). Another technology that is being explored currently is the use of nanoparticles in cleaning up toxic pollutants from contaminated sites. Nanoparticles have highly desirable properties that favour their application in remediation of recalcitrant pollutants from soil and water.

19.2 Properties of Nanoparticles

Nanoparticles possess unique physicochemical properties and therefore, nanotechnology has gained a lot of attention in the last decade. Nanoparticles are nanoscopic particles having dimensions within the range of 1–100 nm. Due to their nanoscale size these particles exhibit exceptional physicochemical properties such as high energy, large specific surface area, and unique visible properties (Fig. 19.1). Nanoparticles by virtue of their small size have properties that differ from the bulk metal. They exhibit physical and chemical properties that are a virtue of their nano-size. The nano-size of the particles imparts them with unique chemical properties such as large surface per unit area and high reactivity. Nanoparticles exhibit plasmon resonance as owing to their small size they have the ability to confine their electrons and produce quantum effects. The media used in the synthesis of nanoparticles and the number of bioactive compounds present in the media directly influence the chemical and morphological properties of nanoparticles (Yadav et al. 2017).

Based on the chemistry, the nanoparticles are broadly classified into organic and inorganic. Organic nanoparticles include carbon nanoparticles (like carbon nanotubes (CNT)), while inorganic nanoparticles include metals (such as nanoscale zerovalent iron (nZVI), palladium, cadmium), noble metals (gold and silver), semi-conductors (copper, zinc oxide, and titanium oxide), and magnetic nanoparticles (maghemite, magnetite) (Guerra et al. 2018).

Nanoparticles have different ways of interacting with each other, some tend to remain as individual moieties, while others tend to group together, depending upon the attractive or repulsive forces acting between them. Agglomeration of nanoparticles is often linked with oxidation-induced-instability, which leads to decrease in the surface area and reactivity of the particles. Coating of nanoparticle with suitable stabilizers increases their adsorbing capacity while decreasing their

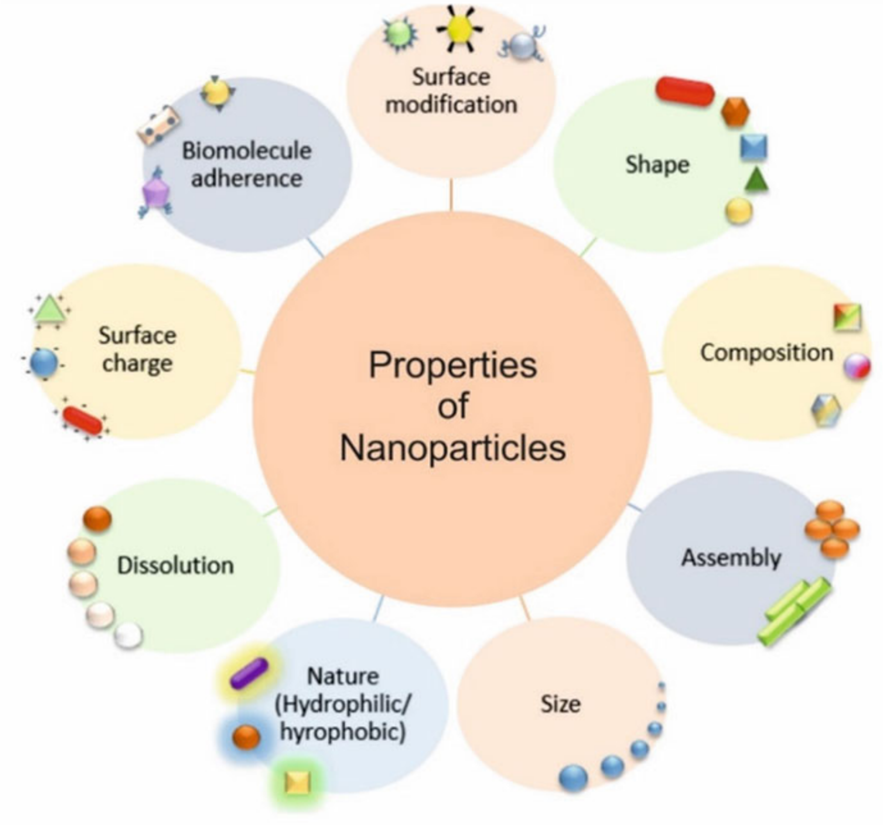

Fig. 19.1 Properties of nanoparticles

tendency to agglomerate. Immobilization with organic polymers such as lactate, gaur gum, gellan gum, etc. enhances their interaction with the toxic compounds by improving nanoparticle mobility, stability, and reactivity. Nanoparticles can be designed to exhibit specific physical properties and chemical composition in order to target specific pollutants (Sakulchaicharoen et al. 2010).

19.3 Nanoparticles and Nanomaterials

Morphologically, nanoparticles can be spheres, sheets, cylinders, and tubes (Pal et al. 2019). However, they differ from nanomaterials owing to their dimensions. Nanomaterials have been defined as "a manufactured or natural material that possesses unbound, aggregated, or agglomerated particles where external dimensions are between 1 and 100 nm size range", according to the EU Commission (Jeevanandam et al. 2018). Nanomaterials therefore have a length of 1–1000 nm in at least one dimension. Based on the shape, size, structure, and composition, nanomaterials can be classified into nanoclusters, nanofibres, nanotubes, nanoshells, and nanocomposites.

Nanomaterials have successfully demonstrated their ability to degrade environmental pollutants from soil and ground/surface water. Metal-based nanomaterials composed of silver (Ag) nanoparticles have been used for disinfection of water and soil from *Escherichia coli* and *Pseudomonas aeruginosa*. Titanium dioxide (TiO_2) nanoparticles have been proven efficient against *Escherichia coli,* MS-2 phage and hepatitis B virus. Other titanium-based nanoparticles have been reportedly used for remediation of aromatic hydrocarbons (phenanthrene), chlorinated compounds (2-chlorophenol), organic pollutants (endotoxins), microorganisms (*Escherichia coli* and *Staphylococcus aureus*), dyes (Rhodamine B), and biological nitrogen (nitric oxide) (Guerra et al. 2018). Binary mixed oxides, iron nanoparticles, and bimetallic nanoparticles have been used for the treatment of water containing methylene blue, heavy metals, and chlorinated and brominated compounds, respectively (Jeevanandam et al. 2018). Due to their minute size and surface properties, they can enter very small spaces in the soil and attain access to contaminants well below the subsurface level. Since movement of these nanoparticles is governed by Brownian motion, they can remain suspended in groundwater facilitating wider transport of the particles and more efficient interaction with the contaminant (Tratnyek and Johnson 2006).

19.4 Synthesis of Nanoparticles

The modification of surface properties of the nanoparticle improves its interaction and compatibility with the pollutant of interest. Nanoparticles, in general, are synthesized using two approaches: top-down and bottom-up. The top-down approach centres on gradual degradation of bulk materials to nanosized particles, while the bottom-up approach involves assembly of atoms and molecules into a nanoparticle (Narayanan and Sakthivel 2010). The former approach involves usage of expensive and energy-intensive physical methods, while the latter can be further sub-classified into chemical and biological methods. The employment of high-priced toxic solvents and extreme physical conditions (such as high pressure and temperature) in chemical synthesis of nanoparticles renders the chemical process as environmentally unfriendly (Narayanan and Sakthivel 2010). Biological methods, which utilizes plants and microbes (algae, bacteria, yeasts, actinomycetes, and fungi) serve as an eco-friendly and less expensive alternative to top-down synthesis of nanoparticles (Fig. 19.2) (Sastry et al. 2003).

19.4.1 Biogenic Production of Nanoparticles Using Plants

The biosynthesis of nanoparticles generally entails oxidation–reduction reactions. Plants and microorganisms have enzymes and produce antioxidizing and reducing

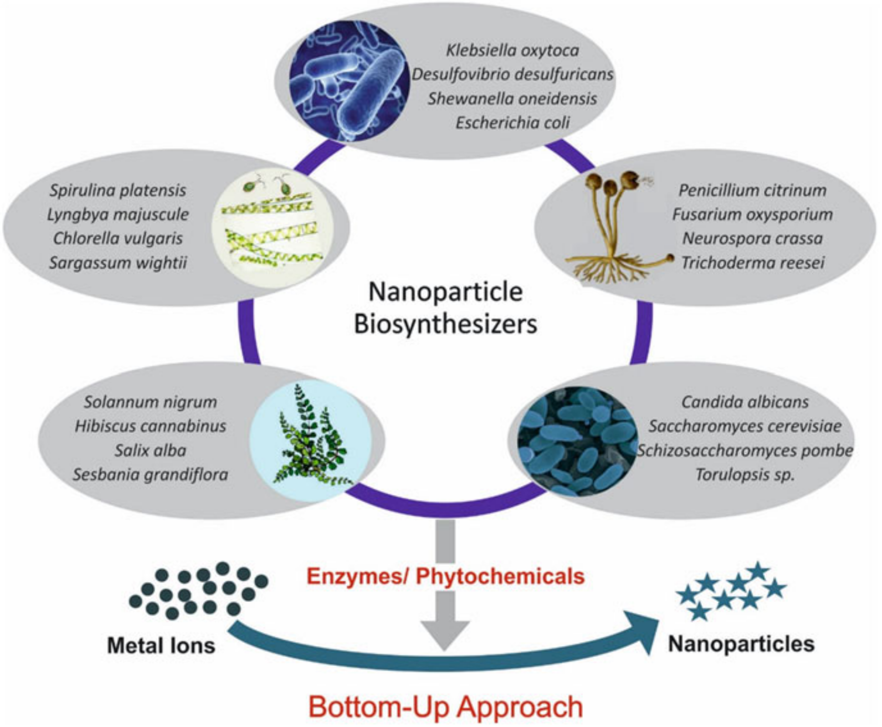

Fig. 19.2 Biogenic synthesis of nanoparticles using bottom-up approach

phytochemicals, which facilitate reduction and detoxification of accumulated metal ions. In the synthesis of metal/metal oxide nanoparticles, plant extracts (from roots, leaves, flowers, stems) are reported to be effective as they contain phytochemicals such as amides, aldehydes, ascorbic acids, carboxylic acids, flavones, ketones, phenols, and terpenoids. These compounds have been reported to have ability to reduce metal salts into metal nanoparticles. Plants such as Alfalfa, oats, Tulsi, lemon, Aloe vera have been reported to be used in production of silver and gold nanoparticles (Singh et al. 2016). Through optimization of process parameters, nanoparticles of desired sizes and morphologies can be biosynthesized (Iravani 2014). The application of whole plants or their phytochemical extracts in synthesis of nanoparticles has been demonstrated through numerous studies (Hussain et al. 2016). Biogenic production using plants is a preferred method as it is easier to scale-up (Megharaj et al. 2011).

19.4.2 Biogenic Production of Nanoparticles Using Microorganisms

Microbes possess highly versatile and effective catalytic mechanisms that enable degradation of various toxic compounds (Watanabe 2001). Additionally, microbes are ubiquitous, much easier to culture and manipulate, have high growth rates, and require low cost investment. Silver nanoparticles have been biogenically produced by using bacteria such as *Arthrobacter gangotriensis, Aeromonas* sp. SH10, *Bacillus amyloliquefaciens, Bacillus cecembensis, Bacillus indicus, Bacillus cereus, Corynebacterium* sp. SH09, *Escherichia coli, Enterobacter cloacae, Geobacter* sp., *Lactobacillus casei, Phaeocystis antarctica, Pseudomonas proteolytica,* and *Shewanella oneidensis.* Gold nanoparticles have been reported to be extensively produced using *Bacillus subtilis* 168, *Bacillus megaterium* D01, *Desulfovibrio desulfuricans*, *Escherichia coli* DH5a, *Plectonema boryanum* UTEX 485, *Rhodopseudomonas capsulate,* and *Shewanella alga*. Fungi have been used to synthesize zinc, gold, silver, and titanium metal/metal oxide nanoparticles. Biosynthesis of silver and gold nanoparticles by *Saccharomyces cerevisiae* has been reported (Singh et al. 2016).

Microorganisms synthesize inorganic nanoparticles by assimilating metal ions from the surrounding environment and converting them to their elemental form using enzymes. Heterotrophic sulphate reducing bacteria have been reported to reduce gold-(I)-thiosulphate complex (Au $(S_2O_3)_2^{3-}$) to elemental gold (Au^0) (Lengke and Southam 2006). Similarly, *Stenotrophomonas maltophilia* SELTE02 mediated transformation of selenite (SeO_3^{2-}) to elemental selenium (Se^0) (Gregorio et al. 2005). Microbial biosynthesis can be achieved through intracellular and extracellular routes. The intracellular method consists of transporting metal ions into the cell, followed by enzymatic reactions, whereas the extracellular method involves adsorption of the metal ions on the cell surface, followed by enzyme-moderated reduction (Zhang et al. 2011). Microorganisms are known to synthesize various types of nanoparticles including metallic nanoparticles (gold, silver, cobalt, chromium, and other metals), magnetic, non-magnetic nanoparticles, and alloy nanoparticles (Li et al. 2011).

The biogenic method of nanoparticle production is an enzyme-mediated "green" synthesis of nanoparticles (Fig. 19.2). It allows elimination of costly, inefficient methods that involve use of expensive, hazardous solvents (such as sodium borohydride, ammoniacal silver nitrate) and produce toxic by-products. Furthermore, the particles generated by biogenic processes have greater surface area and higher catalytic reactivity (Mohanpuria et al. 2008). Table 19.1 lists microorganisms involved in the biogenic synthesis of various nanoparticles.

19.5 Nanoparticles: Mechanism of Action

Nanoparticles exhibit surface and chemical properties that are distinct from the bulk metal due to their nano-size. The nano-size increases the mechanical, magnetic, electrical, and optical properties of the nanoparticles. Nanoparticles catalyse processes such as adsorption and chemical reactions such as photocatalysis, precipitation, reduction, oxidation, and hydrogen peroxide dependent oxidation (Fenton reactions). The adsorption capacity of nanoparticles is being used to develop sorbents like carbon nanotubes and zeolites that have demonstrated efficient removal

Table 19.1 Biogenic production of nanoparticles by microorganisms

Biogenic production of nanoparticles by microorganisms		
Nanoparticle	Microorganism	References
Iron (Fe)	*Pleurotus* sp.	Mazumdar and Haloi 2011
	Bacillus subtilis	Sundaram et al. 2012
	Escherichia coli	Arcon et al. 2012
	Klebsiella oxytoca	Anghel et al. 2012
	Chaetomium globosum	Elcey et al. 2014
Zinc (Zn)	*Desulfobacteriaceae*	Labrenz et al. 2000
	Lactobacillus sp.	Selvarajan and Mohanasrinivasan 2013
	Streptomyces sp.	
	Aspergillus terreus	Raliya and Tarafdar 2013
	Sphingobacterium thalpophilum	Raliya and Tarafdar 2014; Rajabairavi et al. 2017
Palladium (Pd)	*Bacillus sphaericus*	Creamer et al. 2007
	Desulfovibrio desulfuricans	Gurunathan et al. 2015
	Bacillus benzeovorans	Omajali et al. 2015
	Shewanella sp.	Zhang and Hu 2017
	Geobacter sulfurreducens	Yates et al. 2013
Copper (Cu)	*Penicillium aurantiogriseum*	Honary et al. 2012
	Penicillium citrinum	Cuevas et al. 2015
	Penicillium waksmanii	Tiwari et al. 2016
	Stereum hirsutum	Parveen et al. 2016
	Bacillus cereus	Parveen et al. 2016
	Pseudomonas sp., *Serratia* sp.	Parveen et al. 2016
Silver (Ag)	*Bacillus licheniformis*	Kalimuthu et al. 2008
	Trichoderma reesei	Nanda and Saravanan 2009
	Cladosporium cladosporioides	Balaji et al. 2009
	Candida sp.	Kumar et al. 2011
	Streptomyces naganishii	Alani et al. 2012
Gold (Au)	*Rhodococcus* sp., *Streptomyces* sp.	Ahmad et al. 2003
	Aspergillus fumigatus, A. flavus	Gupta and Bector 2013
	Rhodopseudomonas capsulata	He et al. 2007
	Stenotrophomonas maltophilia	Nangia et al. 2009
	Penicillium brevicompactum	Mishra et al. 2011
Titanium (Ti)	*Lactobacillus* sp.	Prasad et al. 2007
	Bacillus subtilis	Vishnu Kirthi et al. 2011
	Aspergillus flavus	Rajakumar et al. 2012
	Aspergillus terreus	Raliya and Tarafdar 2014
	Bacillus amyloliquefaciens	Khan and Fulekar 2016
Cadmium (Cd)	*Escherichia coli*	Sweeney et al. 2004
	Rhodopseudomonas palustris	Bai et al. 2009
	Fusarium sp.	Reyes et al. 2009
	Bacillus amyloliquefaciens	Singh et al. 2011
	Bacillus licheniformis	Shivashankarappa and Sanjay 2015

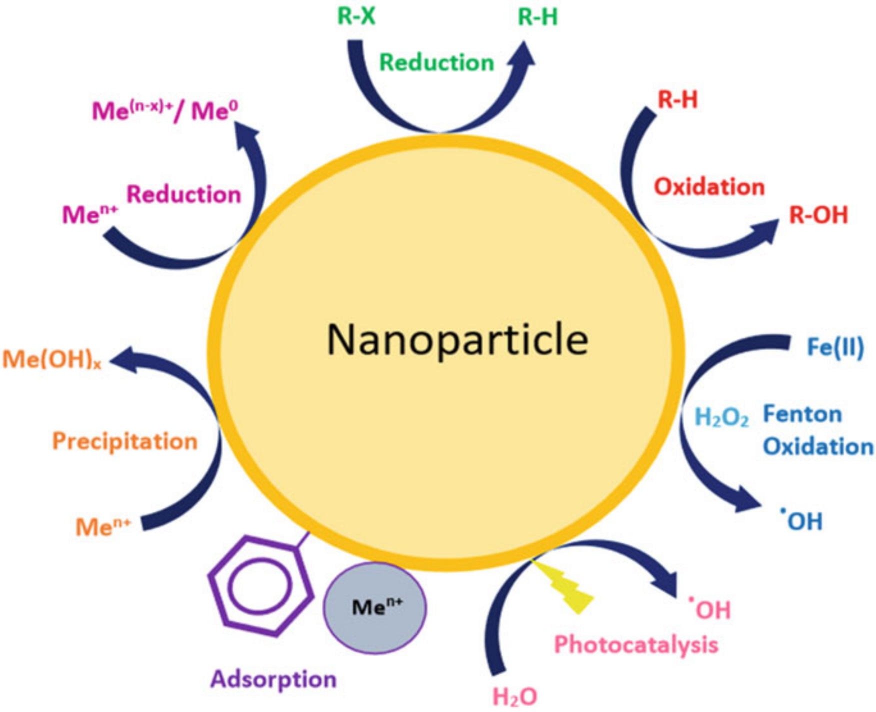

Fig. 19.3 Mechanisms catalysed by nanoparticles in degrading toxic pollutants

of anions and metals from drinking water (Yaqoob et al. 2020). Nanoparticles mediate the transformation of toxic metals into their respective hydroxides by precipitation. Nanoparticles play a crucial role in nanobioremediation by catalysing reactions and generating hydrogen ions that aid the microorganisms to further detoxify and transform the compound. The high reactivity and larger surface area for interaction offer the nanoparticles the characteristic property of having high oxidation potential. Metal oxide nanoparticles have been shown to catalyse oxidation reactions that can transform toxic pollutants such as hydrocarbons. Nanoparticles can absorb photons and act as nanophotocatalysts. The larger surface area of nanoparticles increases the oxidation of organic pollutants at the surface of the nanoparticles resulting in their degradation. TiO_2 is the most commonly used nano-photocatalyst in treatment of wastewater, due to its low cost, chemical stability, easy availability, and zero toxicity. Composite nanomaterials like copper oxide doped (CuO-doped) zinc oxides (ZnO) have been used to catalyse the Fenton oxidation. Fenton oxidation is a H_2O_2-assisted photo-decomposition of toxic pollutant in the presence of solar radiation (Banik and Basumallick 2017). Figure 19.3 summarizes the mechanisms catalysed by nanoparticles in degradation of toxic pollutants.

19.6 Remediation of Toxic Metals Using Nanoparticles

Heavy metals constitute a group of metals and metalloids that have atomic density higher than 4000 kg/m^3 (Edelstein and Ben-Hur 2018). Although plants need various heavy metals such as molybdenum, zinc, iron, etc. for basic metabolic activities, at higher concentrations, these metals are harmful to the plant (Vardhan et al. 2019). Heavy metals are toxic to humans even at low concentrations. Due to urbanization, population explosion, and rapid industrialization, soil and water resources end up as heavy metal sinks. Bioremediation measures thus play an important role in restoring balance within these contaminated environments, failure of which would lead to bioaccumulation and biomagnification of these toxic metals at the cellular level.

Nanomaterials such as bimetallic nanoparticles, metal oxides, nanoscale zeolites, and carbon nanotubes have been considered for metal remediation. Iron oxide nanoparticles have been extensively studied in metal detoxification owing to their ability to be separated easily from the reaction media and due to their low toxicity. Immobilization of accumulated heavy metals in soil plays a crucial role in their transformation and detoxification. Nanoparticles such as nano-alginate, bentonite-nZVI, zerovalent iron nanoparticles, nanocarbon, and dendrimers have been used to immobilize the heavy metals in soil (Helal et al. 2016).

Nano-hydroxyapatite, a phosphate-based nanomaterial has demonstrated significant results in clean-up of Pb contaminated soils. It has also been reported to immobilize other heavy metals such as Cr, Zn, Cd, and Cu. Studies on both graphene oxide nanoparticles and nZVI nanoparticles have been reported in relation to increasing the bioavailability of arsenic and other metals in polluted soils (Baragaño et al. 2020). Similar studies using graphene as the adsorbent showed removal of arsenic by 80% from wastewater. The advantages of this nanomaterial are its ability to be recycled and reused. A nanocomposite with reduced graphene oxide and Fe_3O_4 has been studied for the removal of Pb^{2+} ions from water by co-precipitation and has been found to be efficient. Other graphene-based nanomaterials have been successfully used for the removal of heavy metals such as Cu (II), Fe (II), Mn (II), and Pb (II). Activated carbon nanomaterial has been successfully applied in the removal of heavy metals such as Zn^{+2} and Al^{+3} ions and has demonstrated an efficiency up to 92%. In wastewater treatment, it showed an absorption capacity of up to 50% for Cu^{+2} ions. Other activated carbon nanomaterials have been successfully employed in remediation of heavy metals such as Pb^{+2}, Cd^{+2}, Cu^{+2}, Ni^{+2}, and Zn^{+2} (Baby et al. 2019). The role of various environmental factors affecting the remediation of heavy metals by iron-based nanoparticles has been studied. This study also focused on the toxicity of these nanoparticles on the living organisms (Latif et al. 2020). Hydrous iron oxide-based nanomaterials have been found to remove heavy metals like Pb (II), Cu (II), Cd (II), and Ni (II). However, they have been found to be most effective in removal of arsenic (V) from drinking water. Nanomaterials based on manganese oxides have been used for the treatment of metals such as Tl (I), U, Pb (II), Zn (II), Hg (II), Cd (II), and Cu (II) and have now been considered promising in removal of heavy metals from polluted water. Polyvinylpyrrolidone-coated magnetic nanoparticles (PVP-Fe_3O_4 nanoparticles) have shown significant efficiency (100%) in the removal of Cd, Cr, Ni, and Pb. Hexavalent chromium (VI) is a prevalent inorganic pollutant that is known to be toxic, mutagenic, and carcinogenic (Valko et al. 2005). Remediation of Cr (VI) involves its reduction to trivalent Cr (III), a less toxic, non-carcinogenic form that can be precipitated into hydroxides. This reaction serves as a key step for the removal of Cr (VI) from aqueous solutions (Mabbett et al. 2004). Iron nanoparticles such as ferromagnetic carbon-coated nanoparticles have been used to remove 95% of Cr (VI) from aqueous solutions. Table 19.2 shows the use of nanoparticles in heavy metals remediation.

19.7 Remediation of Hydrocarbons Using Nanoparticles

Hydrocarbon pollution refers to the contamination of the environment by organic polycyclic aromatic hydrocarbons (PAH) or crude oil (petroleum hydrocarbons) compounds. Oil pollution has severe environmental and ecological consequences. Crude oil and its derivatives are considered as some of the most pervasive environmental pollutants. The leakage of crude oils into aquatic systems results in wide-ranging contamination. Oil sludge is a thick complex emulsion made up of various petroleum hydrocarbons, heavy metals, sediments, and water. It is composed of alkanes, aromatics, resin, and asphaltenes and contains volatile and semi-volatile organic compounds, which are reported to be genotoxic (Srivastava et al. 2019). Unintentional and deliberate spillage of oil into the environment leads to transfer of toxic organic materials into the food chain.

Due to their unique physicochemical properties, nanoparticles have gained tremendous interest in oil biodegradation. Nanoparticles can decrease the hydrophobicity of these hydrocarbon compounds and thus increase their bioavailability for bioremediation. Graphene-doped TiO_2 nanoparticles have demonstrated adsorption and photodegradation of phenanthrene, fluoranthene, and benzopyrene to phthalic and benzoic acid; oxygenated and hydroxylated PAHs; acyclic hydrocarbons and alcohols (Bai et al. 2017). Similarly, iron hexacyanoferrate (FeHCF) nanoparticles have been employed in degradation of anthracene, chrysene, and fluorine. It was also established that aromatic hydrocarbon adsorption by the FeHCF followed a molecular weight dependent trend: anthracene > phenanthrene > fluorene > chrysene > benzopyrene (Shanker et al. 2017). Bimetallic magnetic Pt/Pd nanoparticles supported on magnetic silica reduced anthracene to non-toxic partially hydrogenated species. Furthermore, compared to monometallic nanoparticles, the bimetallic particles displayed enhanced activity post recycling (Zanato et al. 2017). Nanoparticles are efficient in degrading organic compounds such as benzophenone and phenol. Benzophenone-3 is an ultraviolet absorber, and thus they can be degraded using catalytic ozonation. Manganese oxide and cobalt oxide nanoparticles immobilized on ceramic membrane displayed remarkable

Table 19.2 Nanoparticles used in remediation of heavy metals

Nanoparticles used in remediation of heavy metals		
Pollutant	Nanoparticle	References
Copper (Cu)	Amino-functionalized magnetic nanoparticles	Hao et al. 2010
	Polydopamine nanoparticles	Farnad et al. 2012
	Maghemite nanoparticles	Rajput et al. 2017
	nZVI	Boente et al. 2018
	Graphene oxide–manganese oxide nanoparticles composite	Wan et al. 2018
Chromium (VI) (Cr)	Chitosan-nZVI (nanoscale zerovalent iron) nanoparticles	Geng et al. 2009
	Magnetite–maghemite nanoparticles	Chowdhury and Yanful 2010
	Cerium oxide nanoparticles	Contreras et al. 2015
	CTAB modified magnetic nanoparticles	Elfeky et al. 2017
	Magnetic alkaline– Lignin−dopamine nanoparticles	Dai et al. 2019
Arsenic (As)	Magnetite–maghemite nanoparticles	Chowdhury and Yanful 2010
	Iron oxide nanoparticles	Shipley et al. 2011
	Cupric oxide nanoparticles	Reddy et al. 2013
	γ-Aluminium oxide nanoparticles	Ghosh et al. 2019
	Magnetic iron-titanium binary oxide composite	Deng et al. 2019
Cadmium (Cd)	Cerium oxide nanoparticles	Contreras et al. 2015
	Iron phosphate (vivianite) nanoparticles	Qiao et al. 2017
	EDTA functionalized iron oxide nanoparticles	Huang and Keller 2015
	Silica-coated iron oxide nanoparticles	Ghafoor and Ata 2017
	Graphene oxide–manganese oxide nanoparticles composite	Wan et al. 2018
Lead (Pb)	Iron phosphate (vivianite) nanoparticles	Liu and Zhao 2007
	Cerium oxide nanoparticles	Contreras et al. 2015
	EDTA functionalized iron oxide nanoparticles	Huang and Keller 2015
	L-cysteine stabilized nZVI nanoparticles	Bagbi et al. 2017
	Maghemite nanoparticles	Rajput et al. 2017
Mercury (Hg)	Carboxymethyl cellulose stabilized iron sulphide nanoparticles	Gong et al. 2012
	Citrate-coated gold nanoparticles	Ojea-Jiménez et al. 2012
	Silica-coated magnetite nanoparticles	Mohmood et al. 2016
	Inorganic magnetic sulphide nanoparticles	Patel et al. 2018

catalytic ozonation of benzophenone-3 (Guo et al. 2016). Reduced graphene oxide silver nanoparticles (rGO-Ag) were demonstrated to successfully breakdown phenol (Bhunia and Jana 2014). ZnO and magnetite-zinc oxide (Fe_3O_4-ZnO) hybrid nanoparticles have been studied in the degradation of phenols and the hybrid nanoparticles were found to be more efficient (Feng et al. 2014). UV-irradiated semiconductor catalysts such as titanium dioxide have been used in photodegradation of organic contaminants (Banik and Basumallick 2017). Calcium peroxide nanoparticles have been reported to exhibit remarkable degradation of benzene and toluene (Mosmeri et al. 2017; Qian et al. 2013). Removal of benzene from aqueous solutions has also been carried out using magnetite nanoparticles. The nano-magnetic particles have been reported to decompose 98.7% and 94.5% of the benzene in batch and continuous conditions, respectively. Furthermore, these particles can easily desorb benzene and be reused for its removal (Amin et al. 2013). Magnetite nanoparticles catalysed decomposition of p-nitrophenol to aromatic intermediates such as benzoquinone and hydroquinone, which were further oxidized by hydrogen peroxide. The nanoparticles exhibited the ability to be magnetically separated from the sludge and reused (Sun and Lemley 2011). Magnesium doped magnetite nanoparticles have been reported to effectively decompose hexachlorobenzene, a precursor of carcinogenic and mutagenic compounds (Su et al. 2014).

The remediation of petroleum-based hydrocarbons using nanoparticle-stabilized surfactants has been explored (Ali et al. 2020). Iron nanoparticles produced biogenically from *Vaccinium floribundum* showed a significant removal of up to 86% and 88% in the total petroleum hydrocarbons from polluted soil and water, respectively (Murgueitio et al. 2018). Raw and distillate forms of petroleum oil were treated with nanocarbon scavengers which efficiently sequestered these hydrocarbons by 80% and 91%, respectively (Daza et al. 2017). Polyvinylpyrrolidone (PVP) coated magnetite nanoparticles (NP) have demonstrated remediation of lower chain alkanes by 70% and higher chain alkanes by 65% after incubation of 1 h. However, the efficiency of degradation of these alkanes increased significantly on incubation of the nanoparticles with oil degrading bacteria (Alabresm et al. 2018). Table 19.3 enlists integrated systems studied for hydrocarbon degradation. Other studies have shown significant results in degradation of hydrocarbons using nanobioremediation, which has been discussed further in this chapter.

19.8 Remediation of Hormones, Antibiotics, and Medicinal Drugs Using Nanoparticles

Antibiotics and hormones are emerging pollutants. Modern healthcare and their extensive use in farming results in their release in effluent and wash waters leading to contamination of groundwater and soil. Their recalcitrant nature makes them persist in the soil and water and lead to serious effects on the environment and human health.

Table 19.3 Nanoparticles used in remediation of hydrocarbon pollutants

Nanoparticles used in remediation of hydrocarbons		
Pollutant	Nanoparticle	References
Polycyclic aromatic hydrocarbons (PAHs)		
Pyrene	Haematite nanoparticles	Jorfi et al. 2016
Phenanthrene, fluoranthene, benzopyrene	Titanium dioxide nanoparticles	Bai et al. 2017
Anthracene, phenanthrene, chrysene, fluorene, and benzopyrene	Iron hexacyanoferrate nanoparticles	Shanker et al. 2017
Anthracene	Bimetallic magnetic Pt/Pd nanoparticles	Zanato et al. 2017
Benzophenone-3	Manganese oxide and cobalt oxide nanoparticles coated on ceramic membrane	Guo et al. 2016
Phenol	Magnetite and zinc oxide hybrid nanoparticles Reduced graphene oxide silver nanoparticles (rGO-Ag)	Feng et al. 2014; Bhunia and Jana 2014
Petroleum-based hydrocarbons		
Total petroleum hydrocarbons	Iron nanoparticles	Murgueitio et al. 2018
Raw and distillate forms of petroleum oil	Nanocarbon nanoparticles	Daza et al. 2017
Alkanes	Polyvinylpyrrolidone (PVP) coated magnetite nanoparticles	Alabresm et al. 2018

19.8.1 Remediation of Antibiotics

Nanoparticles have been reported to clean up even low concentrations of these compounds. Many nanoparticles like zerovalent iron nanoparticles have exhibited the ability to remove antibiotics such as sulfacetamide from the aqueous solution by 61% (Table 19.4). Bimetallic CuFe20$_4$ nanoparticles have been efficiently used for the removal of amoxicillin from aqueous solutions. Photocatalytic degradation of ciprofloxacin has also been reported using graphene oxide/nanocellulose composite. Similar degradation studies have also been reported on ciprofloxacin using zerovalent iron nanoparticles. Tetracycline degradation was successfully carried out by nanoscale zero-valent iron (nZVI) and Fe/Ni bimetallic nanoparticles in aqueous solution. Although Fe/Ni nanoparticles performed better that nZVI, the removal efficiency of both the particles was reported to decrease with increase in pH, thus asserting that the degradation process is pH-dependent (Dong et al. 2018b). UiO-66, a zirconium based nanoparticle doped with cobalt was reported to adsorb and degrade tetracycline via photocatalysis. Factors affecting the adsorption process included dosage of the nanoparticles, coexisting ions, pH, and initial concentration of the antibiotic (Cao et al. 2018). The Oxone process has been utilized to degrade organic compounds. In this process, Oxone [peroxymonosulfate (PMS)] is

Table 19.4 Nanoparticles used in remediation of antibiotics, medicinal drugs, and hormones

Nanoparticles used in remediation of antibiotics, medicinal drugs, and hormones		
Pollutant	Nanoparticle	References
Antibiotics		
Amoxicillin	Copper-iron bimetallic nanoparticles	Malakootian et al. 2019
Ceftriaxone	Fe_3O_4 nanoparticles	Malakootian et al. 2019
Sulfacetamide	Zerovalent iron nanoparticles	Malakootian et al. 2019
Tetracycline	Fe/Ni bimetallic nanoparticles Cobalt-doped UiO-66 nanoparticles Martite nanoparticles Cu/Fe bimetallic particle ZnS nanoparticles Titanium oxide nanocomposite	Dong et al. 2018b; Cao et al. 2018; Soltani et al. 2018; Malakootian et al. 2019
Ciprofloxacin	Zinc oxide nanoparticles Fe-doped zinc oxide nanoparticles Titanium oxide nanoparticles Cupric oxide nanoparticles Graphene oxide/ nanocellulose composite Zerovalent iron nanoparticles	Gharaghani and Malakootian 2017; Das et al. 2018; Malakootian et al. 2020
Levofloxacin	Zn oxide nanoparticles, Graphene oxide sheets	El-Maraghy et al. 2020
Hormones		
Estrone	Polystyrene nanoparticles Titanium dioxide nanoparticles	Akanyeti et al. 2017; Czech and Rubinowska 2013
17-ß-Estradiol	Manganese oxide nanoparticles Magnetic biochar nanoparticles	Han et al. 2014; Dong et al. 2018a
Medicinal drugs		
Paracetamol	Activated carbon nanoparticles	Baby et al. 2019
Carbamazepine	Haematite nanoparticles Magnetite nanoparticles	Rajendran and Sen 2018; Liu et al. 2018
Ibuprofen	Nanoscale zerovalent iron (nZVI)	Machado et al. 2013

combined with a source of transition metals to generation sulphate ions, which catalyse the redox process. Martite (α-Fe_2O_3) nanoparticles have been found to activate the Oxone process to degrade the recalcitrant antibiotic (Soltani et al. 2018).

The degradation of ciprofloxacin, another commonly used antibiotic, was proved both spectrophotometrically and microbiologically by the loss of antibiotic activity, using Fe-doped-ZnO nanoparticles (Das et al. 2018). Immobilized nanoparticles allow easy placement and removal of aqueous contaminants. Moreover, it resolves complications related to separation of catalysts from the solution, as well as allows reusability of nanoparticles. ZnO immobilized on a glass plate exhibited nanophotocatalysis of ciprofloxacin with high removal efficiency (Gharaghani and Malakootian 2017). Similarly, TiO_2 nanoparticles immobilized on a glass plate were shown to adsorb and photodegrade ciprofloxacin and also resulted in decreased sludge production (Malakootian et al. 2019). Other antibiotics such as ampicillin, amoxicillin, and penicillin were reduced by bentonite-supported Fe/Ni nanoparticles (Weng et al. 2018).

19.8.2 Remediation of Medicinal Drugs

Medicinal drugs such as paracetamol, carbamazepine, and ibuprofen not just pollute water bodies, but pose a significant threat to aquatic communities. As in case of other organic compounds, a variety of nanoparticles have been researched for their applicability in degrading these recalcitrant compounds. Ibuprofen reduction can be carried out by nZVI nanoparticles. While effective on lab scale, simulation of the nanoremediation with ibuprofen contaminated soil concluded that the degradation process is slower in aqueous systems, but without any significant impact on contaminant degradation efficiency (Machado et al. 2013). Haematite nanoparticles were demonstrated to be effective adsorbents of carbamazepine and thus offer a potential remediation method for the adsorptive elimination of drugs from contaminated aquatic systems (Table 19.4) (Rajendran and Sen 2018). Magnetite nanoparticles were also confirmed to effectively remove carbamazepine (Liu et al. 2018). Nanoparticles have also been proved effective in reducing chlorhexidine, a commonly used antiseptic component. Photocatalytic degradation of chlorhexidine was successfully concluded using titanium dioxide nanoparticles as photocatalyst (Das et al. 2014). Activated carbon nanoparticles have been reportedly used for the bioremediation of methylene and paracetamol from hospital wastewaters (Baby et al. 2019).

19.8.3 Remediation of Hormones

Naturally synthesized and synthetic hormones are one of the most potent trace contaminants released into soil and water bodies. Apart from excretion and disposal of hormones, application of animal faeces as manure to fields allows transmission of endogenous hormones into soil and ultimately in water bodies. These hormones and endocrine disruptors are known to affect the reproductive health of various animals by disrupting sexual function and promoting abnormal sexual development. As with other organic compounds, nZVI, under oxidative conditions, was found to adsorb and degrade 17β-estradiol (Table 19.4) (a popular endocrine disrupting chemical) and 17α-ethinylestradiol (a synthetic birth control drug) into less bioactive estrone (Jarosova et al. 2015). Biochar, a pyrogenic black carbon product of biomass pyrolysis can be used to derive nanosized biochar particles due to their nanoporous structure, good stability, multiple functional groups, and easy availability. Magnetic biochar nanoparticles (Mag-BCNPs) are a composite of nanosized biochar nanoparticles and magnetic iron nanoparticles (Fe_3O_4). This composite was demonstrated to effectively reduce 17β-estradiol. Post remediation, the Mag-BCNPs can be recovered using a magnet, and the biochar can be desorbed by purging with ozone, thus allowing easy regeneration of the nanoparticles (Dong et al. 2018a). Carboxymethyl cellulose (CMC) stabilized manganese oxide nanoparticles have also been studied for their 17β-estradiol degrading activity (Han et al. 2014). Estrones can be removed from wastewater using TiO_2-assisted photocatalysis (Czech and Rubinowska 2013). A hybrid polystyrene nanoparticle-ultrafiltration system with renewable nanoparticles acts as a lucrative solution to filtering estrone from contaminated water. However, due to the higher permeability of the filtration system compared to that of nanofiltration/reverse osmosis systems, estrone removal capacity of 40% was achieved. However, replacing the filtration system with a finer one can increase success of the designed system (Akanyeti et al. 2017). Table 19.4 shows the use of nanoparticles in remediation of antibiotics, medicinal drugs, and hormones.

19.9 Remediation of Dyes and Organic Solvents Using Nanoparticles

With the onset of industrialization, the synthesis and utilization of various organic compounds have increased exponentially. These organic compounds include dyes which are released into the environment through anthropogenic activities. These pollutants are known to have neurotoxic, mutagenic, and carcinogenic effects on biological systems (Das and Chandran 2011). Various studies using nanoparticles have been carried out on degradation of the dyes. Nanomaterials such as reduced graphene oxide, (rGO)-TiO_2 has been successfully applied for the bioremediation of Alizarin Red S. Other studies have also reported the use of graphene oxide nanomaterials in association with TiO_2 or ZnO in photodegradation of methylene blue. Bimetallic nanoparticles of iron (Fe) and nickel (Ni) showed significant results in cleaning up of the azo dye Orange G from wastewater (Foster et al. 2019). Similarly, remarkable efficiency was exhibited when absorbent made of ZnO nanoparticle was used to remove azo dyes, amaranth, and methyl orange from aqueous solution (Zafar et al. 2019). Tara and others (Tara et al. 2020) have summarized the nanoparticles used in the removal of Azo dyes and the efficiency of removal of these

Table 19.5 Nanoparticles used in remediation of dyes and organic solvents

Nanoparticles used in remediation of dyes, and organic solvents		
Pollutant	Nanoparticle	References
Dyes		
Dye containing effluents	Nickel nanoparticles	Kale and Kane 2017
Azo dyes	ZVI nanoparticles Cerium loaded copper oxide Iron nanoparticle	Tara et al. 2020
Methylene blue, Congo red	Copper oxide nanoparticles Copper oxide nanoneedles Graphene oxide sheets	Tara et al. 2020
Cationic and anionic dyes	Nickel doped zinc oxide nanoparticle	Tara et al. 2020
Coomassie brilliant blue, Amido black 10B	Copper oxide nanoneedles Graphene oxide sheets	Tara et al. 2020
Malachite green, methyl violet	Magnetic NPs coated with poly (dimethylaminoethyl acrylamide) and methyl acrylate on modified with Fe_3O_4 nanoparticles	Tara et al. 2020
Methylene blue	Copper oxide nanoparticles activated with montmorillonite clay	Tara et al. 2020
Methylene blue, methyl orange, rhodamine B, organic dyes	Silver nanocomposite, Silver nanoparticles	Tara et al. 2020; Bhakya et al. 2015
Amaranth and methyl orange	ZnO nanoparticles	Zafar et al. 2019
Orange G	Fe and nickel nanoparticles	Foster et al. 2019
Organic solvents		
TCE	Zerovalent iron nanoparticles	Ibrahem et al. 2012
p-Nitrophenol	Magnetite nanoparticles	Sun and Lemley 2011
Hexachlorobenzene	Magnetic micro/nano Fe_xO_y-CeO_2 composite Mg-doped iron oxide nanoparticles	Jia et al. 2010; Su et al. 2014
Benzene	Magnetite nanoparticles Calcium peroxide nanoparticles	Amin et al. 2013; Mosmeri et al. 2017
Toluene	Calcium peroxide nanoparticles Tungsten doped titanium dioxide nanoparticles	Qian et al. 2013; Poorkarimi et al. 2017

dyes by the respective nanoparticles. Table 19.5 summarizes different nanoparticles that are involved in remediation of dyes and organic solvents.

Nanoscale iron nanoparticles have shown significant efficiency in removal of chlorinated organic solvents contaminating groundwater (Zhang and Elliott 2006). Zerovalent iron nanoparticles have been used for the remediation of trichloroethylene (TCE). It was considered an efficient reducing catalyst and resulted in fast degradation of TCE from contaminated soils (Ibrahem et al. 2012).

19.10 Remediation of Agro-Based Compounds Using Nanoparticles

Agro-based compounds such as herbicides, fungicides, pesticides, weedicides are extensively used in agriculture. These compounds leach and contaminate the surrounding soil and water bodies. Due to the complex chemical structure of these compounds they are recalcitrant in nature and tend to persist in the environment for a long time. Nanoparticles have been found to be efficient in removal of pesticides from contaminated sites by adsorption and photodegradation of these compounds (Table 19.6). Nanomaterials such as zinc oxide, titanium dioxide, and silver have been reported to photocatalyse the degradation of pesticides. Metal nanocomposites and polymer matrix nanocomposites have been successfully used in the removal of organic and inorganic pollutants. Iron nanoparticles have been successfully used in remediation of carbamate pesticides such as methomyl. Fe_3O_4 nanoparticles have

Table 19.6 Nanoparticles used in remediation of agro-based compounds

Nanoparticles used in remediation of agro-based compounds		
Pollutant	Nanoparticle	References
Aldrin	Fe_3O_4 nanoparticles	Sahithya and Das 2015
Alachlor	Nanoscale zerovalent iron (nZVI)	Bezbaruah et al. 2009
Eldrin	Fe_3O_4 nanoparticles	Sahithya and Das 2015
Lindane	Fe_3O_4 nanoparticles, silver nanoparticles	Sahithya and Das 2015
	Nanoscale zerovalent iron (nZVI)	Elliott et al. 2009
Organophosphate pesticides	TiO_2, ZnO, Au-TiO_2, CuO nanoparticles	Sahithya and Das 2015
Atrazine	Nanoscale zerovalent iron (nZVI)	Bezbaruah et al. 2009
Chlorpyrifos	Silver and gold nanoparticles	Bootharaju and Pradeep 2012
DDT	Mixed metal oxides nanoparticles	Manav et al. 2018
Profenofos (organophosphorous pesticide)	Fe/Ni bimetallic nanoparticles	Mansouriieh and Khosravi 2015
Malathion	Iron oxide nanoparticles and iron oxide/gold nanoparticles Magnetite nanoparticles and gold coated magnetic nanoparticles	Fouad et al. 2015
Acetamiprid	Fe/Ni bimetallic nanoparticles	Marcelo et al. 2016

been applied for their efficiency in clean-up of organochlorine pesticides such as aldrin, endrin, and lindane. Silver nanoparticles have also been efficient in remediation of pesticide lindane. Organophosphate pesticides such as monocrotophos, malathion, chlorpyrifos, dichlorvos have been photo-catalytically degraded using nanoparticles such as titanium dioxide, zinc oxide, gold-titanium dioxide, and copper oxide, respectively.

Gold-titanium dioxide (Au-TiO_2) nanoparticles have been reported to photocatalyse the degradation of chloridazon (Sahithya and Das 2015). Rapid anoxic degradation of pesticide alachlor (2-Chloro-2′,6′-diethyl-*N*-(methoxymethyl)-acetanilide) has been reported using nZVI. The reaction resulted in dechlorinated alachlor, which was significantly more biodegradable in comparison to its parent compound (Bezbaruah et al. 2009) (Table 19.6). The nZVI nanoparticles have been documented to degrade lindane (γ-hexachlorocyclohexane), a commonly used organochlorine pesticide, into benzene, diphenyl, and di/tetra/penta forms of the compound (Elliott et al. 2009). Silver and gold nanoparticles have exhibited remarkable ability to decompose chlorpyrifos, an organophosphorothioate pesticide, to 3,5,6-trichloro-2-pyridinol and diethyl thiophosphate at room temperature. These nanoparticles have also demonstrated an ability to be regenerated and reused (Bootharaju and Pradeep 2012). Catalytic degradation of Profenofos (an organophosphorous pesticide) and acetamiprid (a neonicotinoid insecticide) using Fe/Ni bimetallic nanoparticles has been reported (Marcelo et al. 2016; Mansouriieh and Khosravi 2015). $MgCeO_3$ and $MgFe_2O_4$ are mixed metal oxides that have been studied for degradation of DDT (dichlorodiphenyltrichloroethane), a well-known harmful organochlorine insecticide. Both mixed oxides degraded DDT to less toxic compounds DDD (dichlorodiphenyldichloroethane), DDE (dichlorodiphenyldichloroethylene), and simpler compounds within the first reaction hour (Manav et al. 2018). Zerovalent metal nanoparticles, semiconductor nanoparticles, and some bimetallic nanoparticles have been documented to treat environmental pollutants such as azo dyes, pesticides (chlorpyrifos and organochlorines), nitroaromatics, hormones, and antibiotics (Foster et al. 2019).

19.11 Remediation of Organohalide Compounds Using Nanoparticles

Organohalide compounds such as polybrominated diphenyl ethers (PBDEs), dioxins, polychlorinated biphenyls (PCBs), and chlorinated aliphatic hydrocarbons (CAH) are omnipresent, highly toxic fat-soluble compounds. Being insoluble in water, their low bioavailability hinders biodegradation by aquatic microbes. PCBs are toxic organohalide compounds classified as persistent organic pollutants. Various nanoparticles have been studied for their remediation. Pd/Fe bimetallic nanoparticles and nZVI have been reported to catalyse hydro-dechlorination of hexachlorobiphenyl (Chen et al. 2014). Carbon-modified titanium dioxide (CM-*n*-TiO_2) nanoparticles were reportedly used in photocatalytic degradation of PCB mixtures Aroclor 1254 and Aroclor 1260 (Shaban et al. 2016). Surfactants enhance

Table 19.7 Nanoparticles used in remediation of organohalide compounds

Polychlorinated biphenyls (PCBs)		
Pollutant	Nanoparticle	References
2-chlorobiphenyl	Palladium–aluminium (Pd/Al) bimetallic nanoparticles	Yang et al. 2013
Penta, hexa, hepta, and octobiphenyls	Nanoscale zerovalent iron (nZVI)	Gomes et al. 2014
2,2′,4,4′,5,5′-hexachlorobiphenyl	Nanoscale zerovalent iron (nZVI)	Chen et al. 2014
Aroclor 1254 and Aroclor 1260	Carbon-modified titanium dioxide (CM-*n*-TiO_2) nanoparticles	Shaban et al. 2016

solubilization of hydrophobic organic compounds, hence their integration with nanoparticles may lead to increase in bioremediation efficiency. In a combined electro-remediation set-up consisting of electrodialysis, non-ionic detergents (Saponin and Tween-80), and nZVI nanoparticles, degradation of up to 76% PCBs was reportedly achieved within 5 days. However, in a set-up with just surfactant and nanoparticles, the remediation efficiency was low, thus supporting the assumption that the surfactant will not always enhance nanoparticle activity (Gomes et al. 2014). Similar observations were made pertaining to remediation of 4-chlorophenol and 2-chlorobiphenyl using palladium-aluminium (Pd/Al) bimetallic nanoparticles (Table 19.7). While the nanoparticles by themselves were capable of degrading the PCBs, addition of ionic and non-ionic surfactants led to decrease in hydrodechlorination of the organic compounds (Yang et al. 2013). Polychlorinated aliphatic compounds such as trichloroethylene can be remediated using nanoparticles. Polymethyl methacrylate coated nZVI have also been reported capable in reducing trichloroethylene (Wang and Chiu 2009). Bimetallic Ni/Fe nanoparticles immobilized in hydrophilic nylon-66 membrane have been reported to completely dechlorinate trichloroethylene within 25 min. The immobilization of nanoparticles improved the reactivity and longevity of the nanoparticles (Parshetti and Doong 2009).

19.12 Nanobioremediation Using Integrated Nano-Bio Systems

Microbial bioremediation or nanoremediation, by itself offers multiple advantages over conventional treatment methods, but also has multiple noteworthy limitations. Microbial degradation of toxic compounds is a time-consuming process that can take over a year. Its effectiveness varies with conditions such as pH, nutrients, temperature, and other environmental conditions (Abatenh et al. 2017; Kumar et al. 2018). Integration of nanotechnology with microbial bioremediation can overcome these limitations and provide a better alternative to pollutant remediation. The reaction of the toxic pollutant with nanoparticles transforms the pollutant into compounds more easily metabolized by microorganisms. Therefore, nanobioremediation is a promising alternative in remediation technologies involving detoxification of toxic pollutants.

Nanobioremediation can be described as a combination of nanotechnology and bioremediation systems, wherein the former enhances the effectiveness of the latter. Therefore, nanobioremediation offers the benefits of both nanotechnology and bioremediation. The application of nanobioremediation can be done using two approaches. The sequential approach involves subjecting the contaminant to nanoparticles followed by exposure to the bioagent. The nanoparticles break down the contaminants to simpler compounds, allowing the bioagent to metabolize it further. In the concurrent or combined approach, the nanoparticle and biological agent is injected into the system simultaneously (Tratnyek and Johnson 2006; Karn et al. 2009). While both these methods seem to be practical alternatives to conventional technologies, more research and development is needed for their execution on a larger scale.

The most significant advantage of using nanoparticles in remediation is their application in both in situ and ex situ conditions. In ex situ remediation, the contaminated soil is excavated, while the contaminated groundwater is extracted and treated with nanoparticles on-site or off-site. In in situ treatment methods, nanoparticles are directly injected at the site of contamination where it degrades the contaminant. Compared to conventional methods, nanobioremediation is best suited for in situ treatment of contaminated soil and groundwater as the exceptional properties and colloidal nature of nanoparticles allow deep penetration up to the water table, a feat that is not possible to achieve with ex situ methods. Furthermore, nanoparticles enhance the reaction rates of microorganisms, thus allowing better degradation of pollutants (Karn et al. 2009). The ability of nanoparticles to degrade pollutants in association with biological systems presents opportunity for development of more efficient nano-bio integrated technologies. Apart from treatment and remediation of contaminated sites, nanoparticles can be applied to pollution sensing and pollution prevention.

19.13 Nanobioremediation of Toxic Heavy Metals

Integrated systems have great scope in metal bioremediation. Nanoparticles in combination with microorganisms have been used successfully to remediate heavy metals. Nanoscale zerovalent iron (nZVI) is smaller and more reactive than microscale zerovalent iron (ZVI) and therefore offers elevated reactive surface area, higher reactivity, and better injectability into aquifers, thus making them valuable in bioremediation of polluted sites (Li et al. 2006). However, due to their tendency to agglomerate and form larger particles, the reactivity of the nanoparticles decreases. Thus, direct application of free nZVI in remediation of contaminated soil and water could lead to overall decrease in efficiency of nanoparticles and leaching of iron into aquatic bodies. The immobilization of nZVI onto biodegradable, porous materials (beads) helps to overcome agglomeration. The toxic pollutant diffuses into beads and comes in contact with the entrapped nanoparticles. Similar studies on

Table 19.8 Nano-Bio integrated systems for remediation of Chromium (VI)

Integrated systems for remediation of toxic Chromium (VI)			
Metal pollutant	Nanoparticle	Bioagent	References
Bacteria			
Chromium (VI)	CNTs	*Shewanella oneidensis* MR-1	Yan et al. 2013
	CNTs	*Pseudomonas aeruginosa*	Pang et al. 2011
	Bio-Pd	*Clostridium pasteurianum* BC1	Chidambaram et al. 2010
Consortium			
Chromium (VI)	nZVI	Whey microbiota	Nemecek et al. 2016
Chromium (VI)	nZVI	Consortia of *Bacillus subtilis*, *Escherichia coli,* and *Acinetobacter junii*	Ravikumar et al. 2016

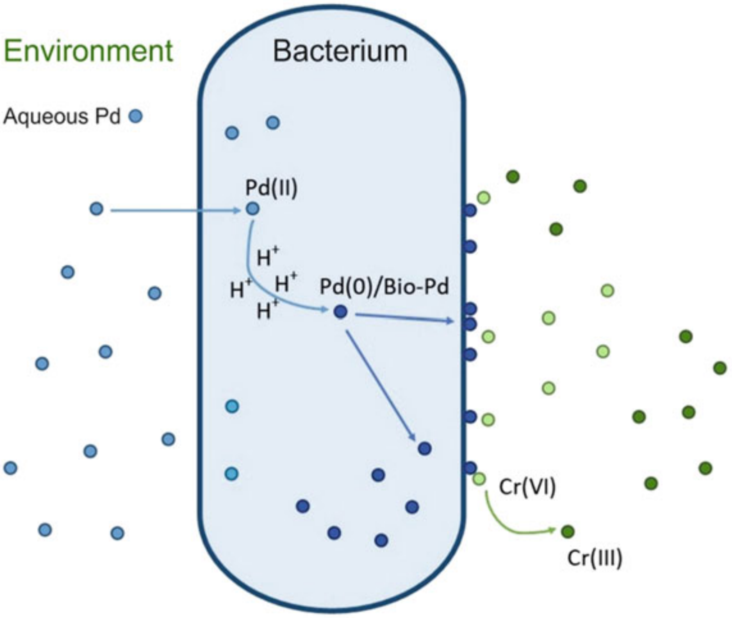

Fig. 19.4 Integrated Bio-Pd system in chromium remediation. The anaerobic hydrogen-producing bacterium accumulates aqueous palladium and reduces it to Bio-Pd, which further reduces toxic chromium (VI) to its less toxic form, Cr (III)

immobilization of nZVI on calcium alginate (nZVI−C − A beads), in presence of microbial biofilm has been shown to be effective in reducing Cr (VI) to Cr (III) (Ravikumar et al. 2016). Table 19.8 depicts various studies carried out using integrated nano-bio systems for remediation of chromium (VI).

The Bio-Pd (bio-reduced-Pd) integrated system is an innovative method for in situ remediation of toxic metals (Fig. 19.4). Bio-Pd generation is a novel system wherein bacterium, in the presence of hydrogen, reduces and precipitates accumulated palladium, Pd (II) into Pd nanoparticles (Pd (0)). The two-step remediation system involves synthesis of Pd nanoparticles (bio-Pd) followed by reaction with the contaminant. Although this two-step process is suitable for ex-situ remediation, hydrogen supply acts as a technical and commercial challenge. *Clostridium pasteurianum* BC1, an anaerobic hydrogen producer, allows coupling of in situ production of H_2 with in situ synthesis of nanoparticles, which further catalyses the degradation of contaminants. The bio-Pd synthesized by *Clostridium pasteurianum* BC1 successfully demonstrated the reduction of Cr (VI) to Cr (III) (Chidambaram et al. 2010).

Nanomaterials have been used to augment the metal-reduction efficiency of microorganisms. Compared to suspended cells, immobilized microorganisms allow continuous and stable bioreduction of Cr (VI). However, the alginate used for immobilization can lower the reduction efficiency due to its effect on electron and mass transport. Impregnation of organic nanomaterial such as carbon nanotubes (CNTs) has proved to enhance the mechanical strength and bioreduction capacity. The immobilization of *Shewanella oneidensis* MR-1 in alginate/CNT beads was shown to yield a higher reduction efficiency compared to the controls, possibly due to accelerated electron transfer (Yan et al. 2013). CNT-modified polyvinyl alcohol and sodium alginate matrix using immobilized *Pseudomonas aeruginosa* also enhanced bioreduction efficiency of the microorganism (Pang et al. 2011). Additionally, these modified beads can be reused effectively multiple times. This technique of CNTs impregnated immobilization can be applied to various other biological reduction processes and can be tested on various other pollutants.

19.14 Nanobioremediation of Polycyclic Aromatic Hydrocarbons (PAHs)

Hydrocarbons and organic pollutants are persistent in nature. The chances of degrading these compounds increase on application of nano-bio integrated systems. Hydrophobic polycyclic aromatic compounds (PAH) such as carbazole and indenopyrene are toxic and carcinogenic environmental pollutants. *Sphingomonas* sp. XLDN2–5 cells magnetically immobilized in Fe_3O_4 nanoparticle containing gellan gum matrix were proved to be effective in degrading carbazole. The addition of Fe_3O_4 nanoparticles to immobilized bacterial cells significantly enhanced its biodegradation activity (Wang et al. 2007). Yeast strains of *Candida tropicalis* NN4 have been reported to enhance indenopyrene biodegradation activity of zerovalent iron nanoparticles by producing glycolipid biosurfactant (Ojha et al. 2019). *Rhodococcus erythropolis* IGTS8 combined with magnetite (Fe_3O_4) nanoparticles have been found to effectively desulphurize dibenzothiophene (DBT), a recalcitrant organo-sulphur compound released on combustion of fossil fuels, to 2-hydroxybiphenyl (2-HBP). The nanoparticles have been reported to enhance cell growth rate, in comparison with the controls containing either the bacteria or the nanoparticles (Karimi et al. 2017). Immobilized *Pseudomonas*

Table 19.9 Integrated nano-bio systems for remediation of polycyclic aromatic hydrocarbons

Integrated nano-bio systems for remediation of polycyclic aromatic hydrocarbons			
Nanoparticle	Bioagent	Pollutant	References
Polycyclic aromatic hydrocarbons			
Fe^0 nanoparticles (ZVI)	*Candida tropicalis* NN4	Indenopyrene (InP)	Ojha et al. 2019
Pd/nFe bimetallic nanoparticles	Laccase enzyme from *Trametes versicolor*	Triclosan	Bokare et al. 2010
Magnetite (Fe_3O_4) nanoparticles	*Pseudomonas delafieldii*	Dibenzothiophene	Shan et al. 2005
Fe_3O_4 nanoparticles + gellan gum gel beads	*Sphingomonas* sp.	Carbazole	Wang et al. 2007
Magnetite nanoparticles	*Rhodococcus erythropolis* IGTS8	Dibenzothiophene (DBT)	Karimi et al. 2017
Nitro-aromatic compound			
Fe^0 nanoparticles (ZVI)	Methanogenic anaerobes	RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine)	Oh et al. 2001

delafieldii coated with magnetite nanoparticles are also effective in degrading DBT (Shan et al. 2005). Successful degradation of a pollutant depends on its chemical structure. Some pollutants can be degraded completely, while others are broken down to less toxic moieties.

Triclosan, a halogenated aromatic hydrocarbon compound, is a commonly used antibacterial and antifungal component of soaps, toothpaste, and deodorants. Although triclosan is not considered as chemical pollutant of high concern currently, its degraded by-products have been detected in soil, wastewater, drinking water, and even human breast milk. Triclosan has been reported to bioaccumulate in various aquatic species, raising concern of it being an emerging toxic contaminant (Dhillon et al. 2015). Complete biotransformation of triclosan to non-toxic oligomers has been reported via sequential nanobioremediation. Pd/nFe bimetallic nanoparticles, under anaerobic conditions, dechlorinated triclosan to 2-phenoxyphenol, which, in the absence of nanoparticles, was oxidized into non-toxic products by laccase enzyme isolated from *Trametes versicolor* (Bokare et al. 2010). Table 19.9 lists some of the integrated nano-bio systems used for bioremediation of polycyclic aromatic hydrocarbons.

19.15 Nanobioremediation of Petroleum-Based Hydrocarbons

Although the studies conducted on nanobioremediation of oil sludge are few, researchers have demonstrated successful degradation of aliphatic and aromatic hydrocarbons of oil sludge using an integrated system of nanoparticles and microorganisms. The nanoparticles decrease the hydrophobicity of the hydrocarbons allowing them to be accessible to the microorganisms for degradation. The bacteria,

Table 19.10 Integrated systems for remediation of petroleum-based hydrocarbon pollutants

Integrated systems for remediation of petroleum-based hydrocarbon pollutants			
Nanoparticle	Bioagent	Pollutant	References
Fe_2O_3 and Fe_3O_4 nanoparticles	*Thalassospira* sp.	Oil sludge	Rizi et al. 2017a
Fe_2O_3 and Fe_3O_4 nanoparticles	*Chromohalobacter* sp.	Oil sludge	Rizi et al. 2017b
Consortium			
ZnO nanoparticles	*Bacillus, Pseudomonas, Achromobacter,* and *Microbacterium*	Crude oil	Ismail et al. 2013
NiO nanoparticles	*Halomonas xianhensis* A, *Halomonas zincidurans* B6, *Pseudomonas stutzeri* ATCC 17588, and *Halomonas salifodinae* BC7	Crude oil	El-Sheshtawy et al. 2017

Thalassospira sp. and *Chromohalobacter* sp. isolated from an oil site in the Persian Gulf has been studied to successfully degrade oil sludge into various non-toxic compounds. The addition of Fe_2O_3 and Fe_3O_4 nanoparticles, at low concentrations, further enhanced degradation of the compounds, without negatively impacting bacterial growth rate (Rizi et al. 2017a, b).

The interaction between nanoparticles and bacteria may not always be synergistic; nanoparticles can have toxic effects on the microbe and thus reduce its bioremediation potential. Crude oil degradation by the isolated bacteria: *Bacillus, Pseudomonas, Achromobacter,* and *Microbacterium sp.* was deemed successful; but addition of ZnO nanoparticles to *Pseudomonas* decreased its growth rate and lowered bioremediation potential (Ismail et al. 2013). This reduction can be attributed to inhibitory effect of the nanoparticles on the bacterium.

Low bioavailability of crude oil and their poor aqueous solubility obstructs microbial degradation. Nevertheless, evolved mechanisms allow many aquatic microbes to utilize these hydrophobic compounds as a source of carbon. Crude oil degrading bacteria produce biosurfactants and bioemulsifiers that permit bacterial adhesion to hydrocarbons and increase aqueous solubility of crude oil components, thus enhancing its biodegradation. Microcosms containing consortia of *Halomonas xianhensis, Halomonas zincidurans, Pseudomonas stutzeri,* and *Halomonas salifodinae*, along with nickel oxide (NiO) nanoparticles and biosurfactants were found to degrade different membered ring polyaromatics, and 90% of the crude oil sample, compared to microcosms with either biosurfactants or nanoparticles (El-Sheshtawy et al. 2017). Table 19.10 lists some of the integrated nano-bio systems used for remediation of petroleum-based hydrocarbons.

Nanoparticle assisted microbial degradation of hydrocarbon plays a significant role in hydrocarbon decontamination. However, many aspects of nanobioremediation need to be studied such as the innate properties of the nanoparticles, their impact on the microorganisms, the reaction conditions and whether sequential or combined treatment systems need to be applied. Also, the effect of biosurfactants and bioemulsifiers on the biodegradation of hydrocarbon contaminated sites needs to be evaluated prior to large-scale application of the integrated system.

19.16 Bioremediation of Organic Solvents and Antibiotics

The organic solvent, trichloroethylene (TCE), is an industrial solvent and is a common soil contaminant which is toxic at low levels. Due to its mobility in groundwater and high density, remediation of TCE can be challenging. Combination of nanoscale zerovalent iron (nZVI) along with bacteria *Dehalococcoides* sp. (Table 19.11) has demonstrated successful dechlorination and degradation of TCE to non-toxic compounds in comparison to controls that either contained the microorganism or the nanometal. It was also reported that the combination enhanced the rate of degradation as the nZVI stimulated bacterial growth by providing the bacteria with hydrogen which was utilized to dehalogenate the chlorinated compound (Xiu et al. 2010).

Antibiotics find their way into soil and aquatic systems due to their incessant use in farming and poultry. Due to their continual input into the environment, antibiotics have been classified as pseudo-persistent organic pollutants (Ma and Zhai 2014). These compounds resist biodegradation due to their antimicrobial properties. While nanoparticles and a few microorganisms are known to individually degrade these compounds to certain extent, integrated remediation can offer a cost-effective and more efficient alternative. A combined nano-bio system using MgO nanoparticles has been reported to accelerate the rate of degradation of the antibiotic Cefdinir, by enhancing the cell membrane permeability of yeast *Candida* sp. (Table 19.11) (Adikesavan and Nilanjana 2016). Table 19.11 also enlists some of the other contaminants that have been studied for their remediation using an integrated system of nanoparticles and microbes. Thus, nanoparticles are known to assist microbial activities, but their effect on microbial reaction rates is yet to be studied.

19.17 Bioremediation of Organohalide Compounds

Organohalide compounds are the most persistent toxic compounds that contaminate the soil and water ecosystems. Under aerobic conditions, nZVI has been reported to enhance the degradation of polybrominated diphenyl ethers (PDBE) such as tetrabromo-diphenyl-ether (BDE-47) by *Pseudomonas stutzeri* with increase in incubation time (Huang et al. 2016). PDBEs such as di-, tri-, and deca-BDEs can be degraded into bromophenols by subjecting it to nZVI followed by biological treatment using *Sphingomonas* sp. PH-07. The combination of *Sphingomonas* sp. PH-07 and nZVI is also effective in degrading tetrachlorodibenzo-p dioxin (TCDD), the most toxic dioxin compound (Kim et al. 2012). Nanoparticles integrated with biosurfactant producing bacteria can potentially remediate PCBs. The sequential treatment of PCBs with Pd/Fe nanoparticles followed by bioremediation with

Table 19.11 Nano-bio integrated systems for remediation of recalcitrant organic pollutants

Nano-bio integrated systems for remediation of recalcitrant organic pollutants			
Nanoparticle	Bioagent	Pollutant	References
Organic solvents			
Fe^0 nanoparticles (ZVI)	*Methanosarcina thermophila*	Carbon tetrachloride and chloroform	Novak et al. 1998
nZVI	*Dehalococcoides* sp.	Trichloroethylene (TCE)	Xiu et al. 2010
Antibiotics			
MgO nanoparticles	*Candida* sp. SMN04	Cefdinir (antibiotic)	Adikesavan and Nilanjana 2016
Organohalide compounds			
nZVI	*Sphingomonas* sp. PH-07	Polybrominated diphenyl ethers (PBDEs)	Kim et al. 2012
Pd/nFe bimetallic nanoparticles	*Sphingomonas wittichii* RW1	2,3,7,8-Tetrachlorodibenzo-p dioxin	Bokare et al. 2012
Carboxymethyl cellulose (CMC)-Pd/nFe bimetallic nanoparticles	*Sphingomonas* sp. NM05	γ-Hexachlorohexane (insecticide)	Singh et al. 2013
Magnetite nanoparticles	*Enterobacter aerogenes*	Organophosphate (pesticide)	Daumann et al. 2014
Pd/nFe bimetallic nanoparticles	*Burkholderia xenovorans*	Polychlorinated biphenyls (PCBs)	Le et al. 2015
Pd^0 nanoparticles	*Shewanella oneidensis* MR-1	Polychlorinated biphenyls (PCBs)	Windt et al. 2005
nZVI	*Dehalobacter* sp., *Sedimentibacter* sp., *Dehalogenimonas* sp.	Chlorinated aliphatic hydrocarbons (CAH)	Koenig et al. 2016
nZVI	*Pseudomonas stutzeri*	Polybrominated diphenyl ethers (PBDEs)	Huang et al. 2016
nZVI	*Bacillus* sp.	Polychlorinated biphenyls (PCBs)	Zhang et al. 2016

biosurfactant producing *Burkholderia xenovorans* resulted in formation of less toxic and harmless compounds (Le et al. 2015). The Bio-Pd-*Shewanella oneidensis* MR-1 system serves as a self-sustaining model for remediation, wherein the bacteria adsorb palladium nanoparticles, reduce it to zerovalent state, and precipitate it. These bio-reduced Pd (bio-Pd) nanoparticles were able to dechlorinate a wide range of chlorinated PCB congeners, without any selectivity (Windt et al. 2005). Culture medium dominated by organochlorine respiring bacteria *Dehalobacter* sp., *Sedimentibacter* sp., and *Dehalogenimonas* sp. when combined with nZVI completely reduce CAH such as dichloroethane and trichloroethane to ethane (Koenig et al. 2016). Carboxymethyl cellulose (CMC) stabilized bimetallic nanoparticles (CMC-Pd/nFe0) integrated with *Sphingomonas* sp. have been demonstrated to degrade γ-hexachlorohexane (γ-HCH), a commonly used insecticide. The stabilized nanoparticles demonstrated to have a biostimulatory effect on the bacterial cells (Singh et al. 2013). Likewise, zerovalent iron (ZVI) has been reported to enhance *Methanosarcina thermophila* mediated dechlorination of compounds such as chloroform and carbon tetrachloride, by serving as an electron donor (Novak et al. 1998). Table 19.11 lists nano-bio systems that are used for remediation of recalcitrant organic compounds.

19.18 Fate of Nanoparticles

While it is implicit that nanoparticles have various applications in the field of bioremediation, the extensive use of these nanoparticles and their subsequent release into the environment is a major concern, especially in cases of in situ remediation. Therefore, the zerovalent iron nanoparticles are currently the only nanoparticles on field application (Kharangate 2015). These particles, once released into the environment, may find channels to enter the food chain, deposit in various organisms, and manifest toxic effects. Nanoparticles have been studied to have toxicity affects that can be attributed to its size. Even nanoparticles of inert metals such as gold have shown to have toxic effects on biological systems (Jeevanandam et al. 2018). Due to the shortage of investigations of the toxicological effects of these nanoparticles, a sub-speciality of nanotechnology, known as nanotoxicology has been developed (Colvin 2003; Niazi and Gu 2009).

Compared to plants, invertebrates, and vertebrates, microorganisms exhibit widespread and diverse reactions to nanoparticles (Oberdorster et al. 2009). The toxic effects depend on the nature of the nanoparticle and its interaction with the microbial species. In case of rhizosphere resident bacteria *Pseudomonas chlororaphis* O6, CuO nanoparticles were demonstrated to neutralize the charge on the EPS colloids and release ions that disrupt the homeostatic control within the cell. Similar mechanisms of disrupting homeostatic mechanisms of the cell have been observed with ZnO nanoparticles (Dimpka et al. 2011).

Application of nanoparticles in remediation processes results in the discharge of these nanoparticles in the soil and aquatic ecosystems wherein they encounter and interact with various microorganisms, which are sensitive to these particles. Due to their nano-size, large surface area, and high reactivity, nanoparticles can destroy the microbial membrane and generate reactive oxygen species (ROS) that are known to disrupt cellular processes (Cecchin et al. 2016). Studies conducted on nanoparticles released in natural aqueous environments confirm that the nanoparticles react and conjugate with biological molecules such as DNA, RNA, proteins as well and lysophospholipids which facilitate their solubilization in water (Ke and Qiao 2007; Niazi and Gu 2009). Since microbes can assimilate nanoparticles, it can lead to accumulation in the food chain and ultimately build-up to toxic levels in humans.

Recovery of released nanoparticles from natural systems seems impossible, extensive research is needed to understand their potential toxic effects on various biological systems, prior to their large-scale application in nanobioremediation of contaminated sites.

Furthermore, soil microorganisms play an important role in regulating biogeochemical cycles and also possess natural mechanisms to degrade contaminants. Drastic reduction in populations of these beneficial organisms can lead to ecological imbalance. Despite their adaptability, nanoparticles used for in situ remediation can have a bactericidal effect on the inherent microbiota. Thus, determining the interactions between native microorganisms, the contaminant and the nanoparticle to be used prior to application is imperative for sustainable remediation of polluted sites.

19.19 Conclusion

Integrated systems have a lot of potential in remediating various organic and inorganic contaminants from polluted environments. Nanobioremediation has the ability to reduce the overall cost for environmental clean-up on large-scale application. While ex situ nanobioremediation is still at an infant stage, in situ application of nanoremediation and nanobioremediation to soil and ground/surface water can reduce contaminant to near-zero levels. Microbe-assisted intracellular/extracellular synthesis of biogenic nanoparticles acts as a novel, environment friendly, cost-effective strategy to supply tailored nanoparticles for remediation projects. Additionally, the possibility of intentionally tuning nanoparticles opens up new avenues in nanoremediation. Although this approach is a favourable alternative to conventional methods, nano-toxicity associated environmental risks are still unclear and need further research. Moreover, the effect of parameters like pH, temperature, ionic strength, presence of competing or inhibitory substances, etc. on remediation efficiency of the nanobioremediation method needs to be evaluated. But once these gaps are filled, integrated nano-bio systems can be applied on a larger scale.

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Bioremediation of Wastewaters

20

Oluwadara O. Alegbeleye

Abstract

Wastewater generation, handling, management, and disposal or recycling is an important issue, globally. Wastewater treatment and reuse is a critical socioeconomic issue, due to several reasons including increased strain on freshwater resources and environmental protection. This overview covers the main types and sources of wastewaters, together with their characteristics. The major alternative uses for (treated) wastewaters are highlighted, exploring the agronomic and socioeconomic intricacies and benefits of wastewater reuse. Over time, there has been extensive research and commercial optimization of suitable wastewater treatment strategies that can ensure reuse or safe environmental discharge. Bioremediation is regarded as a sustainable approach because it is relatively cheap and environmentally friendly. Activated sludge, an important precursor or driver of pollutant removal due to wide abundance and diversity of microorganisms is discussed in this chapter, as well as other technologies such as the use of membrane bioreactors, aerobic granulation technology and hybrid technologies for biological remediation of wastewater-associated pollutants. Known pollutant-degrading microbial groups including bacteria, fungi, and microalgae are discussed and finally, key research gaps are identified.

Keywords

Bioremediation · Activated sludge · Bioreactors · Microalgae · Wastewater

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20.1 Introduction

The main sources of wastewaters include domestic, agricultural, and industrial activities (such as petroleum exploration, textile production, pharmaceutical activities, as well as other chemical and manufacturing processes) (Changotra et al. 2020). Wastewaters may contain potentially hazardous biological and chemical pollutants including heavy metals, other organic and inorganic chemicals, nitrogen, phosphorous, or other nutrients, microplastics, suspended solids, dispersed oils, salts, clinically relevant pathogens, antibiotic resistance genes, radioactive substances, endocrine disrupters, and so on (Changotra et al. 2019b). Wastewaters are typically characterized based on appearance, temperature, pH, salinity, biological oxygen demand (BOD), chemical oxygen demand (COD), total nitrogen (TN), total phosphorous (TP) levels of total suspended solids (TSS), total dissolved solids (TDS), and non-biodegradable organic compounds (Fazal et al. 2018). Management and disposal of wastewaters constitute a significant technical problem for governments, industry leaders, and other relevant stakeholders since the continuous discharge of raw or poorly treated wastewaters into the natural environment may pose substantial ecological and human health risks (Ferronato and Torretta 2019). Wastewater-associated contaminants may be washed off into surface waters via runoff or seep through soils to contaminate groundwater resources (Alegbeleye and Sant'Ana 2020) and could enter into the human food chain, posing significant human health risks.

20.2 Alternative Uses of Wastewaters

First, a definition of terminologies used in this section is provided, for proper context. Graywater refers to all wastewater that does not contain sewage, i.e. water from a po
source that has been used for laundry and other domestic purposes. Urban wastewater refers to combined effluent that contains sewage. Water that has been adequately treated and is considered suitable for particular specified uses such as domestic purposes, irrigation, etc. is known as reclaimed water. Green water is reclaimed water that has been comparatively highly treated, making it suitable for general purposes, as a non-potable source in parallel with a potable source. Drinking water is very high-quality water certified suitable for human consumption.

Generally, water sources are ranked in the following order in terms of microbiological and chemical quality: rainwater or potable water, deep groundwater, shallow groundwater, surface water (e.g. rivers, lakes, and so on), and raw or poorly treated wastewaters (Alegbeleye et al. 2016; Alegbeleye et al. 2018). Wastewater recycling options depend on the amount and quality of wastewater available, but also on the intended end use (Corominas et al. 2020). For example, in residential or domestic settings, available graywater is usually comparatively limited and treating domestic wastewater generates considerably larger volume of reusable water

(Radingoana et al. 2020). Wastewater treatment however generates significant amounts of sludge (discussed in later sections), which require further management.

Globally, particularly in semi-arid, arid, and other water-stressed regions, freshwater resources are increasingly becoming scarce (Mizyed 2013). Wastewater (and graywater) reuse is thus becoming attractive, as it is technically and logistically advantageous for many reasons (Alegbeleye et al. 2018). Fundamentally, the reuse of wastewaters contributes meaningfully to the conservation of natural resources. In certain cases (such as agricultural farming), it serves as a source of nutrients and eases economic and environmental pressures, providing a suitable alternative to environmental disposal of industrial or municipal effluents (Power 2010). Some of the most popular alternative uses of wastewater include: for irrigation of non-food and food crops as well as urban green areas, domestic sanitation, in industrial cooling or other industrial processes, fire systems, recovering arid land, and so on (Englande et al. 2015; Dery et al. 2019). It is important to clarify that the unregulated reuse of graywater is not recommended, because even though graywater does not include sewage, it may contain human pathogens. Many countries, especially advanced countries have stipulated safety standards regulating the recycling and use of (treated) wastewaters. Generally, standards for effluent treatment are based on the required water quality criteria to protect the well-being and beneficial purposes of the end-user or receiving environment. This broadly cuts across the following categories: (1) protection of terrestrial and aquatic ecosystems, (2) agricultural water uses, (3) recreational water uses, (4) groundwater and soils, and (5) human consumption or food production.

While treated wastewaters are usually of slightly poorer quality compared to rainwater, most conventional treatment strategies sufficiently reduce human pathogens and other pollutants to safe levels rendering it colorless, odorless, and suitable for most domestic purposes and agricultural farming (Yadav et al. 2019). Generally, wherever possible, such as in regions with adequate rainfall such as Latin America and sub-Saharan Africa, it is better to use rainwater or potable water for higher-grade purposes such as drinking. The use of raw or poorly treated wastewater for drinking or irrigating crops that will be consumed raw or minimally processed is not recommended (Alegbeleye et al. 2018).

The unintended (or indirect) use of wastewaters, which occurs when untreated, partially treated or treated wastewater is released into environmental resources such as canals and rivers that supply agricultural water is one of the most significant problems associated with the discharge and recycling of wastewaters (Jeong et al. 2016). This is prevalent in developing countries and poses significant public health hazards as the end user is unaware. The probable human and ecological health hazards include: occupational, i.e. (risks to growers, fishermen, and others working on or within the area), residential (residents or those who otherwise have to frequently be in the contaminated area), and the risk of subsequent animal or human infection via the handling or consumption of contaminated foodstuff or contaminated animal (Narain et al. 2013). As urbanization steadily outstrips urban planning infrastructure/provisions in many parts of the developing world, indirect wastewater use is projected to rise (Satterthwaite et al. 2010; Butsch and Heinkel

Table 20.1 Pollutants that may be present in raw or ineffectively treated wastewater (Buechler and Scott 2006; Jechalke et al. 2015; Jaramillo and Restrepo 2017)

Category	Example
Biological	Pathogens Antibiotics, mobile genetic elements (MGEs), class 1 integrons
Metals (especially heavy metals)	Cadmium, nickel, chromium, arsenic, lead, mercury
Nutrients and salts	Phosphorous, nitrate
Organic chemicals	Hydrocarbons, pesticides, other toxic organic compounds
Inorganic chemicals	Fluoride Cyanide Hydrogen sulfide
Emerging contaminants	Pharmaceuticals Endocrine disrupters Other veterinary residues Detergents Other active pharmaceutical ingredients (API)
Other	Suspended matter/solids, acids, and bases

2020). Types of pollutants that are typically occurring in wastewaters are shown in Table 20.1.

The reuse of treated wastewater is also fraught in that the safety at the point of use depends not only on the source and efficaciousness of treatment, but also on the storage or holding conditions and distribution systems (Alegbeleye et al. 2018). All of these contiguous factors and systems must thus be optimized to yield the full benefits of wastewater recycling. Human perception and attitudes are also significant as people are mostly averse to consuming treated wastewaters (Murray and Ray 2010; Wester et al. 2015). For example, in Singapore wastewater is treated to drinking water standard using membrane filtration, but the water is rarely used for drinking because most people will not knowingly consume treated wastewater (Ormerod 2017; Tortajada and Nambiar 2019). The primary consideration for wastewater reuse is not the direct or indirect municipal or economic benefits, but public health protection (Janeiro et al. 2020). Therefore, the most critical goal of all wastewater reuse endeavors should be to eliminate or at best, minimize potential health risks.

20.3 Treatment of Wastewaters

Wastewaters are treated to sufficiently improve their chemical and microbiological quality such that they can be safely released into waterways or reused for agricultural farming or certain domestic purposes, without exerting any significant environmental or human health hazards (Kehrein et al. 2020). To protect public health, it is important to approach wastewater collection, treatment, and disposal (or recycling) as constructively as possible.

Table 20.2 Wastewater treatment options (Scott et al. 2002; Deegan et al. 2011)

Physicochemical	(i) Coagulation. (ii) Filtration. (iii) Sedimentation. (iv) Flocculation. (v) Chemical disinfection, e.g. chlorination.
Biological	(i) Aerobic, e.g. activated sludge (continuous, fill, and draw), membrane batch reactors (crossflow, submerged), sequence batch reactors. (ii) Anaerobic, e.g. anaerobic filters, anaerobic sludge reactors, anaerobic film reactors
Membrane processes	Nanofiltration, ultrafiltration, microfiltration, electrodialysis reversal, reverse osmosis, membrane bioreactors, combinations of membranes in series
Advanced oxidation processes	Hydrogen peroxide, ozonation, perozonation, transition metals and metal oxides, Fenton reactions, photolysis, photocatalysis, electrochemical oxidation, ultrasound irradiation, wet air oxidation
Hybrid technologies	For example, advanced oxidation processes + biological treatment
Other	(i) Phytoremediation. (ii) Bioremediation. (iii) Biosorption.

Most times, treatment strategies and sequence depend on the source and characteristics of the wastewaters. Wastewaters typically contain various particles of differing sizes categorized as supracolloidal (> 100–100 mm), settleable (> 100 μm), dissolved (< 0.08 μm), and colloidal (0.08–1 μm) (Kinyua et al. 2016). Generally, physicochemical and biological treatment strategies are popular as they are deemed cheaper and more sustainable (Barak et al. 2020). Popular wastewater treatment approaches are shown in Table 20.2.

Physicochemical treatment may represent the sole stage/phase in wastewater treatment or may be incorporated as an auxiliary strategy during treatment to improve biological degradation or secondary treatment (such as polishing). Physicochemical wastewater treatment works fundamentally based on the separation of colloidal particles (Samer 2015). Addition of chemical destabilizers such as flocculants and coagulants can alter the physical state of colloids, enhance their stability and in turn, their ability for particle or floc formation, thereby improve settling properties (Sánchez-Martín et al. 2012; Tetteh and Rathilal 2019). Examples of physicochemical or mechanical wastewater treatment processes include: filtration, clarification, dissolved air flotation, aeration, coagulation, sorption, ion exchange, sedimentation, and chlorination, among others (Table 20.2). These processes remove large particles such as fillers, coating materials, bark particles, and other suspended organic solids from wastewaters (Mohan and Pittman 2007). Passing the water through a filter or screen typically can remove large solid compounds and then the water could be passed through grinders or grit chambers to further disintegrate the residual solid wastes or sift out gravel, sand, and other inorganic materials.

For proper perspective/context, very fine particles (colloids), which are highly stable and do not aggregate and subsequently settle, cannot be efficiently separated by flotation, settling, or filtration as they will pass through any filter. In such cases though, separation via other physicochemical treatments like activated carbon filtration and other advanced oxidation processes is possible (Kehrein et al. 2020). Comparatively large particles can be separated by settling using flotation or gravity, depending on the relative densities of water and solids. Physicochemical treatment of wastewaters is evidently not specifically suited for the elimination of microorganisms (Bello et al. 2008; Skouteris et al. 2020). Urban wastewater treatment plants typically consist of a pretreatment step (screening, oil removal, grit removal), a primary settling treatment, designed to retain suspended solids and reduce turbidity. This is followed by secondary treatment (i.e. biological treatment) using microorganisms to catalyze the oxidation of the biodegradable organic matter, which in many cases is the activated sludge (Bertrand et al. 2015).

20.4 Bioremediation of Wastewaters

Bioremediation exploits the metabolic capability of bacteria and other microorganisms to degrade organic compounds and other pollutants into less hazardous compounds, carbon dioxide, water, and minerals (Balseiro-Romero et al. 2019). Aerobic lagoons, anaerobic biological processes, activated sludge systems, and fungal treatment are some of the approaches applied to improve the overall physicochemical properties and neutralize (or at least reduce the toxicity) of chemicals and other hazardous compounds occurring in wastewaters (Pant and Adholeya 2007; Ullah et al. 2020).

Bioremediation technologies can be categorized into two: in situ and ex situ, where in situ refers to the application of bioremediation at the place or point of contamination using natural conditions and ex situ indicates the treatment of wastewater at a separate facility as in the case of centralized and/decentralized wastewater treatment (Kumar Singh et al. 2020). In situ treatment uses natural conditions at the contaminated site, is believed to be relatively cheaper but might be slower. Ex situ treatment approaches are comparatively more expensive as they require waste excavation and transport (Azubuike et al. 2016). In practice, particularly in natural habitats, in situ biodegradation of contaminants is achieved by synergistic interactions among a wide variety or consortia of microbial groups, rather than a single species with known degrading capabilities (Li et al. 2018). In any case, microorganisms with known degrading capabilities may not satisfactorily degrade contaminants in situ (Li et al. 2020a), a trend demonstrated by studies showing that microbial consortia can better degrade pollutants attributable to structural and functional co-operations among diverse members of microbial communities including direct degraders and the so-called non-direct degraders (NDDs) (Hesnawi et al. 2014). Bacterial, fungal, and microalgal species secrete unique enzymes and possess unique degrading genes, which are different in terms of substrate specificity and function over a range of pH and temperature (Roccuzzo et al. 2020). Conversely, however, there is the possibility for interrelationships other than symbiosis such as competition, antagonism, parasitism, neutralism, or commensalism to occur potentially altering the efficacy of co-cultures. In addition, these associations are not static and can in fact evolve over time, which necessitates research on the specific and co-operative roles that the various microbial groups play, specific or co-metabolic degradation steps, and metabolic pathways to permit optimum process control (Roccuzzo et al. 2020). Several strategies including bioventing, biopiling, and bioaugmentation among others are some of the processes that have been developed for the manipulation/modulation and optimization of microbial metabolism of hazardous compounds, colorants, and nutrients occurring in contaminated wastewaters (Ruberto et al. 2009; Alegbeleye et al. 2017a).

Ex situ bioremediation uses bioreactors and there are many different types whose process parameters have been optimized, including aerobic, anaerobic, advanced aerobic, and other wastewater treatment systems (Vikrant et al. 2018; Villegas-Plazas et al. 2019). In one common approach, raw wastewater is suspended in the presence of autochthonous or exogenous microorganisms (in the case of exogenous strains, it is usually those that have been characterized as proficient degraders), thoroughly homogenized and aerated (Samer 2015; Jesus et al. 2019). In another approach, the wastewater can be sprayed over trickling filters or beds of stone covered with microbial biofilms or a cocktail of microbial slime, which act on it to break them down into less toxic byproducts (Ahmed 2007).

The highly controlled and usually conducive conditions in a bioreactor significantly enhance pollutant degradation as well as process rates and efficiency (Alegbeleye et al. 2017a). In most cases, the conditions (such as continuous agitation) in bioreactors improve contaminant bioavailability since it facilitates improved contact between inoculants and pollutants, which enhances contaminant mass transfer phenomena (Bakri et al. 2011). Treatment in bioreactors also offers a dilution effect, which may reduce the impact of pollutant toxicity on degrading microorganisms (Balseiro-Romero et al. 2019). Fundamentally, bioremediation parameters (temperature, pH, and redox conditions) can be more easily manipulated and optimized, but also electron acceptors, solvents, and surfactants can be used to enhance the bioavailability of pollutants (Robles-González et al. 2008; Alegbeleye et al. 2017).

One of the major advantages of ex situ treatment approaches is that it makes the use of exogenous strains with known degradation capacity more feasible while avoiding potential pitfalls such as ecological disruption/stress associated with in situ treatment approaches (Azubuike et al. 2016). Ex situ approaches are also useful because they can be used to assess bioremediation potential, i.e. a pre-validation approach to verify whether or not pilot or field scale remediation may be feasible.

Apart from the management or treatment approach, another critical, yet fundamental factor that influences the type and success of bioremediation is the type of wastewater (Robles-González et al. 2008). The microbial community (diversity and prevalence) depends on the type of wastewater, and this directly affects the success of bioremediation. Increased levels of novel, emerging or recently emerged contaminants such as polychlorinated biphenyls and pharmaceuticals constitutes significant public health challenge particularly because they might not be readily biodegradable. Pharmaceutical wastewaters, for example, might be relatively more challenging to bioremediate seeing as many groups of pharmaceuticals are toxic to microbes; some are antimicrobial agents that can significantly reduce microbial populations in wastewater treatment systems (Iranzo et al. 2018; Changotra et al. 2020).

20.5 Conventional Activated Sludge Methods

Activated sludge is one of the most conventional technologies for the biological treatment of wastewater in wastewater treatment plants (WWTPs), where a suspension of bacterial biomass (i.e. the activated sludge) initiates the biological treatment of pollutants and nutrients (Salama et al. 2019). The process utilizes a dense microbial culture in suspension to aerobically biodegrade organic compounds and form a biological floc for solid separation in the settling units (Tyagi and Lo 2013; Fang et al. 2018; de Rollemberg et al. 2019). The mechanism of treatment is contingent on establishing and maintaining a population of proficient microbial degraders, assuring adequate levels of dissolved oxygen and other environmental/physicochemical parameters, as well as suitable contaminant–microbe contact (Salama et al. 2019). In some treatment systems, biomass may grow attached to a surface (broadly referred to as biofilms) as, for example, in trickling filters, rotating biological contactors/reactors, granular media biofilters, fixed media submerged biofilters, fluidized bed reactors, among others (Rusten et al. 2006). Some other types of biological suspension systems are moving bed biofilm reactors (MBBR) (discussed in subsequent section 20.4.1), and integrated fixed-film activated sludge systems (which can be regarded as a variation of the MBBR process) (Gernaey and Sin 2011).

Activated sludge treatment removes organic carbon compounds, nutrients such as nitrogen and phosphorous as well as pathogens. In some cases, further treatment (thermal or anaerobic) may be applied to efficiently denature pathogens (Wang et al. 2014). Biological decontamination of pollutants may be brought about by a combination of processes including volatilization, surface binding, and microbial decomposition (Fang et al. 2018). Crucial factors such as environmental variables (including pH, temperature, and oxygen), nutrients (usually suitable, biodegradable waste from the bulk of the "nutrients"), microbial diversity, and abundance influence the overall efficiency of activated sludge systems (Zhai et al. 2020; de Rollemberg et al. 2019). Microbial decomposition may not always proceed at a desirable rate, or effectively eliminate, or reduce hazardous compounds due to unfavorable environmental or physicochemical conditions and sub-optimal levels of proficient microbial degraders (Zhao et al. 2017a; Rastogi et al. 2020). These drawbacks can be countered by strategies such as prior acclimatization (or adaptation) of the microbes to contaminants, i.e. biostimulation (Alegbeleye et al. 2017b; Nikolopoulou et al. 2013; Yang et al. 2019). Oxygen conditions and aeration may be improved by diffused or mechanical aeration, such as in bioreactors (e.g. introducing air via agitation, in the form of bubbles, or through diffusers), or the use of models to determine, forecast, and monitor suitable environmental factors for the elimination of respective compounds in activated sludge systems (Brdjanovic et al. 2015).

Activated sludge systems are designed depending on factors such as the ratio of the microorganisms (or activated sludge) to the substrate (waste) and other characteristics of the waste. In most systems, healthy, active microbial groups/ population that will feed on new, incoming batch of organic compounds is maintained by replenishing the microbe concentration (sludge) that has drained through the tank and settled out in a secondary sedimentation tank and disposing part of the settled material. For domestic sewage, adsorption of most organic compounds by the sludge floc occurs within 15–45 min, although most conventional plants are designed to provide up to 90 min contact time to ensure adequate adsorption by the sludge floc.

The efficaciousness of activated sludge systems for pathogen inactivation or removal varies tremendously. For instance, there is some indication that despite high removal efficiency and rates, parasites can survive the activated sludge process and that the treatment does not completely inactivate them. Parasites are mostly inactivated during secondary sedimentation, where some studies have reported enhanced protozoa settling during secondary sedimentation, although this seems to vary depending on the type of protozoa. Cryptosporidium removal seems to be comparatively poorer and slower, and both primary and secondary sedimentation may be necessary for the removal of helminth eggs. Researchers have detected the presence of helminth eggs of *Ascaris* spp., *Trichuris trichiura*, Hookworm, *Taenia saginata*, *Hymenolepis* spp. and protozoan oocysts of *Giardia* spp., *Cryptosporidium*, and *Entamoeba* spp. in activated sludge effluents (Ben Ayed et al. 2009). Helminth eggs are the infective stage of a variety of intestinal worms and although not all helminths are the same, all known helminth eggs are enclosed in a strong protective membrane that consists of an internal lipoidal shell, an intermediate quitinose layer, and a proteic external shell (Robles et al. 2020). This feature makes them highly resistant to most conventional treatment protocols (Robles et al. 2020). Reported removal percentage may, however, depend on the sampling pattern (i.e. if the effluent samples were collected after aeration and sludge separation, or following activated sludge treatment (after secondary sedimentation).

Though activated sludge effectively improves sanitation and minimizes overall environmental health impacts, drawbacks such as associated complex process design, large land footprint, bad odor emissions, and management of treatment byproducts have over time created the need for advancements (Ferronato and Torretta 2019; Cichowicz and Stelęgowski 2019; Guo et al. 2019). In addition, activated sludge processes generate significant amounts of sewage sludge, which may themselves be heavily contaminated (Cichowicz and Stelęgowski 2019; Al-Gheethi et al. 2018). For example, Iranzo et al. (2018) reported sufficient degradation of pharmaceuticals in wastewaters, but elevated levels of the pharmaceuticals were detected in resultant sewage sludge. Sewage sludge can be managed, but imposes additional financial and logistical costs. Sewage sludge management practices vary depending on the type and properties and includes agricultural land application, land reclamation, land filling, anaerobic digestion, energy recovery through incineration, and so on (Kehrein et al. 2020). In recent times, sewage sludge is to a large extent, not regarded as waste per se, but as a source of organic matter, energy, and nutrients (Lalander et al. 2016; Kehrein et al. 2020). There are several strategies for decontaminating sludge such as composting and anaerobic digestion, while composting eliminates most pathogens, as well as a wide range of environmental pollutants, it does not eradicate all pharmaceuticals.

Although several physicochemical and biological approaches such as the use of biofilters, bioscrubbers, and biotrickling filters have been developed over time to minimize the nuisance of bad odors (Barbusinski et al. 2017), odor emissions from activated sludge processes persist as a public health problem. Part of the problem is that certain challenges such as accumulation of toxic metabolites in the treatment systems, moisture control, short-circuiting of gas, media plugging, and so on have been identified as significant drawbacks in some of the intervention techniques developed (Fan et al. 2020; Wu et al. 2018). Contemporary approaches such as aqueous activated sludge biotechnologies have been proposed for end-of-pipe odor removal or prevention of odor emissions. Although they still need to be more robustly characterized and optimized, they are promising because they offer the benefit of simultaneously treating odor and decontaminating wastewater and because of associated low cost (since they can use existential WWTPs facilities).

20.5.1 Membrane Bioreactors

Membrane bioreactors combine the features of conventional activated sludge processes with membrane separation (microfiltration or ultrafiltration in the range 0.05–0.4 μm) to remediate pollutants (Barak et al. 2020). The retention of biomass within the reactor promotes the growth and action of slow-growing autotrophic bacteria, which in many cases, translates to enhanced nutrient and pollutant removal. In fact, when nutrient removal is a priority, MBRs offer a competitive advantage (Yeo et al. 2015). There are a variety of commercially available membranes for use in membrane bioreactors and the most important characteristics that determine the choice include pore size, source material, and structure (Subtil et al. 2014). Based on structural characterization, membranes are categorized as anisotropic (i.e. consists of a thin layer of membrane supported by a dense layer of porous understructure) and isotropic (homogeneous composition). The hollow fiber membrane bioreactor is the most commonly used type of membrane bioreactor (Gede Wenten et al. 2020). There are two possible cell immobilization modes in membrane bioreactors: cells are either immobilized within the membrane or on the membrane in the form of biofilms, or cells are separated from the bioreaction medium by the membrane and maintained in a separate compartment (Nemati and Webb 2011). Regardless of how the cells are immobilized, one critical advantage of MBRs is that the membrane protects the cells from existent bubble bursting and shear forces, which are detrimental to plant and mammalian cells (Nemati and Webb 2011). Generally, because MBRs prevent direct exposure of microbial cells to toxic compounds, it may be considered the preferred choice in the treatment of certain types of waste streams that contain hazardous agents (Sun et al. 2019). There is also some research indication that MBRs may have comparatively better potential (20–50%) for removing micropollutants and other emerging contaminants (Kumar Singh et al. 2020), partly attributable to lengthier solids retention time, which permits more complete oxidation of pollutants.

With membrane pore sizes of less than 0.1 μm, MBR can mount a barrier to some chlorine resistant pathogens, an indication that it can eliminate a wider range of pathogenic bacteria and viruses (Giorno et al. 2011). Membrane reactors do not require sedimentation and media filtration for suspended solids or mixed liquor separation from treated effluent and the secondary clarifier can be eliminated. This is because aeration, clarification, and filtration are merged into a single unit, which makes the process simpler and enables the use of smaller bioreactors, saving space, and exerting low visual impact. Other advantages include reduced CO_2 footprint, high aeration rates, increased separation efficiency, decreased sludge production, and superior effluent quality compared to conventional activated sludge treatment approaches (Barak et al. 2020). The rate and efficiency of bioremediation in MBRs is hinged on controlling and monitoring operational parameters such as influent pH, organic loads, nitrogen and phosphate levels, and aeration within the bioreactors to ensure optimal conditions for microbial species (Awolusi et al. 2015). Careful selection of microbial species and the carrier material for use is also necessary to ensure high exposure area and provisions of sufficient reaction sites to avoid problems such as limited diffusion or enhanced toxicity (Roccuzzo et al. 2020). The use of MBRs offers simultaneous product separation and bioconversion, usually in form of a concentrated stream and in the last decade, their use for municipal and industrial wastewater treatment has increased. Cost-effective design and operation that has easily built on available technologies makes MBRs more attractive. For example, activated sludge models (ASMs), an important advancement in the modeling and operation of conventional activated sludge processes, though developed for use in activated sludge systems have been easily transferred and applied to MBR processes. Despite these merits however, certain disadvantages such as the need to periodically replace membranes and the need to control membrane fouling have been identified.

20.5.2 Moving Bed Biofilm Reactors (MBBR)

Moving bed bioreactor is a hybrid, advanced wastewater treatment approach that merges the features of attached growth processes/media and suspended growth in a single aerobic tank, utilizing the whole tank volume for biomass growth, which increases biomass quantity within treatment tanks (Ødegaard 2006; Marques et al. 2008). In addition to suspended biomass, attached biomass is usually grown on some specially designed biocarriers that have a high surface area, which is applied for enhanced pollutant removal. It does not require any sludge recycle since the biomass grow on carriers that move freely in the water volume of the reactors (Rusten et al. 2006). These carriers are held within the reactor volume by a sieve system fitted to the outlet of the reactor.

The media is in many cases, fluidized through aeration or by mechanical mixing. The premise is to achieve a continuous operating bioreactor with high surface for biomass growth and minimal head losses. This process has proven efficient for pollutant removal and its comparative (compared to traditional suspended growth systems) minimal footprint makes it particularly attractive (Kumar Singh et al. 2020). In addition, it is easy to retrofit existential aerated treatment processes to an MBBR process by integrating the effluent screens and plastic media into the system (Rusten et al. 2006).

20.5.3 Aerobic Granulation Technology

Aerobic granules are formed when consortia of microorganisms self-immobilize or self-aggregate in the absence of a support carrier (Liu et al. 2003). Aerobic granulation technology is a development on activated sludge technology targeted at improving among other drawbacks, sludge-water separation issues during wastewater bioremediation (Nancharaiah and Sarvajith 2019). It is a promising wastewater treatment approach because the various occurring microbial species can play different specific roles in the treatment of wastewater-associated contaminants (Li et al. 2014). Aerobic granules are regular in shape and have a dense, compact structure, which enhances settling capacity, multi-microbial functions, higher biomass retention, as well as enhanced tolerance to toxicity and shock loading (Li et al. 2020c; Maszenan et al. 2011). So many studies have explored granulation mechanisms, the extracellular polymeric substance matrix (EPS) (i.e. sticky polymers secreted by bacteria consisting of lipids, phospholipids, polysaccharides, proteins, and humic acids, which trigger cell adhesion and formation of aerobic granules), as well as other factors that contribute to the physical and chemical structure of the granules. The factors responsible for the long-term stability of AGS and other related factors that influence the rate and efficiency of wastewater remediation have also been abundantly explored (Franca et al. 2018; Alshabib and Onaizi 2019; El-sayed 2020; Li et al. 2020b; Ogura et al. 2020; Pei et al. 2020; Phong Vo et al. 2020). Granulation is according to some research (Barr et al. 2010) rooted in the formation of biofilms, i.e. aggregation of microbes (similar to that in AS), facilitated by polymeric entanglement, cations, granules shaping, and then densification and possible disintegration. The consensus, however, seems to be that four important stages: (i) intercellular interactions, (ii) microbial attachment and formation of aggregates, (iii) EPS facilitated attachment, and (iv) shaping of granules in anaerobic granulation (Lv et al. 2014) are involved in the formation of dense aggregates (AGS). The approach for AGS cultivation from activated sludge flocs, which involves operating the sequencing batch reactor with anaerobic, aerobic, and short settling phases in the cycle creates optimum growth conditions for slow-growing microbes such as glycogen accumulating organisms (GAOs), polyphosphate accumulating organisms (PAOs), and nitrifying bacteria as dense aggregates (Bengtsson et al. 2018; Wilén et al. 2018). Results of most studies suggest that the predominant microbial groups in AGS are bacteria: (such as *Dechloromonas* spp., *Thauera* sp., *Nitrospira* sp., zoogloea, among many others). There is, however, some research indication that protozoal and fungal filaments play vital roles in the initial stages of granule formulation, contributing to the development of a core for bacterial colonization (Beun et al. 1999; Weber et al. 2007).

Aerobic granulation technology has in the last several years evolved into a robust biotechnological approach that has been used commercially for full-scale industrial and municipal wastewater treatment in different parts of the world such as the UK, Netherlands, Sweden, Brazil, and South Africa (Li et al. 2020c). Several studies have described remediation of persistent hazardous pollutants including phthalates, nitroaromatics, chloroanilines, pharmaceuticals, azo dyes, phenols, organophosphorous compounds, metal chelating agents, and explosives, in AGS reactors (Sarvajith et al. 2018; Zhao et al. 2015; Ramos et al. 2015). Compared to conventional wastewater treatment strategies, aerobic granulation technology is more effective in terms of energy requirements and land use (Sarma and Tay 2017). The process design is also comparatively simpler because aerobic, anaerobic, and anoxic microenvironments are occurring within microbial granules, eliminating the need for separate aerobic and anoxic compartments for efficient biological nitrogen removal (BNR). As a consequence, it is possible to achieve both biological treatment and biomass separation from treated wastewater in a single treatment tank. Also, secondary clarifiers, key for the AS process is not required because of the good settling velocities of granules (Weber et al. 2007). Some other benefits include lower sludge production attributed to peculiar metabolism of the various involved microbial groups and resourceful utilization of excess sludge (Nancharaiah and Sarvajith 2019). Despite its advantages however, certain drawbacks such as the requirement of complex sequencing batch operation modes and the need for post-treatment to satisfy environmental standards have been identified (Liébana et al. 2018). The technique of a popular commercial brand/application (Nereda®) involves a short fill/draw timer over the cycle time ratio (e.g. 15%) of sequencing batch reactors which imposes a stringent flow requirement on its pumping systems, meaning that it can only handle small treatment demands (Zou et al. 2018).

Considering that most large-scale WWTPs are currently running under continuous-flow operation, instead of upgrading WWTPs to SBR systems like Nereda, which is logistically and financially costly, it is more practical to incorporate aerobic granulation technology into existing continuous-flow operations (Kent et al. 2018). Requirements for cultivating microorganisms in continuous-flow reactors differ significantly from that in SBRs. There are typically low substrate concentrations in CFRs due to constant substrate consumption by microorganisms. Cultivation and utilization of aerobic granulation in CFRs are thus unstable and challenging (Kent et al. 2018; Li et al. 2020c). To mitigate some of these limitations, studies have explored strategies such as the application of selective pressure into CFRs by modifying the configuration to stimulate the growth of slow-growing bacteria (Devlin and Oleszkiewicz 2018; Zou et al. 2018; Li et al. 2020c). Incorporation/implementation of AGS technology into WWTPs for full-scale, routine use requires that certain operational parameters be optimized. Bioreactor conditions such as anaerobic feeding, feast farming regime, and short settling periods select for slow-growing bacteria that have unique metabolic traits and favor granulation (Li et al. 2020c). The maintenance of granular stability is contingent on optimization of anaerobic feeding and sludge removal strategies. In addition, it is important to further explore molecular aspects of granulation. Over time, studies have developed approaches for improved cultivation of aerobic granules. Recently, Li et al. (2020c) developed a reactor to cultivate aerobic granules under continuous-flow and identified key features and operation conditions for sludge granulation and nitrogen removal during municipal wastewater treatment. In addition to reactor configuration, the study found that dynamic feeding pattern enhanced nitrogen removal performance and nutrient removal in AGS.

20.5.4 Hybrid Technologies

Biological treatment approaches, though widely acknowledged as cheap and effective can be disadvantageous in that they are slow, they generate large amounts of sludge and in some cases, unpleasant odor (Gogate et al. 2020; Brillas 2020). In addition, direct biological treatment technologies are for the most part, suitable for the degradation of biodegradable organic pollutants only (Wang et al. 2014; Changotra et al. 2020). Many times, however, wastewater may contain a significant amount of non-biodegradable, recalcitrant compounds and there is good research evidence indicating that biological treatment may be more effective and faster when combined with other techniques such as physical, chemical, or other biological approaches (Changotra et al. 2019a; Paździor et al. 2019; Rahimi et al. 2020; Bhanot et al. 2020). Examples of pretreatment, auxiliary, or sequential approaches include those based on hydrodynamic cavitation, H_2O_2, Fenton, ozone, and other chemical oxidation approaches (Gogate et al. 2020). Of the several possible combination of technologies, advanced oxidation processes (AOPs) and biological treatment is according to several recent studies particularly promising (Ganzenko et al. 2014; Thanekar et al. 2020; Popat et al. 2019; Paździor et al. 2019). Some advanced oxidation processes such as Fenton processes offer the dual advantage of coagulation and oxidation, while more contemporary processes such as electro-Fenton aid the rapid and effective degradation of recalcitrant pollutants (Nidheesh et al. 2018). Some laboratory and field scale studies have designed dual or multi-phased chemical/biological treatment schemes for the treatment of wastewaters. For example, Changotra et al. (2019b) applied phenton (dark, solar driven photo and electro) as pretreatment for biological treatment of pharmaceutical wastewaters. These processes significantly reduced the organic load of wastewater, enhanced the BOD/COD ratio, improved biocompatibility for subsequent biological degradation, and the overall biodegradability. The study indicated that of the three applied pretreatment technologies, photofenton was the most efficient and was not toxic to the microorganisms in the biological treatment setup. A recent study by Gogate et al. (2020) corroborated these findings reporting that the application of an ultrasonic pretreatment significantly reduced biodegradation time (36 h compared to 60 h of biological oxidation without pretreatment). The pretreatment also significantly enhanced the biodegradability index. Another recent study by Ceretta et al. (2020) coupled biological and photocatalytic treatment for decontaminating textile wastewaters. The study applied bacterial treatment first and then subsequently used photocatalytic process (ZnO/polypyrrole) and reported improved decolorization efficiency and bioremediation rates.

Some researchers have proposed integrating aerobic granular technology with membrane bioreactors for wastewater remediation (Liébana et al. 2018). This combination would yield a hybrid system known as aerobic granular sludge membrane bioreactors (AGMBRs), where the aerobic granules constitute the biomass and the water is treated via filtration (Liébana et al. 2018). Already, research has shown that utilizing granular sludge in MBRs reduced fouling likely because granular sludge has a more compact structure, higher density, as well as larger particle size compared to floccular sludge (Liébana et al. 2018). Also, the use of membranes for the separation of aerobic granules from the treated water (depending on membrane pore size) would yield high-quality effluents. In a full-scale WWTP, AGMBRs would be advantageous since it would guarantee high-quality effluent, with associated advantages including low-permeability loss, minimal space requirements, and less fouling. Some challenges such as maintaining granular stability in AGMBRs is a limitation for the technology (Li et al. 2005; Vijayalayan et al. 2014; Liébana et al. 2018).

Although hybrid processes where systems or treatment protocols are integrated and methods applied sequentially or consecutively seem promising, certain drawbacks persist. For example, AOPs are quite expensive and are inefficient in terms of energy use and sludge production. Overall, integrated treatment approaches seem promising, and it is important to optimize operational parameters that can achieve maximum degradation of organic and inorganic components of wastewaters without exerting any tangible human or ecological health impacts. It is crucial to determine the most suitable treatment sequence(s) and design standard methods for the characterization and management of byproducts.

20.6 Microbial Groups Used for Bioremediation

The rate, efficiency, and overall success of wastewater bioremediation depend to a great extent on the microbial communities in the system (Barak et al. 2020). The potential of using microorganisms: bacteria, fungi, yeasts, and algae to remediate wastewaters has been abundantly explored (Dellamatrice et al. 2017; Roccuzzo et al. 2020); and it has been determined that some microorganisms have the capacity to metabolize/mineralize toxic compounds into CO_2, methane, and other simpler compounds, while others contribute to decolorizing wastewaters (Forgacs et al. 2004; Spolaore et al. 2006). Several studies have attempted to elucidate the major microbial groups that catalyze the different processes in wastewater bioremediation streams or reactors (Costa and Duarte 2005; Maintinguer et al. 2013). This is critical, as it forms an important basis for improving overall process efficiency. Bioreactors and other biological wastewater treatment systems typically contain a tremendously complex and diverse microbial community (Valentín-Vargas et al. 2012; Show et al. 2020; Zhang et al. 2020). The advent, advancement, and increased accessibility of molecular identification and characterization methodologies have greatly enabled our understanding of these microbial degraders (Czaplicki and Gunsch 2016; Malla et al. 2018). The microbial groups required to catalyze the bioremediation pathways, processes, and dynamics depend on whether or not the bioremediation process is aerobic or anaerobic (Juwarkar et al. 2010; Azubuike et al. 2016; Alegbeleye et al. 2017a). Where oxygen is the electron acceptor (aerobic bioremediation), aerobic microorganisms including members of the bacterial phyla Proteobacteria, Firmicutes (which include nitrogen-fixing and denitrifying bacteria), and Bacteroides are some of the most predominant bacterial groups associated with degrading or stabilizing wastewater-associated pollutants (Maintinguer et al. 2013; Zhao et al. 2017b). Some popular decomposing bacterial Genera include Pseudomonas, Bacillus, Rhodococcus, Sphingomonas, Burkholderia, and Mycobacterium (Alegbeleye et al. 2017a; Li et al. 2020a). Members of the pathogenic species Enterobacteriaceae and Enterococcus have been found predominant in some surveys, but their use for bioremediation is not recommended due to their potential health relevance (Robinson et al. 2010; Alegbeleye et al. 2017a; Drzewiecka 2016). Anaerobic bioremediation, however, is triggered and progresses through reducing electron acceptors and specific heterotrophic microorganisms. Notable anaerobic metabolic processes that contribute to biodegradation include fermentation, nitrates respiration (including denitrification), and methanogenesis. Examples of studies that have demonstrated the potential for bacterial species to improve the chemical and microbiological quality of industrial, agricultural, and domestic wastewaters abound in the literature. Paisio et al. (2014) reported that *Acinetobacter* sp. and *Rhodococcus* sp. degraded up to 1000 mg/L of tannery and chemical industry associated 2-methoxyphenol, as well as 4-chlorophenol, 2,4-dichlorophenol, and pentachlorophenol efficiently. In addition, after 7 days of treatment, BOD and COD levels had been significantly reduced. Similarly, Hesnawi et al. (2014) used *Pseudomonas aeruginosa* and *Bacillus subtilis* for the bioremediation of municipal wastewaters.

Fungi can efficiently degrade pollutants occurring in wastewaters via biosorption/bioaccumulation, adsorption, or other intra- and extracellular enzymatic mechanisms (Roccuzzo et al. 2020; Sharma et al. 2020). Their use is advantageous because they purify wastewater satisfactorily, yielding good quality effluent, they are renewable, and they produce commercially valuable biomass that can serve as animal feed, biofuel, and fertilizer (Roccuzzo et al. 2020). Examples of proficient fungal degraders are *Aspergillus ochraceus, Scedosporium apiospermum, Aspergillus fumigatus, Aspergillus niger, Aspergillus versicolor, A. terreus, A. cylindrospora Penicillium purpurogenum,* among many others (Martínez-Gallardo et al. 2020; Sharma et al. 2020).

Although several proficient and potential pollutant-degrading microorganisms have been identified and characterized, a significant percentage of possible degraders remain unexplored. Despite advances in microbial detection, identification, and characterization, several biotechnologically relevant microbial groups remain unidentified and unexploited. Certain studies have indicated that NDDs (i.e. degradation augmenting or assistant strains) can play significant roles in in situ biodegradation and their roles or potential in replenishing contaminated sites should be further explored (Li et al. 2020a). A number of contemporary techniques are used to determine metabolic responses and identify functionality of predominant/active microorganisms in their natural environments. An example is the DNA-stable-isotope-probing (DNA-SIP) technique, a cultivation-independent approach that can be used to identify microorganisms involved in the in situ degradation of contaminants including direct and non-direct degraders in complex microbial communities (Li et al. 2020a). While these approaches are not yet scaled up for real time environmental applications, there is some recent research indicating that the so-called non-direct degraders may play critical roles in bioremediation of compounds such as biphenyl in wastewaters.

20.6.1 Microalgae

Microalgae are a group of eukaryotic or prokaryotic photosynthetic microorganisms that grow in marine and freshwater systems and even wastewater (Khan et al. 2018). Although their photosynthetic mechanism is similar to that of higher plants, microalgae's systematics is based on the type and combinations of photosynthetic pigments occurring in the different species (Moejes et al. 2017; Khan et al. 2018). Most species are, however, capable of capturing solar energy up to 10–15 times better than terrestrial plants (Mondal et al. 2017). They have a simple cellular structure, a large surface to volume body ratio, which enables nutrient uptake and comparatively high growth rates, an indication of efficient CO_2 fixation and high biomass productivity (Singh and Ahluwalia 2013). Additionally, few species can tolerate extreme environmental conditions such as high salinity.

Studies have demonstrated the potential for microalgae to phytoremediate industrial wastes such as dyes, metals, nutrients, and other toxicants in industrial wastewaters (Singh et al. 2016; Fazal et al. 2018). There is also some indication that the cultured microalgae may serve as feedstock for biodiesel production, a potentially sustainable strategy for energy generation, although that is a different subject matter and is not within the scope of this chapter. Microalgae can be cultivated in the wastewaters, which may utilize salts, nutrients, metals, and dyes (depending on the kind of wastewater) as carbon sources for growth and proliferation (Renuka et al. 2015). Some pollutants such as dyes may also adsorb onto the surface structure of microalgae, which has a large surface area and strong binding affinity for some contaminants such as azo dyes and metals, thus acting as a biosorbent (Pathak et al. 2015). Utilization of wastes as a carbon source and biosorption/bioaccumulation may according to some studies occur simultaneously, potentially accelerating the rate and efficiency of bioremediation. Examples of microalgae species capable of pollutant or nutrient biodegradation include *Chlorella vulgaris*, *Chlorella pyrenoidosa*, and *Oscillatoria tenuis* (Forgacs et al. 2004). For example, Chlorella alga isolated by Cheriaa et al. (2009) degraded textile dyes indigo, remazol brilliant orange, crystal violet, and direct blue. Studies have reported that microalgae–microalgae and/or bacteria–microalgae mixed populations are more efficient than individual microbial strains for neutralizing nutrients and biodegradation of pollutants (Xiong et al. 2018; Roccuzzo et al. 2020). Microalgal–bacterial symbiotic consortia are potentially more sustainable since microalgae can via photosynthesis, provide oxygen for aerobic bacteria while utilizing CO_2 released from bacterial respiration. This improves aeration in the system and can potentially reduce high electricity inputs for aeration (Roccuzzo et al. 2020).

20.7 Conclusions

As agricultural and industrial activities continue to increase, it can be expected that wastewaters will continue to be generated. The handling, management, and disposal or recycling of wastewaters is an important issue, globally due to the potential public health impacts of poor management. As highlighted in this chapter and several other studies and summaries, wastewater-associated pollutants including human pathogens, endocrine disrupters, and potential carcinogens may enter into terrestrial and aquatic ecosystems, human food chains, and reach humans. Effective and readily accessible treatment technologies are required for the decontamination of wastes prior to reuse or disposal to minimize potential human health and ecological impacts. Bioremediation is widely regarded as a sustainable treatment strategy, as it is a relatively safe and effective treatment approach that degrades toxic wastes into less hazardous compounds. Some of the mechanisms, dynamics and microbial groups and processes, relevant technologies including conventional activated sludge, membrane bioreactors, and aerobic granulation technology have been summarized in this chapter. Despite significant strides, some gaps, which can further improve optimized strategies and contribute meaningfully to protection of public health have been highlighted.

20.8 Future Perspectives

Although wastewater treatment has advanced significantly over time, particularly in response to increasingly more stringent water conservation and public health requirements, there are still some research gaps.

Optimization of critical parameters such as most suitable microbial species, culturing and harvesting requirements/approaches, dynamics, suitable reactors, and other process parameters is necessary. Microorganisms and their potential for biodegradation vary substantially. Some microbes have more versatile biodegradative potential and are thus, more promising biotechnological tools for degradation of wastes. Probably more critical is that of the microbial groups with known biodegradative potential, some groups are more suitable for some types of wastewaters. Wastewaters vary in type and characteristics and some may offer unbalanced nutrient profiles for certain groups of microorganisms. Some pollutants may also be inhibitors to the growth and proliferation of some groups of microorganisms. Adaptability to physicochemical and environmental changes also varies among different types of microbes. It is important to characterize process inhibitors; for example, microbes present in sludge may be unable to degrade the organic compounds in wastewater. Considering that the generation and accumulation of toxic byproducts have been shown to contribute to bacteria die-off and halt or slow down the remediation process, it is important that the generation of metabolites as bioremediation progresses be better characterized and modulated, if need be.

The behavior of pollutants (e.g. their susceptibility to treatment, their persistence potential, their potential for environmental partitioning, their ability to biomagnify along the food chain, their potential non-human hosts, human infection mechanisms, host response, other environmental behavior) has to be properly understood for better design of bioremediation systems/paradigms. Also, future research should evaluate and compare remediation efficiencies of the various remediation approaches in more realistic settings.

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Occurrence and Attenuation of Antibiotics in Water Using Biomass-Derived Materials

21

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Abstract

Annually, large quantities of pharmaceuticals are consumed globally. The presence of pharmaceutical compounds in water bodies is concerning because these compounds are recalcitrant bioaccumulative toxins. Surface water is contaminated by pollutants from storm water overflows, wastewater treatment plants, and run off from non-point sources such as concrete surfaces in urban areas and agricultural land. Depending on the hydrology, antibiotics (Abs) can also permeate into ground water. Among the various pharmaceutical compounds, antibiotics are widely used globally, consequently, water pollution due to Abs has received widespread attention. Because they are weakly absorbed by the human and animal bodies, a significant proportion of Abs are excreted untransformed or as metabolites depending on their physicochemical characteristics. Consequently, a large quantity of Abs enter the aquatic environment directly through aquaculture or effluents from wastewater treatment facilities or landfills. Wastewater treatment plants are not capable of efficiently removing pharmaceuticals in wastewater, thus these pollutants reach the receiving media, which is usually drinking water. In the environment, Abs residues are poorly biodegradable, and can result in antibiotic resistant genes (ARGs) in animals and humans from prolonged exposure at low concentrations. The existence of Abs, antibiotic

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resistant bacteria (ARB), and ARGs in the environment, particularly in wastewater and drinking water and the food chain, is a serious public health concern, and has thus generated significant interest. Antibiotic resistance arising from the intensive usage of Abs compromises their effectiveness in the management of diseases and upsets native microbes in the ecosystem.

Methods that have been used to remove Abs, ARBs, and ARGs from contaminated water include bioreactors, membrane filtration, advanced oxidation processes, and adsorption. Adsorption is an effective method which is simple to operate, with the adsorbent being key to the pollutant removal efficiency. Moreover, numerous studies have used adsorbents produced from readily available biowaste making the method cost effective. One such adsorbent is biochar (BC), which is an environmentally friendly carbon-rich adsorbent with a highly porous structure. Consequently, a number of studies have reported high Abs removal capacities using BC. In this chapter, the removal of Abs from wastewater using BC is explored and compared to other methods. The mechanisms of adsorption, and research gaps were evaluated.

Keywords

Adsorption · Biochar · Emerging pollutants · Microbes

21.1 Introduction

Emerging contaminants represent a new challenge to water quality through potentially severe environmental and human health impacts. Pharmaceutical compounds are emerging contaminants, and their presence in aquatic systems is concerning. A wide range of pharmaceuticals for human and veterinary use are excreted untransformed or as metabolites, and are constantly introduced into aquatic environments (Fekadu et al. 2019). Among the various pharmaceutical compounds, antibiotics (Abs) are a distinct category with selective antimicrobial activity which does not affect cells and tissues (Ahmed et al. 2015; Xiang et al. 2019). Owing to the intensive use of Abs as prescription drugs for humans and animals, their discharge may pollute the aquatic environment and cause ecological harm (Fig. 21.1).

Moreover, Abs are not efficiently removed in wastewater treating plants (WWTPs), as a result, Abs residues have been reported in a range of matrices especially in the water bodies such as drinking water, groundwater, and wastewater (Azanu et al. 2018; Xiang et al. 2019). The situation is compounded by water reuse which is practiced in some communities (Iakovides et al. 2019; Santos et al. 2019). As a result, antibiotic resistance has been reported in many countries around the world (Table 21.1). The discharge of Abs into the aquatic environment occurs via numerous routes such as aquaculture, pharmaceutical production processes, municipal effluent, farmland runoff, hospital effluent, irrigation with water contaminated with Abs, landfills, and inappropriate disposal of unused or expired medicines (Xiang et al. 2019).

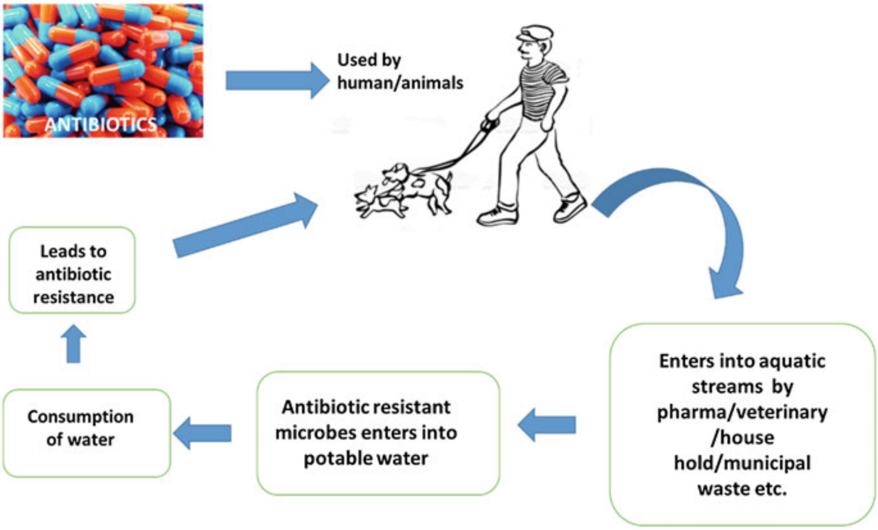

Fig. 21.1 The role of humans and animals in antibiotic resistance development

Table 21.1 Recent studies on the prevalence of antibiotic resistance

Pathogenic organisms	Human health risk	Antibiotic resistant recommended	Country	Observation	References
Acinetobacter spp	Wound infections	Tetracyclines	China	13% ($n = 23$), resistant ESBL isolates reported	Zhang et al. (2016)
Klebsiella pneumoniae	Urinary tract infections	Levofloxacin or ciprofloxacin	Ethiopia	66.6% ($n = 6$) resistant isolates reported	Abera et al. (2016)
Salmonella	Enteric fever	Levofloxacin	India	100% ($n = 36$) resistant isolates reported	Kumar et al. (2013)
Escherichia Coli	Urinary tract infections	Cotrimoxazole	China	25.5% ($n = 99$) isolates were resistant	Chen (2018)

The effects of Abs exposure to animals and humans are varied. Several studies revealed that prolonged exposure to Abs even at relatively low concentrations (μg/L-mg/L) may significantly influence the body weight and growth of biota (Xiang et al. 2019). Other adverse impacts include inducing antibiotic resistant bacteria (ARB) and antibiotic resistant genes (ARGs) owing to: (1) sub-inhibitive Abs concentrations in wastewater, (2) horizontal transfer of ARGs to Ab sensitive microbials, and (3) endocrine disruptive and other harmful ecotoxicological effects (Fekadu et al. 2019; Stange et al. 2019). As a result, the existence of ARB and ARGs in aquatic systems has become the major concern due to their ecotoxicity. Previous studies reported that ARB could be transmitted to consumers from livestock through meat and milk products, causing infections and other adverse effects in humans. Generally, exposure to high concentrations of Abs can compromise the immune system, while some Abs are carcinogenic, mutagenic, teratogenic, and may even inhibit hormonal functions (Sanganyado and Gwenzi 2019; Xiang et al. 2019).

Current WWTPs are designed for removing pollutants such as suspended solids, nutrients, organic matter, and, to some extent, pathogens. They cannot, however, efficiently remove Abs, ARB, and ARGs (Stange et al. 2019). While chlorination, UV radiation, and ozonation as tertiary wastewater treatment methods can effectively remove bacteria, their capacity to remove Abs, ARBs, and ARGs is limited. Thus, ARGs can be potentially transferred to pathogenic microorganisms in the environment following the emission of treated effluent into freshwater or seawater environments. In this regard, effective and sustainable treatment technologies are needed (Stange et al. 2019). A number of methods to remove Abs have been investigated. These include biological processes, filtration, advanced oxidation processes, chlorination, ozonation, adsorption, membrane processes, and a combination of these (Jiang et al. 2018). Among these methods, adsorption is a commonly used method because it is efficient, simple, environmentally friendly, sensitive, cost effective, and easy to scale-up (Chaukura et al. 2016). Moreover, it does not generate secondary pollution. Consequently, adsorption processes have been used for the removal of organics from contaminated streams.

The characteristics of adsorbate, adsorbent, and the chemical composition of the wastewater influence the adsorption efficiency (Xiang et al. 2019). Adsorption using carbon nanostructured materials is a promising and thus commonly used method for removing low pharmaceutical concentrations in aquatic systems (Rostamian and Behnejad 2017; Sarker et al. 2019). One such material is biochar (BC), a carbonaceous material fabricated via biomass pyrolysis under an oxygen-depleted environment. The adsorptive performance of BC is due to its superior physicochemical characteristics such as functional groups, high surface area, high porosity, and surface charge (Teixeira et al. 2019). Although the surface of BC is largely hydrophobic, it also has a variety of polar functional groups from heteroatoms such as O, N, and S. The nature of these functional groups is influenced by the activation conditions and determines the acidity of the surface and, subsequently, to interactions with pollutants. In addition to the properties of BC, the capacity to sorb organics is influenced by the ion strength, pH, and temperature of the aqueous system, along with the properties of the pollutant. The surface charge of BC and the speciation of pollutants are dependent on solution pH, and this subsequently affects hydrophobicity and solubility properties (Teixeira et al. 2019). The physicochemical characteristics of BC, in turn, are influenced by the type of precursor material, and the pyrolysis conditions such as pyrolysis temperature, contact time, heating rate, and reactor design. The feedstock for BC is primarily derived from biowastes such as agrowaste, industrial and municipal solid waste (Jiang et al. 2018). Owing to these properties, BC has found application in the sequestration of Abs in aquatic systems.

21.2 The Occurrence of Antibiotics in Aquatic Systems

The manufacture and consumption of Abs for the prevention and management of bacterial infections in animals and humans have increased. The release of Abs into the environment occurs through a number of pathways including effluents from households, medical practices, agricultural activities, sewage, surface runoff and pharmaceutical industry effluents, and inappropriate disposal of unused or expired medicines (Adegoke et al. 2018; Dires et al. 2018; Anjali and Shanthakumar 2019; Hou et al. 2019; Xiang et al. 2019). In dairy farming, for instance, Abs are generally used to treat a range of diseases and as growth agents to quicken food production and improve the quality of products. A small fraction of the consumed Abs is metabolized while the rest is excreted with little transformation (Cha and Carlson 2019). Thus effluents emanating from animal husbandry activities are a key source of Abs in the environment (Alsager et al. 2018). High concentrations of Abs, ARBs, and ARGs in aquatic systems can be traced back to anthropogenic activities such as the discharge of Abs in wastewater (Huang et al. 2019b). Due to the large disease burden, the quantity of Abs prescribed in low-income countries is increasing, and drug abuse in the developed world contributes to the prevalence of Abs, ARBs, and ARGs in the aquatic environment (Adegoke et al. 2018). Moreover, the release of wastewater contaminants into the environment with little or no treatment is commonly practiced in low-income countries, thus contaminating water bodies (Dires et al. 2018). Although WWTPs are key in reducing and removing Abs, they also act as hot-spots for the accumulation and propagation of Abs, ARBs, and ARGs from a variety of sources (Hu et al. 2019). This way, they enhance the proliferation of ARBs by facilitating the horizontal gene transfer via conjugation, transduction, and transformation, enabling the Abs resistance to spread rapidly to hosts such as animals and humans (Dires et al. 2018; Hu et al. 2019; Huang et al. 2019a; Ma et al. 2019).

Previous studies have predicted the uptake of Abs by crops, and their subsequent entry into the food chain (Azanu et al. 2018). Toxicity in crops can arise when they are irrigated with polluted water, and the cultivars may uptake Abs in the irrigation water. Some of the effects of Abs, ARBs, and ARGs on plants include the inhibition of root elongation (Adegoke et al. 2018). Generally, exposure to Abs may retard growth and reduce the body weight of aquatic organisms (Ahmed et al. 2015). Antibiotics such as fluoroquinolones and sulfonamides interfere with the nitrogen cycle in the environment, resulting in an accumulation of nitrogen, and causing toxicity to living organisms (Larsson et al. 2018).

On transmission into pathogenic bacteria, ARGs express in harmful pathogens which will compromise the efficacy to treat bacterial infections and threaten human health (Dires et al. 2018; Hu et al. 2018). Antibiotics bioaccumulate in living organisms and up the food chain where it causes feminization of male fish, reducing the reproduction process (Anjali and Shanthakumar 2019).

21.3 Removal Strategies of Antibiotics

Residues of Abs have to be removed before discharging wastewater into the environment, but this is usually expensive (Ahmed et al. 2015). Several methods have been used to remove Abs, ARB, and ARGs from wastewater. These include absorption, biodegradation, coagulation, flocculation, sedimentation, membrane processes, and advanced oxidation processes (AOPs) (Pirsaheb et al. 2019; Hiller et al. 2019). However, physical methods like coagulation, flocculation, filtration, and sedimentation are ineffective since they only transfer contaminants from one medium to another requiring follow-up treatment (Alsager et al. 2018). Moreover, membrane technologies such as advanced microfiltration combined with reverse osmosis and UV irradiation cannot adequately remove Abs from wastewater (Alsager et al. 2018).

Conventional WWTPs do not efficiently remove Abs, resulting in the persistence of the pollutants in drinking water sources (Adegoke et al. 2018). While chemical disinfectants destroy pathogens through oxidative impairment of the cell wall, UV radiation can penetrate the water and deactivate pathogens. The antimicrobial effect of UV radiation is however limited to the region in close proximity to the radiation source, and the presence of suspended solids and dissolved organic matter in the water increases the chances of survival of pathogens (Stange et al. 2019).

AOPs have great promise owing to the complete mineralization and non-selectivity for treating a variety of organic pollutants (Kang et al. 2016; Anjali and Shanthakumar 2019). The efficiency of a variety of AOPs in removing Abs, ARGs, and inactivate ARB in wastewater have been widely studied (Iakovides et al. 2019). The major limitation of AOPs is that the generation of radicals requires combinations of reagents, use of toxic elements, or use of secondary sources of energy such as electricity or radiation (Alsager et al. 2018). However, AOPs have become an emerging and promising technique for removing Abs in contaminated water. The AOP techniques include UV irradiation, ozonation, Fenton reactions, persulfate oxidation, and various combinations of these.

Ultraviolet light is commonly integrated into tertiary treatment in WWTPs. However, bacterial regrowth in the distribution system may interfere with the original bacterial culture or encourage the persistence of ARB. Furthermore, previous studies have reported the inefficiency of UV in removing Abs from aqueous media. To circumvent this, catalysts in combination with oxidants such as H_2O_2, $Fe^{2+/3+}$, and TiO_2 have been included to improve removal performance (Saitoha and Shibayama 2016). These technologies constitute AOPs. Due to the environmental friendliness compared to Hg-based lamps, more efficient light conversion, irradiance adjusting capabilities, and a long life span, UV light emitting diodes have attracted significant attention in water treatment. The almost instantaneous switching of the sources of radiation mean pulsed light can now be used in water treatment (Biancullo et al. 2019).

Recently, ozonation has gained wide usage in the treatment of wastewater to enhance pollutant degradation (Anjali and Shanthakumar 2019). It is a strong oxidant that reacts selectively with organic pollutants by directly reacting with molecular ozone, or via an indirect pathway with hydroxyl radical species in alkaline media, which result from the degradation of ozone in aqueous solution. Ozonation can oxidize a range of Abs and inactivate pathogens in water (Alsager et al. 2018; Iakovides et al. 2019; Sanganyado and Gwenzi 2019). The benefits of ozonation include being less energy intensive and ability to achieve high water recovery with minimal waste generation. It, however, has the potential disadvantage of high implementation cost (Anjali and Shanthakumar 2019).

The Fenton reaction depends on the generation of reactive oxygen species (ROS), and is effective for the oxidative treatment of Abs (Kang et al. 2016). In the homogeneous Fenton process, stoichiometric Fe^{2+} and H_2O_2 are used to produce ROS, while heterogeneous systems use iron bearing minerals, iron oxy-hydroxides, or a variety of iron immobilized matrices. Heterogeneous systems have the advantage of limited sludge formation, no ion leaching, operation at circum-neutral pH, and easy catalyst recovery (Kang et al. 2016; Kamagate et al. 2018).

Persulfate oxidation is an emerging AOP with good oxidant stability and strong oxidizing capacity. When subjected to heating, UV radiation, transition metal, or ultrasound, $S_2O_8{}^{2-}$ can be activated to form $SO_4{}^{\bullet-}$, a reactive radical that can attack and degrade Abs (Peng et al. 2019). Consequently, persulfate oxidation has been used to degrade organics in contaminated environmental media.

While AOPs can effectively remove Abs from polluted water, intermediate degradation byproducts can potentially result in secondary pollution of the water. Moreover, AOP methods are expensive and most are still on laboratory scale with limited field application data. In view of these challenges, there is need for alternative low-cost and efficient treatment methods.

21.4 Biomass-Derived Removal Materials

Apart from AOPs, adsorption is the most efficient technology for the removal of Abs from polluted aquatic environments. Adsorption, as a method for the removal of Abs from aquatic systems, is well established, more cost effective, ecofriendly, and more efficient compared to other methods (Chaukura et al. 2016; Guo et al. 2019). However, large-scale application of adsorption is limited by the challenge associated with separating and recovering spent adsorbents from the treated water (Li et al. 2017). A number of adsorbents for Abs removal have been studied. These include raw biomass activated carbon, activated hydrochars, BC, carbon nanotubes, graphene-based materials, metal oxides, porous silica, and organic carbon frameworks (Guo et al. 2019; Liu et al. 2019; Mourid et al. 2019; Peng et al. 2019).

21.4.1 Raw Biomass

Low-cost adsorbents can be fabricated from readily available and abundant feedstock including biowastes from forestry, timber processing, fermentation processes, crop residues, and aquatic weeds (Gwenzi et al. 2015). Aquatic plants such as water hyacinth and algae show rapid growth in nutrient-laden tropical aquatic systems posing significant ecological and public health risks (Gwenzi et al. 2014). Other biomaterials include animal waste and microorganisms which can also be used as biosorbents. Several studies have reported the ability of both live and dead biomass for removal of organic contaminants. The commonly reported live biomass types are bacteria, fungi. and yeast, of which species of the genera *Aspergillus*, *Candida,* and S*accharomyces*, among others have a high sorption capacity for organics. A kind of ectomycorrhizal fungi, *Gomphidius viscidus*, was reported in the phytoremediation of anthracene in soil (Huang et al. 2010). The biosorbent acts as a linker between the plant and the soil. This biosorption process involves several metabolism-independent routes, including physisorption and chemisorption, chelation, and microprecipitation in the cell wall (Aksu 2005). High adsorption capacity (105–419 mg/g) for organic dyes has also been reported for *Corynebacterium glutamicum* (Vijayaraghavan and Yun 2007). Biosorptive components in microbial biomass include peptidoglycan carboxyl groups, sulfonated polysaccharides, glycoproteins, and extracellular polymeric substances.

Dead biomass including crop residues, sludge, sawdust, sea shells, chitosan, and poultry feathers with high adsorption affinities for organic compounds has also been explored as alternatives to live biomass. Commonly used dead biomasses include saw dust, sea shells, and agro-wastes including rice husks (Toniazzo et al. 2013), sugarcane bagasse (Noreen and Bhatti 2014), seed portion of *Abelmoschus esculentus* (lady’s finger) (Le et al. 2018), and nonliving alga *Nostoc comminutum* (Gupta et al. 2014). Although most previous studies have focused on organic dyes, it is possible that such biosorbents may also be effective for the removal of Abs. Despite a considerable number of studies reporting high affinity of dead biomass for inorganic pollutants, raw dead biomass often lacks thermal and chemical stability and the desired specificity towards organic contaminants. To overcome these limitations, activated or engineered biosorbents have been developed and tested.

21.4.2 Biochar as a Low-Cost Alternative

Owing to its porosity, large specific surface area, and surface functional groups, commercial activated carbon (AC) has excellent removal capabilities for a variety of pollutants including Abs (Bardalai and Mahanta 2018). However, it is expensive and unaffordable to low-income countries (Xiang et al. 2019). Therefore, a low-cost adsorbent with fast adsorption kinetics and high adsorption capacity is required (Liu et al. 2019; Mourid et al. 2019; Peng et al. 2019). There are reagent and plant costs associated with the preparation processes of the precursor material, from which the total cost of BC (T_c) can be determined Eq. (21.1) (Ahmed et al. 2015):

$$T_c = P_c + R_c + PL_c \tag{21.1}$$

where P_c is the cost of production, R_c is the cost of regenerating spent BC, and PL_c is the cost of process loss.

Usually, the cost of feedstock is low, depending on local abundance. Overall, the cost of BC depends on the local supply of feedstock, the extent of processing, type of reactor used, pyrolysis conditions, the production of value added byproducts, and reusability (Ahmed et al. 2015). In order to keep T_c low, there is need to establish large-scale supply chains for producing high yield feedstock at low cost.

Several studies have used BC to remove Abs from wastewater (Sun et al. 2018; Liu et al. 2019; Xu et al. 2019; Zhao et al. 2019). Biochar can be produced from a range of biowastes under a range of process conditions, such as temperature and heating rate (Gwenzi et al. 2015). The particle size of biomass plays an important role in the structural transformation of the BC during the rearrangement of the solid phase. During the pyrolysis process, the biomass is heated between 300 and 700 °C in a low oxygen environment (Bardalai and Mahanta 2018). The pyrolysis process can be performed using a range of reactors which include the ablative, auger, fluidized-bed, fixed-bed, vacuum pyrolysis, rotating cone, plasma, solar, and screw type reactors. In addition, rotary kilns, drum kilns, pyrolytic cook stoves, and drum pyrolysers have also been used (Bardalai and Mahanta 2018). Other modification methods include hydrothermal synthesis. While pyrolysis involves carbonization of dry biomass under a limited oxygen atmosphere, low-temperature hydrothermal carbonization involves the treatment of a biomass-water mixture at temperatures in the range of 170–300 °C in a pressurized reactor (Fuertes et al. 2010). Various feedstocks can be used in the production of BC (Table 21.2). These include sludge, municipal solid waste, forest residues, agro-processing wastes, and aquatic weeds. Due to the high temperatures of pyrolysis a variety of chemical reactions occur within the biomass resulting in its conversion into a solid residue and gaseous product.

The characteristics of BC are primarily determined by the preparation temperature and biomass. High pyrolysis temperatures often result in high surface area leading to high sorption capacity for pollutants (Bardalai and Mahanta 2018). Biochar derived from different source materials show varying surface area, ash content, electrical conductivity, porosity, and functional groups (Bardalai and Mahanta 2018). The adsorption capacity of BC can therefore be enhanced via structural and chemical modification, which can be effected through various facile activation techniques such as acid/base treatment, amination, biological modification, impregnation with metal salts, microwave treatment, ozone treatment, and plasma treatment, and introduction of functional groups have been used (Xiang et al. 2019). This produces BC with many desirable properties, making it very effective in sequestering Abs (Liu et al. 2019).

Functionalization alters the surface characteristics such as the surface functional groups, charge, and textural properties of BC. Furthermore, acid modification removes inherent inorganic impurities in the BC, providing additional active sites for the binding of pollutants. This also increases the acidity, and changes the pore structure by oxidizing the water molecules in the pores to produce oxygen-carrying moieties. Adsorption efficiency is determined by the surface chemistry of the BC (Roy et al. 2018). While amination introduces amine moieties on BC surface, modification using $KMnO_4$ via the Hummer's method has been used to increase

Table 21.2 Examples of biomass and the properties of biochar

Biomass source	Pyrolysis conditions	Chemical modification %C %H %O			Characteristics pH EC % ash %moisture				References
Paper and pulp sludge	750 °C under N_2 for 2 h	–	–	–	8.5	0.16	36.2	1.4	Narzari et al. (2017)
Corn stem	600 °C at 10 °C/min under N_2 atmosphere for 1 h	–	–	–	8.9	–	–	16.8	Liu et al. (2019)
Pongamia glabra	350 °C under N_2 for 2 h	61.72	2.24	29.65	8.6	0.76	9.1	13.5	Narzari et al. (2017)
Areca catechu tree dust	450 °C under N_2	54.03	42.14	2.90	8.9	–	24.2	0.1	Bardalai and Mahanta (2018)
Maize	500 °C under N_2 for 2 h	–	–	–	10.5	–	–	0.2	Bogusz et al. (2017)

the number of oxygenated groups such as C=O, C-O, COOH, and phenolics on the BC surface (Jiang et al. 2018; Roy et al. 2018; Yanyan et al. 2018). These functional groups enhance the adsorption of pollutants such as Abs.

Because of its excellent adsorptive properties, BC has been used in water treatment to remove a variety of pollutants including Abs from water bodies (Gwenzi et al. 2014). The capacity of BC fabricated from burcucumber (*Sicyos angulatus* L.) to retain sulfamethazine in loamy sand and sandy loam soils has been investigated (Vithanage et al. 2014). The mobility of sulfamethazine was increasingly retarded with increasing proportions of BC, implying the analyte was progressively retained by BC. Yao et al. (2013) demonstrated the effectiveness of BC derived from various wastewater sludges in removing fluoroquinolone Abs from water. In another study, benzo(a)anthracene, β-estradiol, and bisphenol were bioadsorbed onto chitin, which has attractive features due to its unique molecular structure, physicochemical characteristics, and chemical stability (Krupadam et al. 2011). Two chemically activated BCs fabricated under oxygen-rich and oxygen-starved environments were effectively used for the sequestration of sulfamethoxazole (Jung et al. 2013). A summary of the capacities of a range of biomass-derived adsorbents for the sequestration of Abs is shown in Table 21.3.

21.5 Mechanisms of Removal of Abs Using BC

The sorptive interactions between BC and Abs can be physical adsorption, chemisorption, or electrostatic interactions. These molecular-level interactions include electrostatic, hydrogen bonding, hydrophobic, Lewis acid-base, π-π electron donor-acceptor (EDA), π–π interactions, and van der Waals interactions (Fig. 21.2). Surface functionalities such as -COOH, -OH, $-NH_2$ in BC also influence the mechanism and efficacy of adsorption. The primary interaction between BC and Abs is electrostatic interaction, which usually occur in the adsorption of Abs. For example, previous studies reported that electrostatic interactions and hydrophobic attraction were the major sorption mechanisms of fluoroquinolone on BC (Tan et al. 2016; Gwenzi et al. 2018; Jiang et al. 2018). Hydrophobic interactions are mainly responsible for the adsorption of Abs in aqueous systems, culminating in enhanced removal. In another study, the sorption of quinolone onto powdered activated carbon was reported to be mainly due to electrostatic interactions, hydrophobic interactions, and π–π dispersion forces (Xiang et al. 2019).

The primary mechanisms for the adsorption of Abs onto the BC are largely electrostatic interactions, hydrophobic interactions, hydrogen bonding, partitioning into non-carbonized fractions, pore-filling, π–π interactions, and surface precipitation (Tan et al. 2016). Generally, the adsorption process occurs in four stages: (1) the transportation of Abs in the bulk medium, (2) film diffusion of Abs, (3) pore diffusion of Abs, and (4) the interaction between Abs and the BC matrix. Compared to physisorption, these interactions are strong and more specific, and are confined to the monolayer. The surface chemistry of BC plays a key role in the sorption of Abs since BC has heterogeneous surfaces due to the presence of carbonized and

Table 21.3 Antibiotic removal capacities of biomass-derived materials

Adsorbent	Antibiotic	Adsorption capacity /Removal (%)	Remarks	References
Biochar-derived from swine manure digestate	Sulfadimidine and Tylosin	83.76, and 77.34%	Co-adsorption of abs in the presence of arsenic	Jiang et al. (2018)
Metal organic frameworks	Norfloxacin, Ofloxacin, and Enoxacin	408.2, 450.4, and 425.5 mg/g	Electrostatic interaction between charged functional groups key in adsorption mechanism	Guo et al. (2019)
Activated carbon from walnut shells	Metronidazole, Sulfamethoxazole	107.4 mg/g 93.5 mg/g	pH 8 at 30 °C pH 5.5 at 30 °C	Teixeira et al. (2019)
Aerobic granular sludge	Kanamycin Tetracycline Ciprofloxacin Ampicillin Erythromycin	88.4 ± 4.5%	High protein content from tightly bound extracellular polymeric substances facilitated aerobic granulation.	Peng et al. (2019)
Combinations of up-flow Anaerobic sludge bed, anoxic-oxic tank, and advanced oxidation technologies	Tetracyclines, Sulfamethoxazole, and ampicillin enrofloxacin	62.5–80.9% 73.9%	All antibiotics fully eliminated during the 180 d-operation	Hou et al. (2019)
Drinking water treatment processes	Sulfonamides, sulfamethoxazole		The removal efficiency of advanced process for each antibiotic was higher than that of conventional process, except for sulfameter	Hu et al. (2018)
UVC-activated peroxymonosulfate, UVC irradiation, and PMS oxidation	(ARB) HLS-6, intracellular *sul1* and *intI1*	Reduction rates reached up to 2.9 log and 3.4 log	Reduction rates at pH 5 reached up to 3.1 log (*sul1*) and 3.3 log (*intI1*)	Hu et al. (2019)
Ozonation	Ampicillin, azithromycin, erythromycin, clarithromycin, Ofloxacin, Sulfamethoxazole trimethoprim, and tetracycline	Not stated	Efficiency was mainly ozone dose and contact time dependent. Levels below detection limits were achieved with	Iakovides et al. (2019)

			retention time of 40 min and specific ozone dose of 0.125 gO_3 $gDOC^{-1}$	
Biochar-derived from swine manure digestate	As (III), sulfadimidine and tylosin	83.98, 83.76, 77.34%	Mn-BC was observed as the promising adsorbent	Jiang et al. (2018)
Laterite soil	Flumequine	94%	Laterite exhibited no deactivation of surface sites and an excellent catalytic stability	Kamagate et al. (2018)
Membrane bioreactor systems	Amoxicillin, azithromycin, ciprofloxacin, chloramphenicol, Meropenem, minocycline, Oxytetracycline, Sulfamethazine, and Vancomycin	Mean removal efficiency >70%	Membrane bioreactor outperformed conventional activated sludge in the removal of ARB, ARGs and most targeted antibiotics	Le et al. (2018)
Eggshell membrane-derived $MgFe_2O_4$	Doxycycline	308 mg/g	Adsorbent can be reused after magnetic separation from water and acid treatment	Li et al. (2017)
Graphene and graphene-based nanocomposites			Factors affecting absorbance include pH, temperature, dosage of adsorbent and co-existing ions. Photocatalytic degradation affected by contact time, pH, graphene concentration, and light irradiation condition	Li et al. (2019)
3D hierarchical porous-structured biochar aerogel	Phenicol abs	>90%	Highest efficiency reached in 10 min even with high initial antibiotic concentrations	Liu et al. (2019)
Calcined layered double hydroxide	Sulfamethoxazole	93%	Adsorption is governed by physisorption	Mourid et al. (2019)
MIL-101(Cr) (materials Institute Lavoisier-101(Cr)	Sulfadimethoxine, Sulfamonomethoxine, and Sulfachloropyridazine	100 mg/L.	pH 5–7 adsorption reach maximum and decrease with increasing salt concentration. Oxidation capacity	Peng et al. (2019)

(continued)

Table 21.3 (continued)

Adsorbent	Antibiotic	Adsorption capacity /Removal (%)	Remarks	References
			decrease with increase of oxidation times	

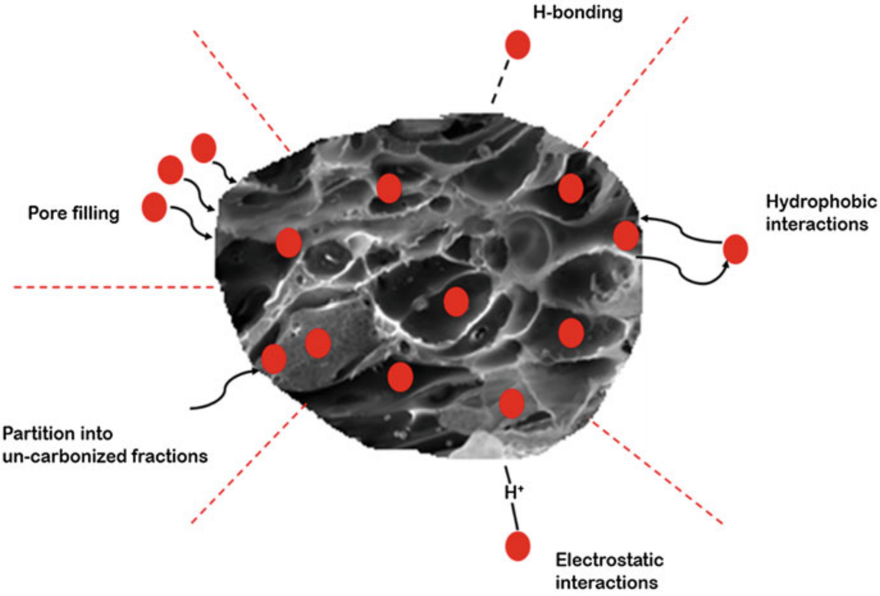

Fig. 21.2 Mechanisms involved in the sorption of Abs on BC

non-carbonized regions, which have different functional groups. For instance, the adsorption of sulfonamides on different BCs depended on the extent of graphitization, indicating π–π EDA interactions between the Abs molecules and the aromatic BC surfaces was the primary mechanism. Similarly, the sorption of sulfamethoxazole on BC under acidic conditions was predominantly through π–π EDA interactions between the protonated aniline rings with the π-electron dense graphitic BC surface, as opposed to cation exchange (Jiang et al. 2018). Under alkaline conditions, the sorption of anionic sulfamethoxazole species enhanced and was regulated by hydrogen bonding. The adsorption kinetics revealed that the predominant sorption mechanism of Abs on BC was chemisorption. The electron density of nitroimidazoles with their aromatic moieties increased π-π Abs-BC dispersion interactions and enhanced their sorption on BC (Ahmed et al. 2015).

21.6 Challenges and Future Outlook

Owing to increasing Abs discovery and usage due to the increasing disease burden, the concentration and variety of Abs, ARB, and ARGs in the aquatic environment are likely to increase. Antibiotics do not only affect aquatic ecosystems, they also compromise the human immune system and inhibit physiological processes. This requires rapid development and up-scaling of removal technologies that will effectively abate these pollutants. A number of promising methods have been explored in this chapter. Of these, the use of biomass-derived materials has been presented as a cost-effective and efficient alternative. Owing to its high porosity and easily modified surface chemistry, BC has great promise in the sequestration of Abs from aquatic systems. With proper modification, the adsorption efficiency of BC can be improved considerably. The properties of BC and the physicochemical characteristics of Abs significantly influence the adsorption processes. Besides, understanding of the interactions between BC and Abs is still lacking. Thus the adsorption mechanisms need further study. Moreover, there is need to study the removal of individual Abs in a multi-component Abs solution, and the influence of competing co-solutes in solution on Abs removal. Use can be made of novel materials, such as nanoparticles, in modifying BC to enhance the Abs removal performance.

Although widely researched on a laboratory scale, the large-scale application of biomass-derived sorbents such as BC is limited by lack of data on reactor design for pilot- and field-scale application. Researchers in various disciplines including chemistry, engineering, environmental sciences, and water engineering need to collaborate to increase the knowledge base and generate unit processes that can be retrofitted and integrated into existing water treatment processes. There is need for state-of-the-art analytical facilities to continuously monitor the concentrations of different Abs in aquatic systems. Another challenge is associated with the disposal of spent adsorbent, which can potentially cause secondary pollution. The cost of the technology can be reduced by establishing large-scale supply chains for producing high yield feedstock at low cost, and using low-cost techniques to regenerate spent BC for multiple reuse. However, at the end of its lifecycle, and with adequate environmental impact assessment, spent BC can be used for such applications as road surfacing and construction (Chaukura et al. 2016). Because of the rich nutrients, other researchers have developed slow-release fertilizers from spent adsorbents (Gwenzi et al. 2018). However, owing to the risk of leaching organics into the soil, spent biomass loaded with organic pollutants will need a thorough characterization before being applied as a fertilizer or any other application.

21.7 Conclusion

This chapter has demonstrated that BC and other biomass-derived materials can be effectively used to remove various Abs from the aquatic environment. Biochar is fabricated through pyrolysis or hydrothermal synthesis of biomass, and the production conditions determine the properties of the resulting product. Adsorption using biomass-derived materials is an attractive technique because: (1) it uses readily available materials, making it cost effective and thus usable even in low-income countries, (2) it effectively removes Abs, (3) it can be regenerated for repeated use, and thus reduce its carbon footprint, and (4) the pollutant-laden material has potential applications as a slow-release fertilizer and soil conditioner. Although experimental studies have been extensively reported, the large-scale use of BC is still lacking. This is mainly because, while there is a lot of data on batch experiments, little data exists on column studies that generate process design parameters for large-scale application.

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Mangrove Forest Pollution and Remediation in the Rhizosphere

22

Ali Ranjbar Jafarabadi, Elham Lashani, and Hamid Moghimi

Abstract

Mangroves are the dominant ecosystems that are lined in transitional regions between the freshwater, seawater, and land around the World, well known for most productive estuarine and marine settings, which support numerous communities and associations, particularly animal and plants. One of the most endangered environments in particular tropical regions is the mangrove ecosystem since these vital ecosystems have an overwhelming role in a productive and complicated food web in the coastal marine environments (subtropical and tropical). At a perturbing and alarming rate, these areas have been swiftly vanishing on the earth since 23% of mangrove ecosystems have been disappeared in the past two decades. These unique natural systems are menaced by both natural (sea-level rise, tropical cyclones, and coastal erosion) and human activities (organic and inorganic pollution, over-harvesting, industrialization, urbanization, aquaculture, and agriculture) factors. Bioremediation is an environment-friendly and efficient technology to *remediat*e organic and inorganic pollutants. In other words, microbial degradation is a potent approach to eliminate organic pollutants from the mangrove areas by uptaking them into the microbial cells and degrading by their active enzymes. This review discusses the vital importance and services and the most threats of mangrove habitats. Also, primary

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organic and inorganic contaminants and the role of the microbial population in mangrove ecosystems for bioremediation have been discussed.

Keywords

Bioremediation · Ecosystem · Hydrocarbons · Mangrove · Metals · Microbes

22.1 Introduction

Mangrove ecosystems are critical coastal ecosystems located in transitional regions between the freshwater, seawater, and land (Barbier et al. 2011). These ecosystems are subject to tidal variations (Ghizelini et al. 2019) in the subtropical and tropical areas of the World (Barbier et al. 2011; Li et al. 2015; Snedaker and Saenger 1993; Viswanathan 2016; Wang et al. 2018) and globally covering approximately 1.7×10^5 km^2 of the coastlines in the World (Li et al. 2015; Snedaker and Saenger 1993; Sandilyan and Kathiresan 2012), it is being reported that 20% of the World's mangrove is located in Indonesia.

Mangrove ecosystems are taxonomically differing groups of tree species in tropical areas. These species have evolved parallel and have developed particular adaptations such as physiological and morphological ones to grow in intertidal settings, like salt regulation strategies and aerial roots (Ellison 2019; Polidoro et al. 2014). Because of intertidal habitat preferences, these ecosystems situate most immensely on low-gradient sedimentary coastlines, among high tide elevations and Mean Sea Level (MSL) (Ellison 2019).

Mangrove construction is specified by "zones" of tree species, in designs that run vertically to the coastline or river margins. Mangrove habitats are also open structures that exchange both matter and energy with offshore coastal ecosystems and upland terrestrial (Ellison 2019). These coastal intertidal wetland forests are composed of different mangrove species that grow with shrub species, submerged bases, and halophytic trees in areas between land and sea interface (Arumugam et al. 2018). Mangrove trees contain relatively 70 vegetation species in 40 genera that are shared characteristics of the sheltered coasts in subtropical and tropical regions (Hamdan et al. 2012; Hogarth 1999). Moreover, it is well documented that fairly 59 mangrove species are wide-spreading global. *Avicennia marina* and *Rhizophora* sp., are cosmopolitan species that are broadly ubiquitous in various coastal habitats like Sri Lanka, Indonesia, India, Australia, Brazil, Eastern Africa, and Persian Gulf (MacFarlane et al. 2003).

22.2 Mangrove Contribution to Ecosystem

The number of contributions these mangrove ecosystems offer to human, plant, and animal populations is undeniable. More importantly, a broad spectrum of ecosystem services profits innumerable human people in different scales from local to regional levels since they are ecologically, environmentally, and economically prominent (Ghizelini et al. 2019; Spalding et al. 2010).

They generally have highly considerable biodiversity and phytoplankton are the prominent flora in the ecosystems that play a part in the primary production, carbon fixation (Gao et al. 2018), and feeds for organisms (especially juveniles and larvae) in mangrove ecosystems directly or indirectly (Alikunhi and Kathiresan 2012; Arumugam et al. 2016; Biswas et al. 2009; Gao et al. 2018). Various studies have confirmed that these unique ecosystems have high biomass of phytoplankton and biodiversity (Aké-Castillo and Vázquez 2008; Al-Hashmi et al. 2013; Arumugam et al. 2016; Aziz et al. 2012; Biswas et al. 2009; Canini et al. 2013; Choudhury et al. 2015; Kannan and Vasantha 1992; Mwashote et al. 2005).

Mangrove ecosystems are very efficient in retaining a broad spectrum of fauna and flora and steading food chains on the coastline (Truong and Do 2018). This coastal area prepares direct economic profits to local communities like charcoal, timber, non-timber forest products, and shellfish/fish (Wang et al. 2018). Also, they provide numerous indirect profits, comprising protecting coastal area (e.g., wave attenuation and controlling coastal erosion), nutrient cycling, water purification, carbon sequestration, research, and education (Wang et al. 2018). Mangrove is also life-support ecosystems in maintaining several aquatic species (Rönnbäck 1999). The mangrove’s vast roots could prepare natural trenches and valuable food source for marine organisms. Also, mangrove roots are a shelter for animals above the seawater (e.g., birds and snakes) (Nagelkerken et al. 2002). Molluscs, particularly mussels and oysters, could utilize the roots of mangrove as a shelter. It is well proved that these highly productive zones are having an overwhelming effect as breeding and nursery grounds for several keys and prominent species (Ingole et al. 2009; Lotfinasabasl et al. 2018). These vegetation are extremely significant to estuarine fisheries due to their role in preparing detritus and organic carbon into the food chain and tree roots that make a habitat for fish and microorganisms such as fungi and bacteria (Holguin et al. 2001).

They also regulate substantial processes like hydrodynamic wave attenuation. In the pond and the mining areas, with a high concentration of metal elements, mangrove also can function as a buffer region (Arumugam et al. 2018), purvey coastal buffer area to protect coastal shelters from the natural calamity (Tamin et al. 2011). These ecosystems have a discernable and overwhelming ecological role in stabilizing and keeping balancing within coastal landforms and marine shelters (Arumugam et al. 2018; Sarika and Chandramohanakumar 2008).

Additionally, the natural food generation in these areas is the highest and essential role that mangroves have in aquaculture. They have a pivotal role in aquaculture due to the natural generation of fry and seeds. Entering shrimp seeds can happen in aquaculture settings naturally or artificially (Rönnbäck 1999). The presence of plankton mostly supports the mangrove food web, microphytobenthos, and detritus (Nagelkerken et al. 2002). A study by Larsson et al. (1994) indicated that mangrove habitat coverage of 25% prepares about 70% of the feed necessity.

Besides, mangroves are regarded as critical ecosystems in reduction programs aimed at declines in nitrogen (N) contamination (Mitsch et al. 2015). Compared to

Table 22.1 The ecological and economic services of mangroves (mean economic value)

Ecosystem service valuations of mangrove ecosystems		The global advantage of ecosystem services	
Average economic value (2007 Int$/ha/yr)		Mangrove ecosystem services	
1. Fisheries (nursery and aquaculture)	17,090	1. Waste treatment	1,62,125
2. Ecotourism and recreation	14,072	2. Habitat/Refugia	17,138
3. Coastal protection	8459	3. Disturbance regulation	5351
4. Pollution abatement	7859	4. Erosion control	3929
5. Food (for wild animals)	1535	5. Recreation	2193
6. Protection from sedimentation	579	6. Water supply	1217
7. Energy resources	306	7. Food production	1111
8.Wood and timber	247	8. Raw materials	358
9. Carbon sequestration	195	9. Genetic resources	311
10. Honey	4.23	10. Climate regulations	65
11. Fodder		11. Nutrient cycling	45
12. Water bioremediation			
13. Protection from salt intrusion			
14. Aesthetic value			
15. Pharmaceuticals			
16. Environmental risk indicators			
Total value per ha (2007 Int$/ha/yr)	50,349	Total value per ha (2007 Int$/ha/yr)	193,843

most terrestrial ecosystems, mangroves sequester more nitrogen per area (Adame et al. 2015; Donato et al. 2011). Mangroves, despite terrestrial woodlands, can store the more substantial part of their nitrogen (Adame and Fry 2016).

Many investigations have tried to evaluate the economic value of mangrove areas services globally (Salem and Mercer 2012; Wang et al. 2018). Table. 22.1 demonstrates a summary of the ecological and economic services and values of these ecosystems (Mukherjee et al. 2014).

22.3 Threats to Mangrove Ecosystem

The degradation of ecosystems is an environmental issue that diminishes the capability of abiotic and biotic compartments of ecosystems. This degradation could occur in invaluable sensitive marine ecosystems, and this degradation is continually accelerating (Jafarabadi et al. 2018a, b; Jafarabadi et al. 2017a, b, c; Jafarabadi et al. 2019a, b, c). Although the mangroves are considered as one of the most menaced tropical ecosystems (Lotfinasabasl et al. 2018), at a perturbing and alarming rate, these areas have been swiftly vanishing on the earth since 23% of these systems have been disappeared in the last 20 years (Giri et al. 2011; Spalding et al. 2010). These ecosystems are persistently perturbed by natural agents, like tropical storms, which can do a great disservice to trees and peat collapse (Kauffman and Cole 2010). The remaining woodlands are under permanent menace from demographic pressure and human activities, like tourism, agriculture, and aquaculture, occurring at or near these woodlands (Duke et al. 2007; Ishtiaque et al. 2016).

Nonetheless, despite its invaluable socio-ecological value, these unique natural systems are menaced by both human activities (i.e., pollution, agriculture) and natural (i.e., coastal erosion, tropical hurricane/cyclones, and sea-level rise) agents (Bhowmik and Cabral 2013; Ishtiaque et al. 2016). Because of the detrimental effects of human activities like aquaculture, globalization, industrialization, and urbanization, the mangrove area has lessened by 30–50% globally across the past few decades (Chen et al. 2009; Feng et al. 2017). These ecosystems have negatively been affected by human activities (i.e., heavy agriculture and wastewater), and these ecosystems biodiversity has altered due to these activities in last years (Gao et al. 2018).

One of the most prominent compartments of mangrove ecosystems is sediment. A significant supply for these areas flexibility to the sea level rise assumptions that are forecasted is mangrove sediment, which depends on the physiographic environments of these ecosystems (Nitto et al. 2014). In mangroves, the sediment supply proceeds from internal and external processes, comprising interactions among both mangrove plants and environments. Moreover, the most variable component of mangrove environments is allochthonous sediment supply, which depends on discrepancies in the current processes operating and geomorphic settings.

22.4 Causes of Mangrove Destruction

The destruction of these ecosystems has been somewhat due to climate change, which increased sea-level, as well as by human activities like shifts of land use for coastal expansion, comprising aquaculture and agriculture activities (Jusoff and Taha 2008). Jayanthi et al. 2018 studied the Sundarbans of West Bengal, mangrove ecosystems of Gujarat, and mangrove forests of Odisha. Their results demonstrated that 8% of mangrove conversion caused by driver's human activities, and the degree of deforestation was lower than that of mangroves grown in India (Jusoff and Taha 2008). In the Sundarbans region, significant mangrove loss occurred mainly due to the inundation of seawater and coastline shifts. Natural factors including changes in rainfall, hypersaline condition, sea-level rise, lack of freshwater supply, sediment supply, and topography played a substantial role than human activities such as agriculture, aquaculture, and deforestation for the general mangrove ecosystems shifts (Jusoff and Taha 2008). Our literature review demonstrated that the main actions, which made deterioration of these vital ecosystems, are as a following (Fig. 22.1).

Detrimental influences have been formerly observed and reported by climate change on these ecosystems (Alongi 2015; Gilman et al. 2008). Elevated salinity (Eslami-Andargoli et al. 2009) has been demonstrated to decrease the growth and generation of mangroves and also augment the vulnerability of them due to the effects of climate change (Ball 2002). Projected results of climate change, like

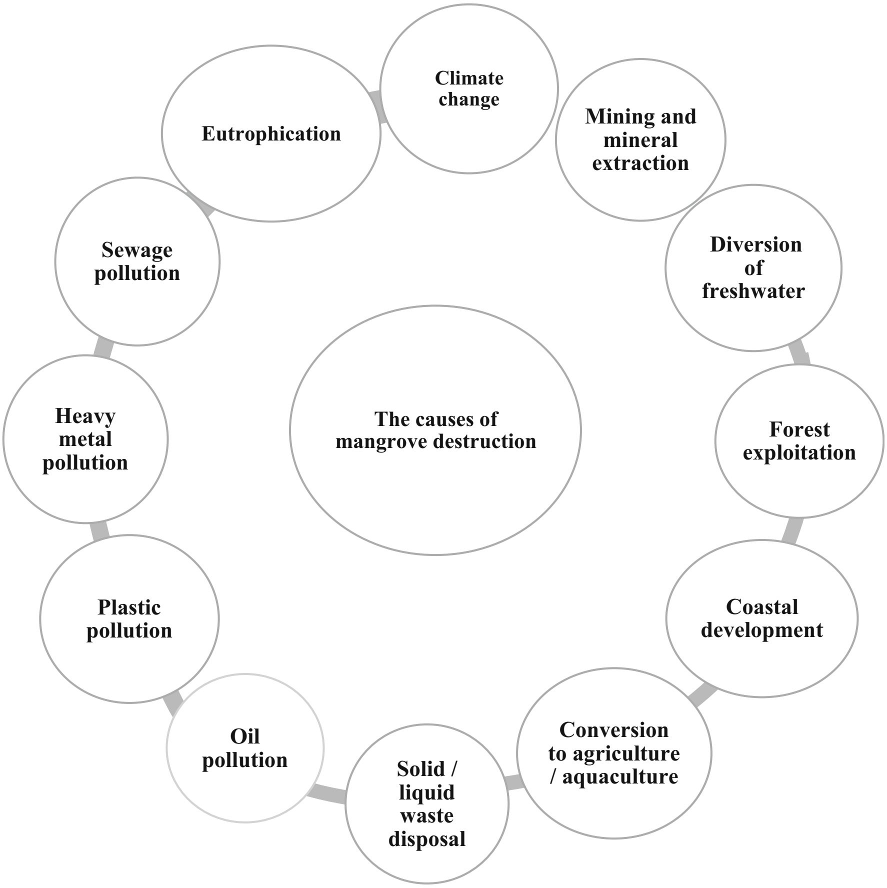

Fig. 22.1 Causes of mangrove forest degradation due to several factors

alterations in increased average temperatures, rainfall patterns, sea-level rise, increased concentration of carbon dioxide, changes in ocean circulation patterns, and increased storm activities formerly seem to have a considerable effect on the growth and expansion of mangroves across the World (Alongi 2015; Galeano et al. 2017; Urrego et al. 2013). Due to a nearby association between rainfall and mangrove habitat situations, any shifts in patterns of rainfall and surface water in watersheds will considerably affect the spatial distribution and growth of these ecosystems. Increasing in the sea level is a chiefly imperceptible menace to these ecosystems, though it is expected to have main effects on the existence of this coastal vegetation in the future (Ellison 2000; Field 1996). Besides, the vulnerability caused by sea-level rise may be exasperated by decision-makers on management decisions like damming on rivers. These choices could decrease external sediment input from fluvial sources like rivers in Vietnam (the Mekong River), in Thailand (Chao Phraya River), and Myanmar (the Ayeyarwady River).

22.4.1 Mining Activities

As the shortage of minerals in industrial sections, there is a parallel augment in mining alluvial mineral sediments. There are rich alluvial sediments of chromium, tin, and other minerals like titanium associated with them in different coastal zone sections. The utilization of ore bodies in the coastline area occurs in different parts of mangrove systems like upstream and downstream. Mining in adjacent regions of mangrove vegetation causes variable destructive effects. In mangrove ecosystems, sedimentation has a remarkable delaying impress in the exchanges of water, gases, and nutrients within the substrate. The loss of mangroves takes place within a period determined in days when this exchange is generally blocked (Saenger 2013) (Fig. 22.2).

22.4.2 Forest Exploitation

Around the World, although domestic fuel and firewood are reducing in supply, the market is swiftly ascending simultaneously. In India and Africa, mangrove vegetation is directly used for firewood. In some mangrove areas, the tree is turned into charcoal for small industrial or domestic usage (Kauffman and Cole 2010). In those areas, the annual regrowth of wood is higher than the annual extraction. In many mangrove regions, the pressure of anthropogenic activities is too much so that the woodlands are swiftly being degraded or are vanishing and more importantly, the extraction far exceeds the annual regrowth (Kauffman and Cole 2010). In some cases, mostly due to the high request for the change to other forms of land use and unsuccessful natural regeneration, exploitation in large-scale has led to a thorough loss of certain regions (Fig. 22.3).

22.4.3 Coastal Development

In high-income countries, a significant problem is a destruction and the exchange of mangrove lands to industrial and domestic expansion. In developing countries, it is beginning to become an issue of consequence. Industry and coastal tourism facilities, like small port development, and housing and residential development, are the most common forms of conversion. Urban, industrial, and airport are the three substantial types of development. Industry and airports are two developments that tend to be nearby to chief population centers (Jusoff and Taha 2008) (Fig. 22.3).

22.4.4 Conversion to Agriculture and Aquaculture

Traditionally, for agricultural and/or aqua cultural generation, coastal woodlands in anaerobic and saline settings have been regarded to be marginal, or inappropriate. Nonetheless, with considerable advancements in cultigen hybridization and

Fig. 22.2 Effects of human activities on mangrove forest destructions (Sources: Little et al. 2018; Dahdouh-Guebas et al. 2005; Duke 2016)

conversion of acidic soils, saline and augmenting demand for arable land, a substantial option for the global rise in agricultural generations is considered the mangrove areas.

Although these ecosystems are broadly recognized for their high economic values, deforestation has dramatically mounted during the last decades; predictions exhibit that if current deforestation rates persist, mangrove coverage will be lost within the next 100 years (Tanner et al. 2019). Deforestation in mangrove lands results in alterations in N and C fluxes to the beach (Lee 2016) and the release of high C quantities (Lovelock et al. 2011). Recovery of these lands can offset these N and C losses (Alongi 2012; Ouyang and Guo 2016).

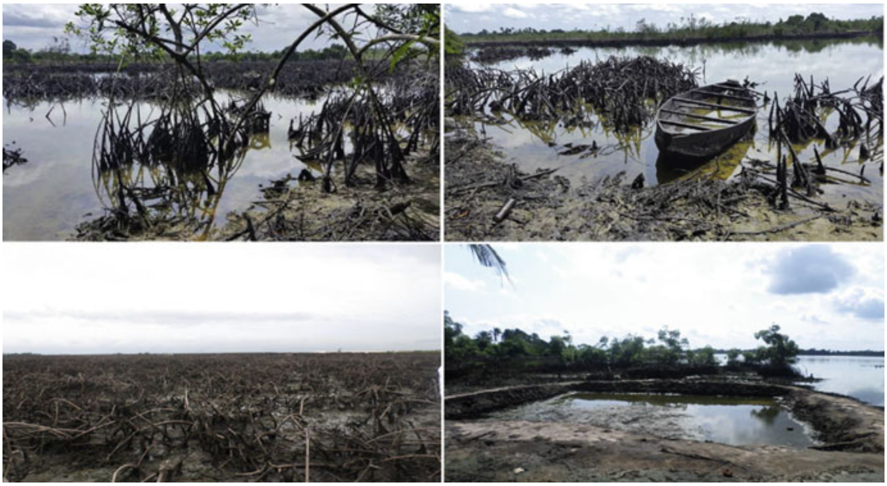

Fig. 22.3 Oil spillage and destructive effects on the mangrove environment (Sources: Onyena and Sam 2020; Sam and Zabbey 2018)

22.4.5 Solid and Liquid Waste Disposal

In the urban areas in most countries, the human populations have been doubled, and it has resulted in a considerable increase in the garbage and solid by three to four times. Additionally, these wastes have been conveyed and discarded where it would not be extremely observable to people. They have been put in the fovea or on flatlands. Much solid waste and garbage refuse have been disposed into these ecosystems. The most significant urban centers in tropical and subtropical regions are placed on estuaries or coasts, and these regions have traditionally been noted as a wasteland. Moreover, disposal of waste so close to waterways has created many unforeseen issues, which can be clearly seen in Fig. 22.2.

22.4.6 Eutrophication

Hypertrophication or eutrophication is a significant and effective factor in coastal areas. When a water body becomes excessively enriched with nutrients and minerals, the excessive growth of algae could happen. This process may lead to deleterious impacts on these forests, comprising oxygen depletion, and mangrove mortality, even killing benthos and fish in the water body (Gao et al. 2018). The swift response to this contamination of coastal areas makes considerable shifts of phytoplankton sensitive bio-indicators in aquatic ecosystems (Sathicq et al. 2017). Manna et al. (2012) studied a tidal creek of Sundarbans estuary, southern Bengal, India. They demonstrated that eutrophication, as well as the existence of toxic Cyanophyceae and Dinoflagellates, has been resulted in deterioration of water quality and consequently menacing the mangrove forests.

As mentioned above, coastal ecosystems, particularly mangrove forests are vital systems and need the supportive efforts of mangrove conservation since it is well reported that these unique trees can apply for phytoremediation for eradication contaminants in the mangrove areas (Moreira et al. 2013).

22.5 Oil Pollutants in the Mangrove Habitats

Impacts of oil spills on shorelines, particularly sensitive habitats such as mangrove are covered in more detail in the International Petroleum Industry Environmental Conservation Association (IPIECA) (Owens and Sykes 2005). Coastal habitats contain plenty of various types of habitats, each of which is characterized by various communities of animals, plants, and microbial associations. Coastal habitats and species will be vulnerable to any coastal oil spill but the scale of the effect and the rate of recovery will be defined mainly by the persistence and condition of the stranded oil, which is itself extremely correlated with wave exposure (Mittal and Singh 2009). Hereupon, effects on coastal habitats such as mangroves are typical could be short/long term since water movement usually removes oil rapidly. However, the natural removal of oil from these habitats is slower. In locations where the intertidal substrate is muddy and dominated by marsh or mangroves, oil residues can persist for years, making long-term effects/impacts (Owens and Sykes 2005).

When the oil is releasing into the environment, such as coastal settings, it becomes subject to some natural processes, known as "weathering," that quickly and progressively shift its character and redistribute much of it into other parts of the environment. The significance of each process on the fate of the oil depends on where the spill occurs, the type of oil, and environmental conditions, such as the chemical and physical (Mittal and Singh 2009; Owens and Sykes 2005). The mechanism and scale of ecological effects are greatly affected by the fate of the oil. Nevertheless, petroleum hydrocarbon contaminants such as PAHs, *n*-alkanes, hopanes, and steranes can be eliminated from the environment via fundamental actions such as natural attenuation, biological, physical, or chemical processes. Hereupon, making a deep understanding of the fate of oil compounds in the ecosystem, particularly these sensitive and productive habitats, is substantially required (Owens and Sykes 2005). When oil spills occur in the environment, several processes happen, such as sedimentation, evaporation, sinking, photo-oxidation, spreading and movement, emulsification, dissolution, dispersion, and biodegradation (Fig. 22.3).

Among coastal ecosystems, rocky coasts have an excellent self-cleaning ability via extremely energetic wave action. Conversely, mangrove habitats are appropriate traps for drifting oil slicks, and this is a fundamental problem of crude oil spillages in mangrove areas. The first is acute and immediate effects. It relates to the physical smothering effect of oil on the plant surfaces responsible for gas exchange (e.g., oxygen and carbon dioxide). It is confirmed that mangrove trees can be killed within 48–72 h via circumstances of a heavy oil spill (Moreira et al. 2013; Souza et al. 2018). The second group of effects pertinent to the long-term chronic poisoning of trees and related fauna by the toxic components of residual oil (Moreira et al. 2013; Souza et al. 2018). Studying petroleum compounds in mangrove environments (biota and abiota) has been recently received more attention because of the toxic effects of oil pollutants. Dadashi et al. (2018) were chosen three sites along with mangrove forests of Iran. Their results demonstrated a main biogenic source of n-alkanes in marginal Qeshm Island stations, which varied from biogenic to petrogenic origins in the Khamir Port areas. In the Khamir Port, sediment samples revealed the significant existence of petroleum pollutants. This investigation indeed indicated that the Hara Protected Area in the Persian Gulf, Iran, was already contaminated by background petroleum contamination as an effect of continuous oil spills and war conflicts in the Persian Gulf.

22.6 Plastic Pollution

Recently, several investigations have been demonstrated that these coastal ecosystems are dramatically vulnerable to natural environmental shifts and anthropogenic perturbations; particularly, micro-plastic contamination. Plastic contamination in the mangrove is receiving great concern. Scientific communities suspect that due to their unique geographical characterizations, the micro-plastic contamination of semi-enclosed seas is considerably discrepant from that of other seaside types. These plastics could be surrounded by pneumatophores and prop roots of mangrove trees. This absorption may lead to a physical barrier affecting the tree itself and the associated fauna through inhibiting exchanging gas and releasing toxic chemicals absorbed by or industrially added to plastic materials (Martin et al. 2019). Moreover, only a few investigations have reported plastic contamination in mangrove areas, which mostly concentrating on micro-plastic in their surrounding sediments (Barasarathi et al. 2014; Lima et al. 2014; Lourenço et al. 2017; Martin et al. 2019; Naji et al. 2017; Nor and Obbard 2014). Recently, many investigations have been directed on micro-plastic in mangrove environments, and the majority of them confirmed that this issue is deteriorating the mangrove environment (both biota and abiota) (Fig. 22.4). Li et al. (2019) studied a typical semi-enclosed sea, the Maowei Sea. Their results demonstrated that the micro-plastic abundances at the oceanic entrance zones were much higher than those of the river estuaries (between 520 ± 8 and 940 ± 17 items/kg). In the observed mangrove sediments, polyethylene (PE), polypropylene (PP), and polystyrene (PS) were the dominant type, color, and size of the micro-plastics, respectively (Li et al. 2019).

22.7 Heavy Metal Pollution

Even though, mangrove ecosystem is involved in the impelling of industrial and domestic pollutant releases (Arumugam et al. 2018). No integrated and practical management has been implemented on these coastal ecosystems, and heavy metal has a significant concern outright of anthropogenic effects, specifically in

Fig. 22.4 Plastic pollution in mangrove habitats (Source: Martin et al. 2019)

contaminated mangrove coastlines (Arumugam et al. 2018; Qiu et al. 2011; Tam et al. 1995; Tam and Wong 2000). These metallic elements could deposit in ambient sediment in mangrove areas and finally bind with oxides such as iron ones and transferred to these trees/plants (Arumugam et al. 2018). Globally, in many places, such as China, Australia, India, and Vietnam (Nath et al. 2013), these kind of inorganic pollutants in mangroves ambient sediments have been reported. Table 22.2 shows some heavy metal polluted areas all around the world. Overall, mangrove contamination with heavy metals can be classified into two-point and non-point sources, and most of this contamination is pertinent to anthropogenic processes via municipal effluent, surface run-off, and untreated industrial wastewater (Bodin et al. 2011). Toxic minerals from tidal waters and riverine sources can be swiftly eliminated from the waterbody and placed in the ambient sediments, eventually causing it to be a depository media for these metals. It is related to the anoxic essence of mangrove sediment. Nonetheless, two major processes, biological and chemical ones, may allow the deposited toxic minerals to be desorbed from mangrove sediments, upon which they are unleashed into the waterbody (Hill et al. 2013; Wang et al. 2013).

In an interesting study, the concentration, partitioning, distribution, and ecological risks of seven metals (Ni, Fe, As, Co, Cu, Cr, and Mn) in ambient sediments and pore-waters were investigated by Thanh-Nho et al. (2019) in the Can Gio Mangrove. They collected three cores within a mudflat, beneath *Avicennia alba* and *Rhizophora apiculata* stands.

Table 22.2 Some of the toxic metal polluted regions in mangrove environments

Contamination site	Metal	Concentration	References
Shenzhen, China	W	377 mg kg^{-1}	Xu et al. (2015)
	Co	129 mg kg^{-1}	
Zambales, Philippines	Pb	Undetectable levels	Paz-Alberto et al. (2014)
Hong Kong	Cu	80 μg/g	McDonald et al. (2006), Tam and Wong (2000)
	Zn	240 μg/g	
	Cr	40 μg/g	
	Ni	30 μg/g	
	Cd	3 μg/g	
	Pb	80 μg/g	
South China	Cr	28.5–86.6 mg kg^{-1}	Liu et al. (2017), McDonald et al. (2006)
	Cu	10.3–30.9 mg kg^{-1}	
	Zn	24.8–87 mg kg^{-1}	
	As	2.44–20.1 mg kg^{-1}	
	Pb	25.6–86.4 mg kg^{-1}	
	Cd	0.07–0.39 mg kg^{-1}	
	Hg	0.061–0.24 mg. Kg^{-1}	
French Guiana	Cu	0.06–0.61 μmol/g	Al-Hashmi et al. (2013), Marchand et al. (2006)
	Co	0.12–0.68 μmol/g	
	Pb	0.08–0.18 μmol/g	
	Ni	0.32–0.76 μmol/g	
	Cr	0.61–1.4 μmol/g	
	Zn	1.25–5.94 μmol/g	
	Mn	4.36–45.4 μmol/g	
	Fe	441–1128 μmol/g	
Brazil, Rio de Janeira state, Guanabara Bay	Hg	0.7–9.78 mg kg^{-1} dry weight	Kehrig et al. (2003), McDonald et al. (2006), McDonald et al. (2006)
	Zn	78–707 mg kg^{-1} dry weight	
	Cr	3.5–480 mg kg^{-1} dry weight	

(continued)

Table 22.2 (continued)

Contamination site	Metal	Concentration	References
	Cu	2.4–300 mg kg^{-1} dry weight	
	Pb	3.6–110 mg kg^{-1} dry weight	
	Cd	0.02–2.6 mg kg^{-1} dry weight	
Brazil, Rio de Janeira state, Sepetiba Bay	Hg	0.017–0.16 mg kg^{-1} dry weight	
	Zn	18.1–795 mg kg^{-1} dry weight	
	Cr	23.9–121 mg kg^{-1} dry weight	
	Cu	2.1–166 mg kg^{-1} dry weight	
	Pb	6.5–85.7 mg kg^{-1} dry weight	
	Cd	0.5–8.7 mg kg^{-1} dry weight	

22.8 Biological Approaches for Remediation in Mangrove Habitats

Ecological parameters affecting microbial hydrocarbon bioremediation include temperature, electron acceptors, pressure, salinity, substrates, type of microorganisms, inoculum size, nutrient accessibility, biosurfactant, and bioavailability of pollutants (Varjani et al. 2017). Several techniques applied for bioremediation of polluted areas listed in Fig. 22.5.

There are two strategies for bioremediation of polluted regions, including biostimulation and bioaugmentation. Bioaugmentation refers to the addition of exogenous strains/mixed cultures to polluted environments to improve or accelerate the degradation of specific compounds. This method can effectively transform the contaminants into less complicated compounds. The genetically engineered bacteria, pre-adapted microorganisms, and a vector containing genes involved in bioremediation are applied in microbial bioaugmentation (Herrero and Stuckey 2015). In contrast, biostimulation is a bioremediation strategy that consists of the optimization of some factors (such as the addition of nutrients, trace elements, electron acceptors or donors) to induce indigenous microbial communities to remove environmental pollutants (Chen et al. 2012).

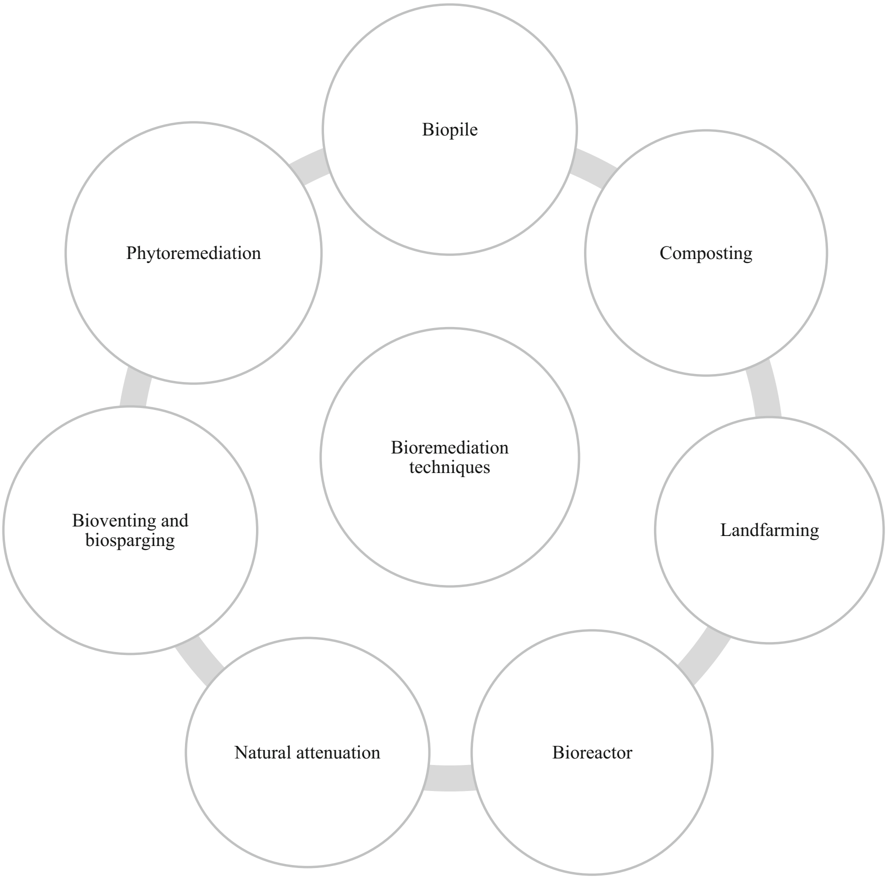

Fig. 22.5 Bioremediation strategies used in polluted environments (Gaur et al. 2018)

These strategies are classified into three groups: In situ, prepared bed/on-site (ex situ), and bioreactor (Wilson and Jones 1993). In situ-bioremediation is a simple, economical, highly efficient technique and without any secondary waste production. In this process, degrading organic pollutants and producing inorganic compounds such as methane and carbon dioxide contamination are treated in place and without excavation and transport (Farhadian et al. 2008; Wilson and Jones 1993). In contrast, ex-situ bioremediation is a costly and challenging technique that requires transportation of contaminated soil or water and can be applied in severe pollution (Tomei and Daugulis 2013).

Natural attenuation is an intrinsic bioremediation process in which diminution of pollutant adverse effects can occur with both physical or biological methods such as biodegradation by natural microorganisms, volatilization, chemical conversion, dispersion, precipitation, sorption, stabilization of contaminants, and dilution (Scow and Hicks 2005).

Bioventing is another technique of the in situ bioremediation techniques that used to aerate the polluted sites to promote microbial eradication of organic compounds. In addition to the oxygenation of the vadose zone, this process involves adding nutrients and moisture to contaminated sites for improvement of indigenous microbial activity. Biosparging is similar to bioventing with this exception that air injection is performed at the saturated area. As a result, volatile organic compounds migrate upward to the unsaturated region and undergo biodegradation (Azubuike et al. 2016).

Phytoremediation is a bioremediation technique that can be applied in large scales and is used for improving soil fertility. In this process, plants are used instead of microorganisms for the treatment of contaminated environments. There are several types of phytoremediation in which rhizofiltration, phytovolatilization, phytoextraction, and phytostabilization are remarkable (Sruthi et al. 2017).

22.9 Microbial Degradation of Organic Pollutants in Mangrove Habitats

Persistent organic pollutants (POPs) are hydrophobic compounds that accumulate in fatty tissues of vertebrates and induce cell apoptosis by producing reactive oxygen species (ROS). These compounds include dioxins, polychlorinated biphenyls (PCB), organochlorine pesticides (OCPs), PAHs, and dibenzofurans and have anthropogenic and natural sources (Gaur et al. 2018). According to the Agency for Toxic Substances and Disease Registry (ATSDR) report, PAH and PCB are, respectively, in the ninth and fifth ranks of 2017 priority list of hazardous substances, which includes metal/metalloid pollutants (Agency for Toxic Substances and Disease Registry 2017, Priority List of Hazardous Substances https://www.atsdr.cdc.gov/SPL). The amount of anthropogenic activity for PAH production in the USA, Sweden, and Norway is 9406 metric tons/year, according to Chan et al. (2006) (Chan et al. 2006). These compounds are composed of two or more attached benzene groups, and as the number of aromatic rings elevates, its carcinogenic effects increase (Ghosal et al. 2016). The remediation strategy must be employed because of the various adverse effects of contaminants such as genotoxicity, mutagenicity, and toxicity on the human health and ecosystem. Some of the microbial enzymes that take part in this process include oxygenases, peroxidases, reductases, hydroxylases, and dehydrogenases. alkA (alkane monooxygenase), alkM (alkane monooxygenase), alkB (alkane monooxygenase), ladA (alkane monooxygenase), assA1,2 (alkylsuccinate synthase alpha-subunit A), nahA-M (Naphthalene dioxygenase reductase), napA (Nitrate reductase), amoA (Ammonia mono oxygenase), dsrAB (Dissimilatory sulfate reductase), and mcrA (A-subunit of Methyl –coenzyme M reductase) are the central genes involved in biodegradation of organic pollutants (Varjani et al. 2017). Table 22.3 listed different enzymes involved in the microbial degradation of the hydrocarbon compounds.

Pure culture of bacteria may degrade few hydrocarbons, while microbial consortia may be capable of eradicating a wide range of contaminants because of synergism observed between its microorganisms (Cerniglia and Sutherland 2010; Uad et al.

Table 22.3 Microbial enzymes identified for degrading hydrocarbon compounds

Enzyme	Name of microorganism	Petroleum hydrocarbon/pollutant compound	References
Dioxygenases	*Acinetobacter sp.*	C10-C30 alkanes	Abbasian et al. (2015)
Bacterial P450 oxygenase system (CY153)	*Acinetobacter, Caulobacter Mycobacterium*	C5-C16 alkanes, cycloalkanes	Abbasian et al. (2015)
Eukaryotic P450 (CYP52)	*Candida maltose, Candida tropicalis, Yarrowia lipolytica*	C10-C16 alkanes, fatty acids	Abbasian et al. (2015), Salleh et al. (2003)
AlkB related alkane hydroxylases	*Pseudomonas, Burkholderia, Rhodococcus, Mycobacterium*	C5-C16 alkanes, alkyl benzenes, Cycloalkanes, fatty acids	Abbasian et al. (2015)
Monooxygenases	*Oxyfera*		Abbasian et al. (2015)
Soluble/ particulate methane	*Methylocystis, Methylomonas, Methylocella, Methylobacter, Methylococcus, Geobacillus thermodenitrificans, Methylomirabilis Oxyfera*	C1-C8 alkanes, C1-C5 (halogenated) Alkanes, alkenes, cycloalkanes	Abbasian et al. (2015), McDonald et al. (2006)

2010; Varjani 2017; Kumar et al. 2018). The first step of the relation between oil contaminants and the microbial community includes direct interaction between them (Souza et al. 2018) and it eventuates on the cell wall structure and its hydrophobicity. Hydrophobicity and surfactant activity favor interaction between microorganisms and hydrophobic substrate (Kavitha et al. 2014). Microorganisms having ability in degradation of oil with biosurfactant generation and anoxic conditions growth ability are more effectual for in situ methanogenesis in oil reservoirs (Zhao et al. 2016).

Similar to bacteria, fungi are potent organisms to possess the capability of biodegradation of persistent organic pollutants (Ramanathan et al. 2008). Mold and yeast can metabolize a variety of hydrocarbon compounds via their active enzymes (Reddy 1995). Mangrove inhabited fungi also involved in the remediation of contaminants in estuarine ecosystems that often exposed to a broad spectrum of organic contaminants.

Yeasts are the most dominant fungal taxon in contaminated ecosystems (Berdicevsky et al. 1993), and they can degrade PAH by consuming of other carbon sources. *Rhodotorula glutinis* is a yeast isolated from a hydrocarbon-polluted stream and can oxidize phenanthrene as well as the rate of degradation by *Pseudomonas aeruginosa* as a bacterium (Romero et al. 1998). Table 22.4 demonstrates some fungi species for biodegradation of petroleum compounds.

Table 22.4 Microbial species able to degrade petro-organic compounds

Target petroleum hydrocarbon/pollutant	Microbial species	References
Aliphatic hydrocarbon	*Acinetobacter sp.*	Foght (2008), Mittal and Singh (2009)
	Alcanivorax sp.	Brooijmans et al. (2009), Harayama et al. (2004)
	Azoarcus sp.	Widdel and Rabus (2001)
	Bacillus sp.	Ghazali et al. (2004)
	Brevibacterium	Leahy and Colwell (1990)
	Desulfosarcina sp.	Jaekel et al. (2013)
	Desulfococcus sp.	Jaekel et al. (2013)
	Marinobacter sp.	Yakimov et al. (2007)
	Micrococcus sp.	Ghazali et al. (2004), Roy et al. (2002)
	Ochrobactrum sp.	Varjani et al. (2015)
	Oleispira sp.	Harayama et al. (2004)
	Pseudomonas sp.	Mittal and Singh (2009), Rocha et al. (2011), Sajna et al. (2015), Varjani et al. (2015)
Aromatic hydrocarbons (poly−/mono-hydrocarbons)	*Acinetobacter sp.*	Batista et al. (2006)
	Archaeoglobus fulgidus	Wilkes et al. (2016)
	Aromatoleum aromaticum	Wilkes et al. (2016)
	Bacillus sp.	Janbandhu and Fulekar (2011)
	Halomonas sp.	Widdel and Rabus (2001)
	Pseudomonas sp.	Meckenstock et al. (2016), Mittal and Singh (2009)
	Rhodococcus sp.	Leahy and Colwell (1990), Salleh et al. (2003)
	Achromobacter insolitus	Janbandhu and Fulekar (2011)
	Bacillus sp.	Mittal and Singh (2009)
	Cycloclasticus sp.	Harayama et al. (2004)
	Phanerochaete chrysosporium	Salleh et al. (2003)
	Pseudomonas sp.	Meckenstock et al. (2016), Widdel and Rabus (2001)
	Vibrio sp.	Widdel and Rabus (2001)
	Penicillium janthinellum	Boonchan et al. (2000)
	Alcaligenes faecalis	Kim et al. (2009)
	Arthrobacter gandavensis	Kim et al. (2009)
	Arthrobacter sp. P1–1	Isaac et al. (2015)
	Mycobacterium fluoranthenivorans	Seo et al. (2006)
	Mycobacterium PYR-1	Hormisch et al. (2004)
	Pseudomonas fluorescens	Ramirez et al. (2001)
	Pseudomonas monteilii	Kim et al. (2009)
	Pseudomonas aeruginosa	Isaac et al. (2015)
	Ochrobactrum anthropi	Varjani et al. (2015)

(continued)

Table 22.4 (continued)

Target petroleum hydrocarbon/pollutant	Microbial species	References
	Rhodococcus wratislaviensis	Ortega-González et al. (2015))
	Sphingomonas formosensis	Isaac et al. (2015)
	Stenotrophomonas maltophilia	Lin et al. (2012)
	Anthracophyllum discolor	Acevedo et al. (2011)
	Aspergillus flavus and Paecilomyces farinosus	Romero et al. (2010)
	Aspergillus sclerotiorum	Passarini et al. (2011)
	Aspergillus terreus	Reyes-César et al. (2014)
	Byssochlamys spectabilis	Rosales et al. (2012)
	Cladophialophora psammophila	Badali et al. (2011)
	Cyclothyrium sp.	da Silva et al. (2004)
	Fusarium oxysporum	Ortega-González et al. (2015)
	Phanerochaete chrysosporium	Bhattacharya et al. (2013)
	Trichoderma asperellum	Zafra et al. (2015)
	Trichoderma longibrachiatum	Rosales et al. (2012)
Resins	*Pseudomonas sp.*	Leahy and Colwell (1990)
	Members of *Vibrionaceae* and *Enterobacteriaceae*, *Moraxella sp.*	Chandra et al. (2013)

22.10 Symbiosis Between Microbes and Mangrove Plants

Diverse groups of organisms can be associated with mangrove-specific species, like *Avicennia marina,* and help in some essential ecological processes such as N_2 fixation, organic sulfate mineralization, phosphate solubilization and providing soluble iron for these species. One of the pivotal ecological relationships is the association of N_2 fixers and mangrove roots. Bacteria and fungi can degrade biopolymers and benefit roots by changing pH, the redox potential of environments, and increasing bioavailability of nutrients. Instead, plants can provide nutrients for bacteria and fungi. Some microorganisms can produce organic acids and solubilize phosphates called phosphate solubilizing microorganisms (Alongi 2005). Because of nitrogen and phosphate limitation in mangrove ecosystems, the cooperation of N_2 fixing and phosphate solubilizing microorganisms can be crucial. Rojas et al. (2001) studied the effect of a co-culture composed of *Phyllobacterium* sp. (an N_2-fixing bacterium) and *Bacillus licheniformis* (a phosphate-solubilizing bacterium) on the development of mangrove tree leaves. The synergism observed between the two species increased the number of leaves and nitrogen incorporation of plants (Rojas et al. 2001).

Effect of several mangrove rhizosphere bacteria and *Azospirillum* sp. on oilseed halophyte *Salicornia bigelovii* was investigated by Bashan et al. (2000). The height and dry weight of S. bigelovii increased in response to the inoculation of a mixture of two *Vibrio* strains. In addition to mentioned effects, a mixture of phosphate solubilizing bacterium (*Phyllobacterium* sp.) and N_2- fixing bacterium (*Bacillus licheniformis*) enhanced the length of spikes while inoculation of the cyanobacterium *Microcoleus chthonoplastes* decreased spike size and had no effect on plant foliage (for more details see Table 22.5) (Bashan et al. 2000).

The symbiosis between mangrove plant species and Arbuscular Mycorrhizal Fungi (AMF) is an exciting subject in Microbial ecology. AMF benefits plants by supporting growth and increasing plant biomass levels and absorption of nitrogen, phosphate, and potassium (5). In this regard, Wang et al. 2010 investigated the symbiosis between six AMF species (*Glomus* and *Acaulospora*) and *Sonneratia apetala* B. Ham (plant species). They suggested that phosphate level and hydrological conditions such as moisture content of rhizosphere soil and flooding duration are the most important abiotic factors influencing arbuscular mycorrhizal fungi colonization of mangrove plants. Survival of AMF, as aerobic microorganisms in flooded conditions (low oxygen), depends on oxygen provided by aerenchyma developed in adult mangrove species. Hence, the AMF colonization rates were increased in the dry and aerobic zones compared to wet and hypoxic regions. Furthermore, a very low or high level of phosphate limits AMF colonization to mangrove species (Wang et al. 2010).

22.11 Microbial Biodiversity in Mangrove Ecosystems

The reaction of mangrove environments to various pollutants is essential for controlling contaminants in this environment. Therefore, the study of microbial diversity of these ecosystems has involved the attention of many studies. Understanding the impacts of pollution on the microbial diversity (such as the fungi) that associated with mangrove ecosystem is of substantial importance for the maintenance of renewable resources in an effective way (Tsui et al. 1998). Microorganisms can also degrade contaminants such as PAHs or other organic pollutants from domestic effluent (Holguin et al. 2001; Jones 2000; Santos et al. 2011). Different studies accompanied by the microbial community structure of contaminated mangrove habitats (Maciel-Souza et al. 2006). Different studies investigated the microbial diversity such as bacteria (Grativol et al. 2017) and fungi (they are well known to be highly potent in the eradication of several contaminants) (D'Annibale et al. 2006).

Microorganisms with petroleum hydrocarbon metabolizing activity are broadly dispersed in the environment (Brooijmans et al. 2009; Lamichhane et al. 2016). For a better evaluating of microbial distribution and abundance in natural ecosystems such as mangrove habitats, the tools are well developed (Varjani et al. 2015).

Table 22.5 Effect of bacteria on mangrove plants growth parameters

Factors	*A. halopraeferens* AU10		*A. brasilense* strains	*Vibrio* strains	*B. licheniformis* + *Phyllobacterium* sp.	*Microcoleus chthonoplastes*
Total phosphate	+		+	+	+	–
The total lipid of seeds	–		+	–	+	+
Total N of seeds	+		+	+	+	+
Total N of plants	–		–	–	–	–
Plant height	+		+	+	+	+
Plant dry weight	+		+	+	+	+
Number of branches	+		–	+	No effect	+
Length of spikes	+		+	+	+	–

Table 22.6 Taxonomic classes on the four different microhabitats

Location	More abundant classes	Less abundant classes
Immersed *A. marina*	*Sordariomycetes Dothideomycetes*	*Leotiomycetes*
Emerged *A. marina*	*Dothideomycetes*	*Leotiomycetes*
Immersed *R. stylosa*	*Dothideomycetes*	*Leotiomycetes*
Emerged *R. stylosa*	*Lecanoromycetes Dothideomycetes*	*Leotiomycetes*

The effects of hydrocarbon pollutants on three Brazilian mangrove forests were investigated by Marcial Gomes et al. (2008). DNA was extracted from samples and 16S rDNA gene fragments denaturing gradient gel electrophoresis (DGGE) was done as a culture-independent method. Despite other natural sites that harbor *Alphaproteobacteria*, *Actinobacteria*, and *Pseudomonads* taxa as predominant groups, the dominant species of these samples like other hydrocarbon polluted sites species have belonged to *Pseudomonadales*, *Burkholderiales*, *Alteromonadales*, *Rhodocyclales*, and *Rhodobacterales* orders (Marcial Gomes et al. 2008).

Metagenomic analysis of Sundarbans mangrove (India) bacterial diversity revealed that *Proteobacteria*, *Firmicutes*, *Chloroflexi*, *Bacteroidetes*, *Acidobacteria*, *Nitrospirae*, and *Actinobacteria* are the dominant taxa of this ecosystem, respectively. Only 5% of sequences are related to a poorly characterized taxon (Basak et al. 2015).

Illumina sequencing method was employed to determine the bacterial diversity of sediments in Mai Po Ramsar mangrove wetland, Hong Kong. The results showed that *Actinobacteria*, *Verrucomicrobia*, *Acidobacteria*, and *Nitrospirae* comprised the dominant phyla in the inner sediments. *Proteobacteria* and *Defferibacteria* were prevalent in the surface sediments. In this ecosystem, *Gammaproteobacteria* and *Deltaproteobacteria* were the abundant taxa among *Proteobacteria* (Jiang et al. 2013).

Arfi et al. (2012) studied the fungal diversity of two mangrove trees (*A. marina* and *R. stylosa*) at Saint Vincent Bay, New Caledonia, by pyrosequencing method. *Ascomycota*, with 82%, was the dominant phyla, and *Basidiomycetes* comprise only 3% of the community. 15% of sequences were related to unknown taxa. *Dothideomycetes* with 25–55% were predominant on emerged and immersed surfaces of these two mangrove trees. The details are presented in Table 22.6 (Arfi et al. 2012).

Molecular tools were applied for characterization of the Cyanobacterial community of mangrove environments of south-east Brazil and showed 19 different genera of cyanobacteria and unidentified taxa. *Nostocales* and *Oscillatoriales* were dominant orders which included N2 fixing cyanobacteria such as *Anabaena*, *Brasilonema*, *Scytonema*, *Symphyonemopsis*, *Fischerella*, *Rivularia*, and *Nostoc* that highlighted the importance of nitrogen-fixing bacteria and nitrogen cycle for decreasing nitrogen limitation in ecosystems (Rigonato et al. 2012).

22.12 Biotechnological Importance of Mangrove Microorganisms

Mangroves are the desired place for isolating cellulase producing microorganisms because of the frequent amount of lignocellulosic substrate for carbon turnover in these environments (Gao et al. 2010). There are three types of cellulase, including exoglucanase (EXG), endoglucanase (EG), and β-glucosidase (BGL), which both bacteria and fungi can produce (Behera et al. 2017). Castro et al. (2014) isolated plant-associated endophytic bacteria of two mangrove environments by culture-dependent methods. *Bacillus* was the most dominant genus isolated from both environments, and the other genera include *Enterobacter*, *Pantoea*, *Brevundimonas*, *Microbacterium*, *Chryseobacterium*, *Novosphingobium*, *Xanthomonas*, *Erwinia*, *Alcaligenes*, *Ochrobactrum*, *Curtobacterium*, *Stenotrophomonas*, and *Sphingopyxis*. Amylase, protease, lipase, endoglucanase, and esterase were produced by 45%, 75%, 52.5%, 62.5%, and 17.5% of these microorganisms, respectively. The highest rate of amylolytic, estrasic, and endocellulolytic activity was observed in *Bacillus*. This finding emphasized the ability of mangrove inhabiting microorganisms for biotechnological applications (Castro et al. 2014).

In addition to bacteria isolated from mangrove ecosystems, yeasts are also capable of producing metabolites such as extracellular hydrolytic enzymes. In this regard, Jiang et al. (2016) isolated 300 yeast strains from mangrove ecosystems and screened them for inulin hydrolyzing activity. This enzyme called β-Fructofuranosidase (FFase) and has two types: extracellular and intracellular. The substrates of FFase are sucrose, raffinose, and inulin, which can be degraded to glucose and fructose. FFase has immense biotechnological applications and can be used in food and beverage, cosmetic, pharmaceutical, fermentation, and paper industries. After screening, the highest insulin-degrading activity (30.98 ± 0.8 U. ml^{-1} after 108 h) was observed in *Aureobasidium* sp. P6 strain (Jiang et al. 2016).

22.13 Heavy Metal Removal in Mangrove Sediments

Heavy metal is referred to as any metal between groups 3 and 16 (Hawkes 1997) with a specific gravity of 5 g/cm^3 or over. These elements have atomic weights between 63.5 and 200.6. Heavy metal pollutions occur by some anthropogenic activities such as paper industries, tanneries, batteries, fertilizers. These elements accumulate in living organisms and promote toxic or carcinogenic reactions. The most major heavy metals with adverse effects on the environment include Cu, Zn, Ni, Hg, Cr, Pb, and Cd (Fu and Wang 2011).

The effect of heavy metal on the microbial community composition of Xiangjiang River was investigated by Zhu et al. (2013). In this study, the microbial diversity of four samples polluted by different heavy metals analyzed by PCR-RFLP as a culture-independent method. As shown in Fig. 22.6, *Proteobacteria* (55%) was the dominant phylum in this environment. *Alphaproteobacteria*, *betaproteobacteria*, *Gammaproteobacteria*, *Deltaproteobacteria*, *Epsilonproteobacteria* comprised

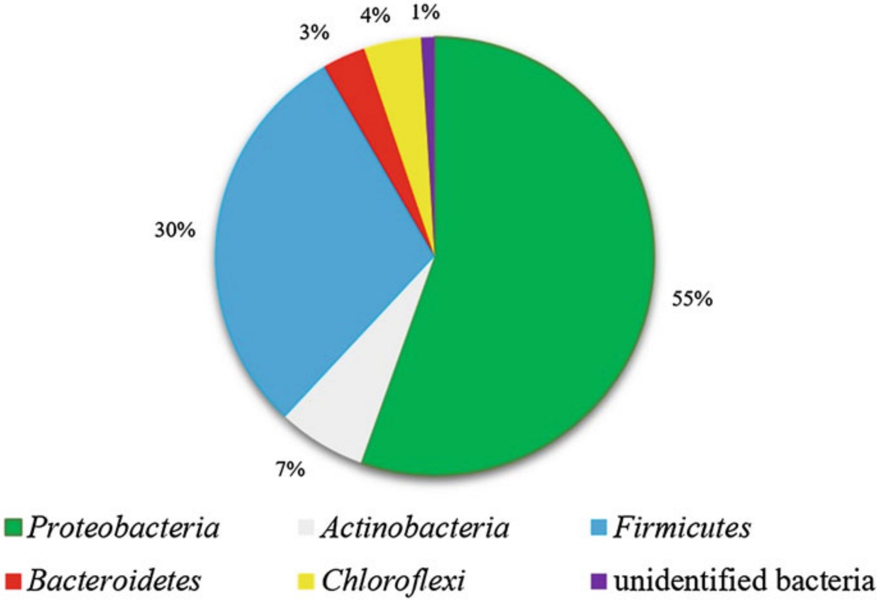

Fig. 22.6 Different operational taxonomical units (OTU) in Xiangjiang river

23.4%, 22.6%, 3.6%, 5.5%, and 0.4% of microbial diversity, respectively. As heavy metal concentration raised, the percentage of *Alphaproteobacteria* elevated (Zhu et al. 2013).

Microbial diversity of two hydrocarbon and heavy metal polluted regions of Brazil (Santos and Itanhaem estuaries) was studied by Pinto et al. (2015). Heavy metal pollutants include Cd, As, Cu, Cr, Hg, Zn, and Pb. Direct counting method applied for quantification of heterotrophic bacteria, cyanobacteria, and yeasts. Because of less pollution of Itanhaem estuary than Santos estuary, the total density of microorganisms (heterotrophic bacteria, yeasts, and cyanobacteria) of Itanhaem estuary was more. Nevertheless, the count of cyanobacteria in sediments of Santos was higher than Itanhaem estuary. It can be for the immense potential of these microorganisms in hydrocarbon biodegradation (Pinto et al. 2015).

Mallick et al. (2018) isolated *Bacillus vietnamensis* AB403 and *Kocuria flava* AB402 from the mangrove rhizosphere of Sundarbans. These halophilic strains were arsenite resistant and can eradicate arsenite from environments by biosorption to their exopolysaccharides and accumulation intracellularly. These mechanisms lead to diminished concentration of arsenite and have some impacts on plants in arsenite polluted sites such as plant growth promotion and decrease of arsenite accumulation (Mallick et al. 2018).

22.14 Conclusion

Mangroves are unique ecosystems in subtropical and tropical areas and represent significant productive habitats for many living things. Despite their great ecological, biological, and economical importance, mangroves ecosystems are exposed to many natural and human-made pollutants. In this review, we suggest that organic and inorganic pollution may be the most threatened in mangrove ecosystems. Bioremediation is an environment-friendly and economical method to reduce the toxic effect of pollutants in terrestrial and aquatic ecosystems. Microbial groups perform the central role in bioremediation. Microorganisms have evolved too many mechanisms that allow them to utilize organic pollutants as an energy source or biotransform inorganic contaminants to a less or non-toxic form. The use of prevention strategies for mangrove ecosystem protection and bioremediation of pollutants by a diverse group of microorganisms, especially in mangrove plant rhizosphere, could help to reduce the risk of mangrove extinction.

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Biotherapeutic Approaches: Bioremediation of Industrial Heavy Metals from Ecosphere

23

Reyed M Reyed

Abstract

Sustainable probiotics are cost-effective, active, friendly biosphere, and viable biotherapeutic mediators that increase positive biome inhabitants in the gut micro-bio ecosystem of living organisms. The critical benefit of the potential treatment effectively utilizing such biological agents as a biotherapy approach is the notable absence of their adverse effects. In recent years, extraordinary interest in the possible use of these therapeutic agents has significantly improved to refer to courteously and typically prevent a significant number of complex disorders in our Macro-bio ecosystem. Probiotics biofilms first and foremost restrain gut microbiota directly or indirectly to scale down using biotransformation of complex chemical compounds. Because of the unique structures on its extracellular matrix "MBBM," so many other probiotic microbial communities could already entangle to organic waste product. All strategies merely enable constructive biofilm development and metal-binding of organic compounds. Probiotics biofilm-mediated bioremediation implemented strategically for contaminants. Prebiotics remain naturally, universally potent ingredients with beneficial phytonutrients, fundamental nutritional sources. They are naturally insoluble fiber with complex carbohydrates. Prebiotics has much more to contribute powerfully than purely and simply the systemic application of autochthonous microorganisms in host micro-bio-environments as well as complex environments of plants and animals. Prebiotic indigenous ingredients naturally have to be metabolized by targeted microbiota and microbial processes in a

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specific order to biosynthesize and extensively develop capsular and extracellular biopolymers Membrane-Bound -Biopolymer Matrix MBBM. MBBM released into the unique environment closed capsules or loosely interrelated biofilm blankets. In summary, comprehensive techniques demonstrated to have been an appropriate therapeutic option that explicitly mentioned in this perusal. However, there is a need for more data analysis to focus on the process challenge the interrogator environments in situ. The author hopes that this chapter will create a good literature review that makes substantial contributions to current and promising environmentally therapeutic initiatives in the long term.

Keywords

Bioremediation · Ecosystem · Heavy metals · Microbes · Probiotics · Membrane Bound-Biopolymer Martix “MBBM” · Micronanoremedation · Prebiotics

23.1 Introduction

Bioremediation is strongly involved in trapping “biosorption” (Giese et al. 2020; Contreras-Cortés et al. 2020) bioprocessing “biostimulation” (Zhang et al. 2020); manipulating “bioaugmentation” (Roy et al. 2018); downgrading “biodegradation” (Lee et al. 2019) and clean-up organic, inorganic compounds (Jaiswal and Shukla 2020) and noxious waste (Igiri et al. 2018) from the contiguous Biospheres through the cooperation of microbiome, mycobiome, and plants. This microbiota assimilates organic compounds by biosynthesis certain metabolites, macromolecules, or biomolecules known by enzymes, which brings alterations the nutrient composition and therefore their ecological accessibility. This coordination has been largely employed in agro-ecosystem.

23.2 Probiotics Microbial Strains for Biosphere Cleaning Up

Probiotics pay attention to the particular instances “pro” and “biotic” from the Greek Term “for growth and development.” The ability microbe cells to live, called probiotics (even though a heat-inactivated pattern seems to have become useful for livestock) (Amenyogbe et al. 2020; FAO 2002, 2001; Gibson and Roberfroid 1995; Hill et al. 2014; Reyed 2020; Parker 1974).“ Additionally, they addressed under “straightforwardly administered microbial, oral consumption of probiotics or probiotics dietary supplements (Vesty et al. 2020).”

Probiotics appropriately represent beneficial microorganisms that would adequately provide therapeutic benefits for the prominent guest just before handled fittingly. Although since it has been the world’s most officially known and widely recognized form (Hill et al. 2014; Reyed 2020; Reyed 2007a, 2007b). Promising Probiotics are significant producer for biosurfactants (Ebrahimi et al. 2019), nanomaterial (Nile et al. 2020), metallic nanoparticles (Mohd Yusof et al. 2020), biopolymer (De Prisco and Mauriello 2016; Reyed 2007c), antimicrobial agent

(Karimi et al. 2018), bacteriocin (Maldonado Galdeano et al. 2019); natural biocides (Soliman et al. 2019), and bioactive compound (Binda et al. 2020). Probiotics are categorized as functional and protected microorganisms that progressively improves the host which may be gut microbiome, Biospheres, plant-soil ecobiome, and aquaculture, with necessary prebiotic metabolites and functional ingredient that positively modulates the host's biosphere, thus improving maintaining a stable internal environment association homeostasis (Brodmann et al. 2017). Secondary metabolites obtained directly from plant flora (Jurić et al. 2020), microbiome (Agamennone et al. 2019), mycobiome (Chin et al. 2020), lichens (Olivier-Jimenez et al. 2019), and seaweed "blue-green algae" (Singh et al. 2017a)—are premium of nature, because of their applications in various fields. Recent advances in modern biotechnology have contributed to innovative feasibilities in the dressing, processed foods, pharmaceutical and medicinal sectors of biological resources.

The differentiation of clear and unambiguous engagement arrays among symbiotic organisms permitted use of potential of microbiota to fix biological remediation issues. This resulted in probiotics being regarded as an approach of symbiotic associations. Probiotics could build a number of specific connections which make a range of mutual bionetworks based on different nano-scales platforms, in order to operate properly. These probiotics encounters frequently in the improvement of disease severity or cause therapeutic effect on living organism, including humans. They could also create accomplishments to substance modification and bioprocessing development. Throughout almost all of the biological and ecological issues, farming, conservational research, food manufacturing as well as healthcare consequently play an increasingly important role in the communication among probiotics microbiota. Probiotics are green "nontoxic for the proposed practice" potential long term, and sustainable valuable biofilms could very well precipitously as expected biospheres affirmative (Chung et al. 2016). Probiotics microorganisms are friendly biospheres (Cutcliffe 2017), viable, and sustainable biotherapeutic promoters that naturally strengthen the functional genomics beneficial biomass. The prevalent of treatment using biotherapy represents a reduction of harmful symptoms, such as antagonistic microbes. In earlier years, intellectual curiosity in the usage of such bioactive agents to suppress and mitigate an enormous number of syndromes in our Biospheres has massively increased in the metabolic pathways of biologically active compounds. These probiotics are ubiquitous in the food sector and generally considered safe. In the biospheres, probiotics can sometimes be isolated and characterized sources (Khangwal and Shukla 2019). This microbiota has numerous desirable characteristics that can promote both humans and the Biospheres. Probiotics could very well counteract health effects triggered by toxic chemicals. And therefore, it provides the necessary effective and reliable protection mechanisms in the long term to reduce effects of oxidative stress and cross-link themselves to confiscate and eliminate out from cell wall ecosystem (Roškar et al. 2017).

The recent research for probiotics can also be encompassed in so many other raw materials traditionally based on the intended utilization and bio-formulation (Mastan et al. 2019). It commercialized as dairy products, nutraceuticals, or nutritional support (Jackson et al. 2019). Even so, while the term probiotics generally marketed as functional ingredients, for instance, capsules/powder (Fu et al. 2018), or as functional foods (Roy et al. 2018), natural yogurt (Scariot et al. 2018), kombucha (Kozyrovska et al. 2012), crop production, biofertilizers (Afzal et al. 2019; Jiménez-Gómez et al. 2017) always improve plant nutrient situation (with positive reinforcement growth and profit harvest) and Feed additive for animal's livestock (Markowiak et al. 2019). Thus, utmost of the present probiotic culture likes all kinds of beneficial microbiota that support their host immune system. Bio-manufacturing probiotic was "universally recognized for all living organisms," necessarily mean that stimulated motivated products are friendly biosphere products, processed foods, and agricultural commodities (Fenster et al. 2019). Many organizations and technologists have officially started using probiotic bacteria on small ruminants, even though they have identified and generally acknowledged agroindustry besides health outcomes and socioeconomic welfare benefit of probiotics in public health and environment safety.

23.3 Potential Prebiotics for Effective Biosphere Biotherapy

Prebiotics are carbohydrates "oligo-fructose or oligo-fructan", that can't be metabolized by living organisms. They are a potential source of nutrition for probiotic microorganisms-beneficial mycobiome and microbiome in the gut of living organisms. That interconnected to endorsing the development of cooperative ecobiome including endophytic fungal, rhizobacterial communities of sustainable autochthonous microbial populations, and as well as in the human microecosystem. Prebiotics are therefore quickly emerging as essential mechanisms of biotechnology as therapeutics, as environmental decontamination agents, and as components for a wide range of developmental handles (Amenyogbe et al. 2020; Davani-Davari et al. 2019; Reyed 2007c). Dietary foodstuffs characterized as a prebiotic or Bifidus Agent (Sasaki et al. 2020; Reyed 2007d, e) on many concepts, such as fermentation tolerance in the upper region of the small intestinal tract and the selective encouragement of the growth of probiotic microbiota. Prebiotic metabolism with appropriate techniques and biological activities is needed if capsular or extracellular polysaccharides generated. Among several others, a membrane-bound biopolymer matrix was established and is well-known as "Membranes-Bonded Biopolymer Matrix" (MBBM) biopolymers. In this specific case, synbiotic (Jost et al. 2015) "living and viable potent microbiota with their metabolites" is used once again to focus on improving their habitat, then will also endorse the macro and microeconomic-bio-ecosystem ex-situ biosorption and biomonitoring process (Goyal et al. 2019).

Beneficial microbes used in bioremediation to neutralize, detoxify, efficiently absorb, purify, break up or break down waste, and other harmful materials into the less volatile or toxic compounds. In organic farming, the beneficial microorganism profitably grows throughout powerfully establishing a relationship with aquaculture and naturally provides straight forward accessibility to the local fish gastrointestinal systems, with gills and nourishment available. In this chapter, I put forward to profitably use the expression "Membrane-Bound Biopolymer Matrix "MBBM" for Extracellular polymeric substance "EPS" (Gupta and Diwan 2017), but did not drift down into review articles. Meanwhile, at that possible moment, the debate nearby the standard abbreviation has been virtually completed with "Membrane-Bound Biopolymer Matrix MBBM" as the practical implication of Extracellular polymeric substances. "MBBM" same as "EPS". MBBM biofilm organizations well-defined as "Microbial biodynamic biopolymer which has been arising as a consequence in direct relation for both the joining or affix (coherence and collective efficacy) together through cells (bond strength for biofilm formation) and some other particulate material "pollutant materials, heavy metals." Biopolymers in common are macromolecules in the exterior membrane (Biopolymer Matrix Membrane Bound). They secreted in microbial organisms as tightly enclosed capsules or loosely connected biofilm sheets. In industrial bioprocessing MBBM is useful for regulation of biotherapeutic agents and functional nanoscale particles.

An excellent selection of extensive uses would carefully cover novelty items, professionally clean-up, home healthcare goods, macro-ecosystem sustainability, nutrition, and rehabilitation. Microbes are responsible for us with an overwhelming and various biotherapeutic essentials of the macro-ecosystem. Such cautiously approaching adverse possessions are identified and improved by the cutting-edge indigenous materials required to counter the situation of chemical combinations, nitrogenous compounds (risky materials), and thus the microorganism of the Biospheres. Nevertheless comprehensive work in progress, only a few microbial origins has been until now to be identified with specific numerous products. Microbial resources can merely contribute to a more advanced production of microbial syntheses by generating a new golden age of environmental bioprocessing, which has sufficiently developed into one important branch of nano-biotechnology. It is a constructive chapter on contemporary bioremediation by probiotics for treasured microbial biomass bio-based materials to merely enhance the biosphere cleanup development of polluted macro-bio ecosystem applications, to promote renewable bio-resources for bionanoformulation.

23.4 Severely Spoilt Biosphere by Heavy Metals

An element of an unexpectedly extensive urban, newly fifth, and fourth-generation industrializing and population growth has been contaminated with various hazardous xenobiotic substances on the planet (Chang et al. 2019). The biosphere polluted with possibly unsafe carbon-based impurities, and the manufacturing sector in current history. Pigments, dyestuffs have become alarming in our biotic systems (azo dyes, commercially available dyestuffs) (Benkhaya et al. 2020). Our biosphere, including humans, animals, and plants, are threatened by pollutants through disruption of the cell wall, DNA derived, altered enzyme activities, and caused death to the birth, liver and kidneys, neurological problems, and premature heart and brain (Giavasis et al. 2020). Conservation pollution by heavy metal caused considerable damage to aquatic systems owing to biotic, abiotic, and industrial overflows. Applications usually involve coal and iron extraction and industrial processes, rechargeable batteries and pharmaceutical discharges, manures, insecticides, and much other heavy industry and inappropriately commonly utilized substrates.

The worst most widely recognized toxic heavy metals found in the biosphere are synthetic polymers, and rare earth metals. The toxic metal seeps into the soil, metastasizes, accumulations, and generally speaking, accumulates in surface and groundwater (Jaishankar et al. 2014); (Hossain and Rao 2014). Contaminants are harmful at less dose that cause serious biosphere oncogenic, xenobiotics, and bioaccumulative threats. They lead to the bioaccumulation of toxic elements by food processing interconnection into animals and floras. These xenobiotic contaminants are created commercially and discharged of extensively in the biosphere. Disclosure to poisonous substances results in the implementation of different food chain concentrations (Bharagava et al. 2018). They look as if to have an antagonistic consequence on “biotic diversity” and not recyclable then poisonous to humans. Innovative technologies are now essential to improve treatments. Numerous physicochemical and biological processes are applied because organic compounds released into the biosphere from industrial effluents. Eco-friendly and efficient remediation process deem necessary to improve this situation. Since several methods for pollutants exclusion and dyestuffs are appropriate, biological treatments are robust today, and cleaner because they are sustainable, globalization economic, not begin producing toxic by-products (Allam 2017). In vitro and in vivo as well as on the field microbial clean-up can be implemented through integrating a variety of harmful organic pollutants into high-end chemical products while using organic, biologically healthy, cost-efficient, and composites reinforced across much of the application of microbiota biotransformation for decontaminating and biodegrading a dangerous macro ecosystem (Dick and Stucki 2020).

Microscopic multicellular entities biofilm sustained biomonitoring, pollutant removal, and photocatalysis procedures are more promising nanostrategies than others currently offered by microbial biodegradation combined with the increasing microbial biomass viscosities and the significantly sophisticated natural cell immobilization capability for surveillance and mechanical resistance of bacteria (Yadav and Singh 2019). The monitoring approaches to the harmful effects of such noxious are most important for sustainable economic growth. Using beneficial biofilms “probiotics” as a tool for bioremediation of potentially toxins allow new technologies to remain biosphere sustainable if integrated methods correctly developed and applied. Such a technique using microorganisms and their products to degrade and cleanup various effluents is beneficial in the long run, so they must incorporate into detecting and preventing the harsh chemical from release into the biosphere. Many studies have completed in the way of how biofilms interconnected to infection, but less focus has given to the probiotics beneficial biofilms related to the biosphere. One striking example, however, relates to the current cleaning of the major oil spill by Exxon Oil on the shorelines of Prince William Sound, Alaska, back in 1989 (Prince and Atlas 2016; Beth Lebwoh 2011).

23.5 Microbial Consortia and Pollutants

Consortia of genetically modified microbes have deployed to detoxify pollutants. Such positive biofilm research in the natural biosphere of soil, sand, and sediments has revealed the potential biofilms to treat pollution. The exosome communication system within microbiomes biofilm taxon, together along with microbial community's chemotaxis, could promptly lead to biocompatibility and bioavailability of harmful pollutants, which is extremely important directly positively linked to the gradual degradation of toxic and organic contamination by biofilm creating microbiome. (Edwards and Kjellerup 2013). For synthetic dyes, textile wastewater pigmentation promptly became one of the most imperative biosphere impacts. It is a root cause of stimulated ecosystem pollution. The oxygenation or continuous renewal of oxygenation possessions of natural water sources and trimmed-off exposure to dying sunlight are also affected by massive quantities of staining and finishing colorings in water boards (Yaseen and Scholz 2019). Textile wastewater that is untreated has negative biosphere and social impacts. Near to the ground dose (< 1 ppm) of dyestuff can efficiently generate sensitive Macro-ecosystems colors, impair compositional quality, inhibit photorespiration, and destruction water and land network. (Sghaier et al. 2019). Biological approach as probiotics biofilms-intermediated bioremediation “PBIB” forming membrane-bound biopolymer matrix (MBBM), are necessarily towards the detoxification of toxic chemicals.

23.6 Probiotics Mediated Bioremediation of Biofilms “PIBB”: An Innovative Comprehension of Environmental Complications

Microscopic organisms are directly relevant to indisposition and ephemerality. It could be something threatening as well as horrible. Even so, together with digital technologies, the microbiota twenty-first century is not always an invader, and therefore might be best friends. Probiotics intermediate bioremediation biofilms soundly supposed to overcome procedures to affect the control side:

1. Competition and participate cautiously in the gradual progression of potentially treacherous microbial communities “pathogenic biofilm-producing and opportunistic microorganisms”.
2. As well as, the nutrient can adhere to the composite surface substrate of mutant cells, through fluid secretion of prebiotic membrane-bound biopolymer matrix (MBBM).
3. Monitoring, controlling, ecobiome eubiosis, and homeostasis augmentations through accelerating hydrogen peroxide emission (Mazzoli et al. 2019), catalases enzymes release (Yu et al. 2019), antioxidant biosynthesis (Chooruk et al. 2017), various prebiotics nanoparticles exudations (Mohd Yusof et al. 2020), and biosurfactant oozing out (Ebrahimi et al. 2019).

Innumerable technological respects of probiotics biofilms-intermediated bioremediation lifecycle, for remarkable instance, water ground remediation by subterranean root system where Phyto-hydraulics biosorption and microbial biotransformation of heavy metals and specific toxins into their gaseous practices. Microorganisms and crops are deteriorating contaminants into several components and carefully withdrawn, modified, changed, and processed for reducing harmful environments. Microorganisms and plants are degrading pollutants into many ingredients and safely removed, modified, adapted, and processed for minimizing hazardous environments. Hopefully, soon, it has been used for all the polluted towns, lines, sediments, reservoirs, and surface water bioconversion systems widely used for extensive irrigation. (Kapahi and Sachdeva 2019). Bioremediation process is used to neutralize, reduce, and remove environmental pollutants by application of probiotics biofilm or metabolite profiling “prebiotics metabolomics” as biological agent for bioremediation or even if plants are used for this purpose, to eradicate, relocation, adsorption, and/or lay off waste product called phytoremediation (Yan et al. 2020). In certain circumstances, Microbial bioremediation, microbiota produced enzymes change the composition and configuration of heavy metals to transform toxic pollutants. The phenomenon is classified as bioconversion or enzyme hydrolysis or microbial degradation. In many deteriorated, the composition of toxic chemicals has been degraded, the structure becomes easier and simple and essentially harmless, ineffective, not harmful, and eventually, metabolites called biomineralization (Zhao et al. 2019).

23.7 Bioremediation Through the Application of Intrinsic or Extrinsic Probiotics Biotherapy

Host protection like plants, aquacultures, animals, and humans, the cognitive processing of these directly linked living organisms, has been understood. The eubiosis and dysbacteriosis (Reyed 2020; Bajinka et al. 2020) protected function of these microbial populations is significant but is very far from putting into corrective action. The probiotic hypothesis being one of the most widely recognized assumptions. It sufficiently indicates a dynamic relation between symbiotic living organisms and environmental conditions that leads to the unique composition of the most valuable meta-organisms. As another advantage, the extensive modification of inhibitory microbiota, including purported soil microbes for the biosphere, may typically have probiotic constructive powers for distinctive florae and faunas. Throughout this approach, it is promising to cooperate with intermediate, bioremediation, and the aggregation of a healthy microbe. This ambitious scheme will naturally inspire the nutrient depletion of emerging contaminants that toxic to ecobiome and other meta-organism. The condition of polybiomics correctly is the impressive array of active viruses, phages, eubacteria, archaea, beneficial fungi, protozoa, and Arthropods stimulating special protection of a host secretion, and many other metabolic abnormalities. Because of higher biomass crosslinking and adsorption capacity with sophisticated defensive and adhesive properties, probiotics biofilms-intermediated bioremediation “PBIB” would correctly be a much more promising approach.

PBIB attribute to the successful genetic modification between ecobiome/phytobiome and other beneficial organisms induced biocompatibility and biotransformation of toxic chemicals by microbial communities certain chemotaxis. Phytobiome, microbiome, mycobiome, and arthropods composition typically play an integral role absolutely in distinct nutrient absorption and therefore colonized with a massive, dynamic group of biota that merely makes a significant contribution in nutrient decomposition forms sustainable harvest. A large variety of unique microbiota in the intestines, from archaea to eukaryotes, just like many of the mycorrhizal phyllosphere and endophytes, generally occupy the plump tissue of the affected plant. Similarly, rhizosphere microbiota factors also include soil type patterns, moisture levels, evolutionary indicators for agricultural production, roots xenografts, etc. (Dong et al. 2019). A hybridization and cross-pollination with both cultivated plants and beneficial microorganism facultative mode of private life or obligate mutualistic interdependence relationship and legumes developing conditions sometimes including Adzuki beans. Anasazi beans, Black beans, Black-eyed peas, Fava beans, Garbanzo beans (chickpeas), organic Kidney beans, and Lentils represent absolutely just another substantial economic agro-processing, and valuable agricultural dynamic relationship. To thoughtfully provide complimentary access, such profoundly grateful bryophytes offer additional keep providing CO_2 resources, mostly as organic compounds, including one that adequately maintains beneficial microorganisms stable and enthusiastic (Harris et al. 2020).

As seen with the residents’ densities of lichen and rhizopus-Azolla, demanding and many-sided chemical compounds enable beneficial bacteria to regulate their biochemical processes with that of the necessary requirements of other representatives of their active populations (Sehar and Naz 2016). Throughout the whole scenario, the single-celled microbiome, mycobiome, their residences inside the vesicles of the rhizobia “nodules” where every day they tighten and help hold nitrogen from the atmosphere to the plants, microbiome “bacterial inhabit” or mycobiome “fungal occupies” that living inside plant soft tissue, dispossessed producing infection. This phenomenon well famous by phytobiomic probiotics microbiomic or mycobiome endophyte and invertebrates “creepy-crawlies, arachnids, myriad pods, and prawns” relationship, this remarkable statement abbreviated by triple genuine compacted network “probiotics biofilm phytobiome” (Kumari et al. 2020).

Probiotic biofilm phytobiome “PBP” Triple interactions amongst Plants, Microbes, and bugs relationship are multifarious, and more than a few complex dynamics possibly will touch its specific configuration, like phytobiome-microbiome and microbiome–microbiome interfaces and macroecolgical distinctions. (Maria 2020). Biospheres potential application of probiotics biofilm phytobiome as green fermentation bioprocess miscellaneous fertilizers, the commonly bio-based product on valuable plant beneficial biofilm connection from probiotic biofilm phytobiome. Additionally, the unique capability to biosynthesize hormones and iron-chelating complexes efficiently are two of the utmost communal

Phyto-improvement stimulating mechanisms discovered by probiotics biofilm phytobiome. Besides, PBP also has bioregulator characterization, performing as phyto-shielding potential mediators alongside pathogens living things of a deferent environment. The successful production of siderophores and cell wall-hydrolytic elevated enzymes like "chitinase, glucanase, protease, and cellulose" are competent to progressively destroy the mycobiome and microbiome cell wall and sufficient possible reasons the cell dissolution of microbiological septicity. As well as release and ecological development of chemotherapeutic polymers via volatile compounds (VC) efficiently is between those biocontrol of phytopathogens.

The appropriate use of probiotics phytobiome not only increases harvest production, then again as well as valuable products typically resulting from these yields. There are specific additional probiotics biofilms-intermediated bioremediation such as *Ralstonia eutropha "Alcaligenes eutrophus"* (Xu et al. 2019) The function of *Ralstonia eutropha* is efficient because all organic carbon, vitamins, and minerals are typically restricted, it is sometimes intracellular biogenerate and continue eagerly to bio produce a massive amount of polyhydroxybutyrate biocomposite (PHB), which is environmental friendly biodegradable and nanocomposites to manufacture hydrocarbons plastics in abundant amounts. Nevertheless, *Ralstonia eutropha* improves for somewhat other than PHB yields, like distilled alcohol, methyl ketone bodies, unsaturated fats, and alkyl and *Deinococcus radiodurans* "*polyextremophile*" (Ott et al. 2017) struggle to particle emission, oxidants, and desiccation and resistance to UV. It is capable of withstanding acute irradiation doses and growth under chronic radiation that could accept high levels of heavy metals and radiation. *Deinococcus radiodurans* (Manobala 2019) would be used in iron, copper, silver, and uranium mines to start cleaning up harmful emissions.

Encouraging microscopic organisms as well as other pathogenic microorganisms, small biotechnology specialists, could perhaps help accelerate huge numbers of biochemical processes that are already unaware of "better" species involved in regulating. Tiny microbes mediated procedures have always been constructive in the long run for each other, but they are still worthwhile for everyone else in the biogeochemical cycles, which would include humans in general. Supposedly, those life structures may not even have originated, notwithstanding these ongoing planet inhabitants, and omnipresence would not function habitually. We recognize and comprehend. Microbial communities consequently frustrate our earth's ordinary production processes wobbling. Through most of the physical and biologically-created bioaccumulation technologies, numerous microorganisms have already used. There are excessively voluminous *Bacilli pseudomonads*, and methane bacteria are listed. These minuscule organisms, for instance, facilitate now over trillion cubic meters of industrial wastewater to be manufactured and cleaned occur annually worldwide. Through several stage systems, including autotrophic and heterotrophic digestion, microorganisms such as bacteria promote the elimination of biomass, organic and inorganic derivatives, while materials remove unwanted poisonous, aromatic hydrocarbons, herbicides, insecticides, and environmental pollutants (Yang et al. 2019). Species of *Candidatus Accumulibacter phosphatis* was a potential probiotics biofilms-intermediated bioremediation that is becoming the predominant phosphorus cleaner coordinator (Nurmiyanto et al. 2017). Of significant relevance, these and many other forms of life sometimes monitor the microbial ecological balance even though no individual in the population may circumnavigate another.

As a direct result, "recycling" wastewater is a precious environmental resource through reasonable standards of microbial. It should have been blatantly coherent, and even so are additionally, that microbes are the strongest bio-indicators harvesters, grinders, and compost piles on the globe! Across the whole of fact, humans and other types of life choose their potential to improve them, both physiological and biochemical. For example, in the case, in arthropod earthworm and bed bug specific microbiota involved, therefore, allow each one to utilize it for consumption lignocellulosic materials as well as other plant materials. Probiotics microbiota from time to time even produce insect-specific compounds, which overwhelmingly support their host and promote biodiversity (Zoghlami and Paes 2019). Beneficial bacteria produce natural chemicals and pesticides designed to fight infectious pathogens, and agrochemicals technology implemented throughout cultivation. Sometimes even antibiotics put an end to many bacteria used to remedy pathogens. They also definitely covet them to discourage infectious agents. The significant development of contemporary beneficial microbial communities in agricultural production regularly tends to avoid like using hazardous and potentially dangerous disinfectant and chemical substances without distinction. The microbial biofilms concept of this innovative model for chemical agents and danger to the public confirms that somehow the biosphere isn't even the first synthetic bioweapons to utilize (ASBMB 2018).

The microbial enzyme that efficiently breaks down and decomposes dying forests and deceased human organisms, which used to historically create biomolecules and will successfully lead to the healthy production of each other as well as other organizations. Naturally, almost any type of healthy food in the biosphere today and at the glorious beginning. Nearly anything else in the global economy could produce future profits from these microbial populations effectively (Leonhardt et al. 2019). Scientists wish to give responsibility to something about microorganisms. There could be another probiotics biofilms-intermediated bioremediation "PBIB" species, and bionetwork has several desirable properties that used to benefit both humans and the environment (Maftei 2019). Mitigating or preventing xenobiotic compound toxic effects. Lichen is a microorganism's life form, which could also thrive on a peculiar stone's exposed surface area. Lichen consists of fungal species which split rock to extract minerals, cyanobacteria that mostly absorb light fuel to produce carbohydrates as well as carbon compounds, and cyanobacteria which absorb nitrogen to generate organic nitrogen compounds. They go forward as on its own bases of nutrition, with ragged stone and used oxygen (Dal Grande et al. 2018). Cyanophyta aquatic fern *Scenedesmus*, and *Anabaena, Azolla*, blossoms, and flourishes together in flowering meadow and wetland in all planet. *Anabaena* blue-green photorespiration series, Cells are translucent or monochrome, distinguished, sprinkled with Units defined as organic process vacuoles focus on providing and act appropriately a resource nitrogen synthesis by the aquatic rhododendrons (Pereira 2017).

Integrating sustainability health-conscious bacterial organisms must have undoubtedly had some attractive features which economically exploited for the maximum potential of both human beings and the natural environment. Strategies to mitigate or attempt to prevent xenobiotic compound with their adverse health effects. Subterranean rhizosphere rhizome, and from the other hand, Underground plant roots, as well, synergistic modalities of biofilms known as “Phytobiotics” or plant probiotics) may also work in superior conjunction much more coherently) Ferdous et al. 2019; Menendez and Garcia-Fraile 2017). For example, Endophytic-type bacteria restore atmospheric nitrogen via transforming Nitrogen gas into ammonia. It may simultaneously involve action potentials between some of these exotic plants and in broad-spectrum and particularly the microbiota subsidizing to the considerable expansion of “nodes” impenetrable and exterior the rhizome, where dissolved used oxygen routinely occurs. Then again, the direct connection between the rhizobia and the rhizospheric organisms and adapted plant would adequately represent the most dynamic contractual relationship (Singh et al. 2017b).

The probiotics biofilm intermediated bioremediation efficiently produces, along with several other items, a probiotics biofilm mostly on the sensitive surface of the rhizobia, and therefore also continues to sufficiently develop a responsible multi-stakeholder synergistic relationship that precisely requires there symbiotic organisms to construct biofilms. Then again, Endophytes precious are acutely powerful positive probiotics biofilms biosphere system (Ancheeva et al. 2020). The endosymbiotic community “Biotic components of microbial endophytes Inhabitants” of probiotics biofilms association with synergistic effect with other rhizospheric organisms—root microbiome, mycobiome, and invertebrate which are unique ecological zones of depleted soil that near to root system—are developmental tool drugs for the acute treatment of various complex illnesses with potential applications in sustainable agriculture, pharmaceuticals, used food, and personal hygiene products (Mashiane et al. 2018). Maybe that is why they need organic farming probiotic microorganisms to focus not only through guidelines recommended benefits but its direct impact on the farming community as well. A twofold availability of probiotics for publics approaches, one through direct feed (blended into a meal) and the other through dilute water with organic matter). Utilization as the direct feed approach improves efficiency and effectiveness nutrient by incorporating probiotic ingredients and dissolution throughout the diet. This way impacts feed quality by integrating them into metabolites that assimilated inside the gut. Consequently, probiotics increasing biomass production enhance mineral bio-availability, escalating fatty acid metabolism, and rising growth performance, towards the nutrient (Wanka et al. 2018). One main reason to progress enhanced productivity of the Soil mantle “Pedo-sphere” must efficiently be through the used implementation of organic matter by probiotics as green organic biofertilizers, and biomass dependent products. In the diverse types of natural bio-based products of agricultural and domestic operations, it is essential to naturally stimulate meaningful amounts of organic or biofertilizer, manufacturing sector, and waste management (Teng and Chen 2019).

Potential biofertilizers or probiotics biofilms intermediated bioremediation intermittently used to undoubtedly constitute biomass technological innovations, boosting the biodegradation of the organic components, that most positively impact plants biomass on contaminated soil a deliberate process as well-known by biodegradation and in agricultures fields by the potential application of Integrated bio-enhanced coffee stirrer organic fertilizer with bio-stimulants coalitions naturally appears to willingly offer a dual opportunity: aiming accurately to improve tremendously the microstructure of soils microorganisms, rheological properties, physiochemical characterization and continuing eagerly to progressively increase the specific content of microbial biomass, upturn organic matter in the exposed soil and personal recovery for soil fertility (Menénadez and Paço 2020). Rhizoremediation is a mechanism where living organisms eliminate rhizospheric topsoil harmful emissions and xenobiotic. Rhizosphere ecobiome that mostly propagate plant growth and development have recovered the infertility complications land for enhancing crop productivity. Rhizoremediation using the root system with sustainable synergism to build up microbiome associations with organisms like Nematodes and earthworm. These invertebrate and plant interconnected with microbial biodiversity to boost hypertrophic degeneration of potential pollutants (Vergani et al. 2019). This property indicates a direct interface between probiotic and bioremediation.

Probiotics provide their host with great benefits. When probiotics handed in sufficient quantity and quality (humans, animals), microbial remediation results in biostimulation of microbial diversity through enough concentration and responsible for diverse range with health benefits, for example, protective effect, ecological benefit, competent size, nutritional value, and rehabilitation of contaminated living beings. The solutions indicated are indeed reasonably cost-effective, straightforward to use, and extremely adaptable for all numerous types of aqueous solution functional groups are convenient (Villela et al. 2019). Chromium is a natural element in the earth's crust and emitted by changing weather patterns into the ecosystem. Bio-eradication of contaminated soil by bioaccumulation and detoxification of hexavalent atomic number 24 "chromium (Cr(VI))," two *Bacillus cereus* species endure extremely resistant strains with reduction potential. Both strains are naturally hyper-entrapment in sodium alginate with diatomite function as more than just a micro-protective agent to mitigate emotional complexities and merely enable bio-absorption, and biotransformation toxic hexavalent chromium to chromium (III) endurance beneath 8 mM 99.9%, that being the case these used species typically displayed high pH and temperature adaptability. *Bacillus* was cautiously removed from Hexavalent chromium in culture in 24 h. It is the most outrageous efficient removal in the historiography that has been seeing until just now (Li et al. 2020).

The highest possible bioaccumulation of 3.562 mg Cdg-1 of cells from the water phase in *Lactobacillus Plantarum* strain HD 48 had shown. The Cd bioavailability through in vitro gastric model diminishes by such culture between 24.71 and 41.62%. In this understanding, probiotics strain *lactobacillus* has the potential to manage and sizeable experience to process Cadmium from water solution that would otherwise, therefore, evaluated to mitigate the morbidity and mortality of the body for a degree of multidimensional economic benefit (Kumar et al. 2017). Contamination of heavy metals in food products directly impacts public health and safety. Food supplemented with probiotic lactic acid bacteria could indeed shield and immunize livestock and humans from toxic metals, but the pathway about biotransformation adequately resolved. Mice were administered here with *Pediococcus spp*, strain BT36. BT36 suppressed biosynthesis of chromate but after 480 h overnight of non-chromate degradation. Oxidative disruption and reduced histochemical disruption of hepatocyte modified mice. Pro-inflammatory cytokine biosynthesized via (Cr VI), BT36 can attenuate the intestinal permeability and carefully preserve potential Cr toxicity (Feng et al. 2020). Higher plasma concentrations from trimethylamine oxide risk for undesirable cardiovascular factors. Trimethylamine oxide enthusiastically encourages the successful establishment of macrophages and thus motivates coronary artery disease to develop. Dropping iso-antibody of trimethylamine oxide "IATMAO" is auspicious methodology in the social inhibition of the vascular syndromes, at an inspired guess of independent investigators. Then again, typically decreasing the dietary supplement originators of "IATMAO" is both improbable and risky. Nonetheless, modulation of the gut by biotransformation to breakdown and preventing trimethylamine synthesized. Unconventional bioremediate of trimethylamine in situ the human gut into an inert compound. Archaeal microbiota has been found suitable to eliminate methylated compounds.

However, some archaea lawfully residing in the human gut may realistically achieve this conversion by efficiently producing methane as a metabolic by-product. We enthusiastic endorse economic theory that specific distinctive archaeal microbiota for forthcoming bioremediation. Glorious blossom unsurprisingly in the gut is succeeding brilliantly generation prospective bioremediation probiotics (Brugère et al. 2018). Just in the similar approach for bioremediation, where new studies are illuminating the ways in which environmental contaminants are affecting, and are affected by microbes. Le and Yang (2019). Showed an exploration on the assessment of two Strains of *Pediococcus pentosaceus* obtained from the fermented aquatic fish as well as then taken into practical consideration extremely significant resistance to Cd. Virtually all species documented resistant to the human intestinal tract. These varieties claimed to have become innovative, effective chelation to prevent and manage cadmium cytotoxic effects in the bodily organism. Cd′s adhesion to bacterial cells characterized by continuous presence on the cell surface of various binding sites includes carbonyl, amine groups, and phosphate. For appropriate responding in situ digestion model, Cd bioavailability dramatically reduced by 44.7–46.8%.

23.8 Micronano-Remediation: For Safe, Protected and Hygienic Macro-ecosystem

A short time ago, Biotechnology of bioaugmentation and biostimulation are essential tools for applications of bioremediation (Titah et al. 2019). For undoubtedly enhancing microbial population at an active site to progressively improve contamination cleanup and sufficiently reduce local time, for the biodeterioration and eradication of dangerous chemical contaminants were increasingly desirable because of their rising resistance to adverse environmental stress. Environmental bioprocess is the most suitable strategy in which positive impacts of the microbial population are widely used as a therapeutic agent, up to the current date. Amicrobial probiotics attack" novel approach naturally create eco-friendly bio-Nano composite components (Durazzo et al. 2020). Sustainable power for enhancing complex bioremediation process of contaminated waters, soils, and poisonous gases. The potential application of functionalized bio preparation constituents. Biodiversity of microbiota provides inherent prospective capacity in bioprocessing development and bio-manufacturing for nanoparticles. Microbial green synthesis of nanoparticles (Ezzeldin 2020) ordinarily has, however, emerged nano-biotechnology multidisciplinary field business (Baptista et al. 2018).

To understand molecular switches, in addition to critical factors genuinely needed to adequately control the specific dimension, complex nature, crystal arrangement of nanomolecules, and molecular tool that intermediate microbial bio-production of nanoparticles progressively improve the unique situation. In actuality, biological processes continue being relatively unexplored. Nanotechnologists use beneficial living organisms for the synthesis of prospect nanomaterials. A sophisticated and engrossing methodology for manufacturing "more eco-friendly" agricultural products and novel materials is the fermentation of metallic nanoparticles through biomass feedstock microbial communities to the ultimate bio-based invention. Depth insight into biogenesis pathway and upcoming opportunities afford by recombinant DNA technology. Naturally tend to encourage manual labor into paradigm change and commercial application in micro-biotechnology downstream processing in nano-biosynthesis for possible economic development and effective implementation. Probiotics technology is the cutting-edge, environmentally safe, and cost-effective nano-manufacture material for biosphere bioremediation by nanoparticles. The biosynthetic pathway of ZnO metallic nanoparticles produces by probiotics. Numerous probiotic bacteria seem to be a component to anything other than the prevention of Zn^{2+} human risk of injury. The highest probiotic value obtained for highly resistant Lactobacillus zinc isolates. Zinc oxide nanoparticles formed by particles at the molecular stage (Mohd Yusof et al. 2020).

23.9 Prebiotics Exobioploymer "Membrane - Bound Biopolymer Matrix" (MBBM).

The prebiotics membrane-bound biopolymer matrix biosecreted and released by probiotics microbiota differ by monosaccharide configuration, charge, connection, the prevalence of recurrent side-chains, and replacements. In general, the prebiotics Membrane-bound biopolymer matrix classified into homopolysaccharides (HoPs) and heteropolysaccharides (HePs), prebiotics Membrane-bound biopolymer matrix (MBBM), with vast functional properties and impacts in the field of medicine, pharmaceuticals, bioremediation, treatment of water, and operations. Microbial polysaccharides are versatile, ubiquitous, eco-friendly, robust, parsimoniously low-cost, and pigeonholed into exopolysaccharides formed and retained in the cell, functional or structural polysaccharides and prebiotics Membrane-bound biopolymer matrix (MBBM). The polysaccharide is multi-efficient, Extracellular biopolymer substances industrialized by prokaryotic organisms, archaea & eukaryotes, fungi, and algae. New algorithms have developed nowadays to substitute their microbial models for the conventional usage of vegetable adhesives. Microbial exo-biopolymers mostly used emulsifying agents and biodegradable polymers, and enormous bioremediation application scenarios for reduction of bioaccumulation, biodynamic environmental responsibility, and natural resources used in adverse weather conditions. Membrane-Bound Biopolymer Matrix (MBBM) is positively outer membrane macromolecules and excreted in microbial species as enclosed capsules or densely interconnected biofilm mats. They naturally make a significant contribution to fighting drying, oxidative metabolism, cell identification, phage invasion, antimicrobials, or harmful substances, and osmotic tension. Alive thanks to their functional efficiency, nanoparticles have enthusiastically received considerable interest from modern scientists and academic researchers in the completed last several eons. The MBBM sustainably harvested from probiotic strains regarding multiple different macronutrient compositions in general addition to especially incorporate a comprehensive range of environmental agents. Membrane-Bound Biopolymer Matrix “MBBM” defined as Microbial biodynamic polymeric materials that almost always attach used cells and some other composites around each other (practical sense of active community) to polymer (mechanical strength) in biofilm architectures (cooperation).

23.10 How Ruinous Exobioploymer Are Created in Real World?

Even if you do not recognize the word biofilm, you have frequently seen biofilms. One type of bacterial biofilm, for example, is the plaque that forms on your teeth and causes tooth decay. A biofilm is also the “sludge,” which blockages the kitchen drainage. If you have ever passed across any lake or river, you can even walk on stones colonized with slim association from different biomes known by biofilm. Dangerous potential biofilm a chronic tight spot infection from a sports injury, so it is biological animations, where you want to be.

MBBM microbiomic polysaccharides are a concrete “cement” significant class of biological polymers in living organisms, could therefore generally speaking be reclassified as a sizable amount of intracellular processing highly hydrated biopolymers polysaccharides, functional polysaccharides” glycogen-capsular polysaccharides closely linked to the cell surface and extracellular bacterial polysaccharides are complex heterogeneous macromolecules biopolymers made up of sugar residual and discharged also, called exopolysaccharides (Xu et al. 2020), or extracellular polymeric substance (Orhan-Yanıkan et al. 2020). For example, Xanthan gum is a common food additive sphingan “associates of the genus Sphingomonas”. It uses in numerous food products, additives, and other agricultural sectors. Alginate found in brown algae as carboxylic acids, natural, and foldable nanoparticles that express with nutritional value in the cell walls of the algae (Pereira and Cotas 2020). MBBM is a natural linear, homopolymer, essential for biofilm creation. It is extracellular heterogeneous, long-chain substances, with high molecular weight, and biosynthesized by microbiota. It becomes a critical component to quantify the physicochemical characteristics, functional and structural integrities of biofilms (Pereira and Cotas 2020). It supposed to be medium from polysaccharides and proteins, although macro components, such as DNA, lipids, and humic material. Membrane-bound biopolymer matrix is the building material of bacterial colonies, and bound to the outer surface of the cell or isolated from its medium of development. These nanoscale molecules are vital for the improvement of exobioploymer and the attachment of cells to surfaces. Membrane-bound biopolymer matrix make up 50% to 90% of the general carbon-based content in an exobioploymer (Staudt et al. 2004; Donlan 2002). Owing to the range of membrane-bound biopolymer matrix structures has been used in different nutritional and medicinal industries. Furthermore, enormous procedures have taken towards the identification and manufacture of new, microbial MBBM for medical and industrial applications (Mody 2009).

23.11 Membrane-Bound Biopolymer Matrixomic Biofilm Hypothesis

Microbiota "Commensal, mutually beneficial relationship and infectious agent environmental ecosystems" are categorized in the mainstream of olden times of microbiology as plankton, freely suspended cells, and have been identified nutritional rich media based on their growth characteristics (Sharma et al. 2019). Regeneration of microbial hypothesis that microbe adheres to something and expand spontaneously on open surfaces. Polymicrobial biofilms formation has nanostrategies for everything from the preliminary commitment of materials, densely inhabited network, biodiversity, and differentiation (Catherine and Matthew 2018). Membrane-Bound Biopolymer matrixomic Biofilm is biotic agglomeration that ultimately hooked up with a substrate (not omitted by delicate cleaning). It incorporates in a framework of mainly polysaccharide product. Non-cells, including mineral stones, decay pieces, limestone, sawdust, and fluid resources, identified in the biofilm matrix depend on more than just the environment under which biofilms have accumulated. (Jamal et al. 2018).

Also, organisms that are associated with Membrane-Bound Biopolymer Matrix Biofilm differ in terms of the genes transcribed from their phytoplankton counterparts. Membrane-Bound Biopolymer Matrix Biofilm on a variety of surfaces, including living tissues, medical instruments, piping of industrial or drinking water systems, or natural aquatic systems, can develop. The modifying composition of Membrane-Bound Biopolymer Matrix Biofilm highlight by the evaluation of electronic micrographs from the biofilm industry and healthcare. The harsh restraining effect of biocides and antibiotics on the development of systematized populations of microbiomic cells identified as biofilms can be lethal thru course operation and in the urinary tract contagions (Jamal et al. 2018). There are thousands of victims in US health facilities alone due to disease in the biofilm surgery of the site and urinary bladder (APA 2018; Lo Giudice and Poli 2020).

Membrane-Bound Biopolymer Matrix MBBM immobilized particles of food and clay and other minerals. The substance stuck in the bodily fluid modes nanometric microclimate, every one possessing a distinctly different extracellular matrix, countenancing microbiota that dissimilar prerequisites to instigate together to run through microbiota association (Sapare 2018). The origin MBBM confined microbes involved in the creation of biofilms to make a positive contribution to gene expression. As well they have water networks for nourishment and microbial activity (Pathak and Navneet 2017). Also, the MBBM encompasses secondary metabolites, termed biosurfactants, which might also penetrate water-insoluble surfactant or other xenobiotic mediums quite effectively eco-compatible and the bio-based way during the reclamation and bioremediation progressions (Selvi et al. 2019). The growth and development of Membrane-Bound Biopolymer Matrix Biofilm usually occur via the five successions of biofilm formation: (1) early adherence, (2) unpreventable, and persistent fitting together, (3) growth and development I, (4). borrowings II, and (5) aggregating and redistributing. The biofilms then regularly interact and to metabolize the resulting Membrane-Bound Biopolymer Matrix MBBM and messages for biofilm development. When the signal increased, nutrients decrease, and cells begin to scatter signals. Biofilm formation considerable effort has been eager to pathogenic microorganisms and their toxic effects (Wang et al. 2020).

Inhabitants of biofilms possess interdependent biological and physiological interplay for micronutrients and gene expression interactions between the enrolled bioecosystem and empower against various biotic and abiotic stresses through intense food insecurity, pH, temperature, biocides stress, and/or opportunistic zooplankton (Karygianni et al. 2020). According to its metabolic capabilities to eradicate toxins, adaptive responses and great promise for survival continued to be enhanced especially in the environmental influence, because they had been produced naturally throughout the matrixomic cell, substantial chemical contaminant resistance, and many biological functions. Microbial communities live together in biofilm formation, which acts as naturally produced and environmental mechanisms that are much more powerful and productive than free-bacterial swimming in heavy metals bioremediation (de Carvalho 2018).

23.12 Role of Membrane Bound Biopolymer Matrix “MBBM”

Membrane-bound biopolymer matrix binding impermeable membranes cover and against desiccation (Ghosh and Maiti 2016). MBBM planktonic microbial population used as an affirmative defense against possible violence (Harimawan and Peng Ting 2016). The physicochemical characteristics of microbial cells should be encouraged by the formulations of a membrane-bound biopolymer matrix which can sometimes have a direct or indirect effect on variables that include the cellular recognition, agglomeration, and resistance of the global environment. (Harimawan and Peng Ting 2016). Many bacterial strains that produce lactic acid have a membrane-bound biocomposite network, such as *Lactococcus lactis* subsp. It makes a significant step towards the enzyme hydrolysis of foodstuffs already bioavailable by polysaccharides (Welman 2009). The usage of panettones and others shows the development of a more membrane-binding biopolymer matrix multiplication in textile industries (Ullrich 2009). MBBM Bionetwork: the membrane-binding biopolymer matrix actually encourages nitrogen-fixing microbes anchor to host tissues and groundwater as a mutually dependent mediator (Ghosh and Maiti 2016).

As a result, it tends to be extremely important for endophytic for the supply of nutrients and an important part of terrestrial ecosystems. As a natural product, it appears to be highly advantageous for rhizobia for nutrients availability and essential element for terrestrial ecosystems and established positive penetration of bioactive material through the aisle (Ghosh and Maiti 2016). Bioremediation of noxious metals aided and abetted by bacterial membrane-bonding biopolymer matrix. This is effective in treating wastewater systems, and just biofilm formation entangles and starts to remove metal ions like cope, plumb, nickel, and cadmium (Pal and Paul 2008). The integrating innate predisposition and predictability of membrane-bound biopolymer matrix depending on a polymeric matrix and maybe even some variables such as compositions as well as on capabilities to adsorption capacity metal cation among other substances dissolved (Pal and Paul 2008). Intrinsic rigidity and binding potency of MBBM show a significant effect on the destruction of natural resources from both biological and environmental perspectives. The interrelationship between MBBM anthropogenic and natural environments allow MBBM to have a direct effect on the operation of the environment (Tourney and Ngwenya 2014).

23.13 Engineering Rebellion Proposal

As an environmentally friendly and infrastructural possible solution to mainstream wastewater management become more extremely important. The sectors of the economy give attention to something like the mechanism of microorganisms and their membrane-binding biopolymer matrix in the removal of heavy metals (Biswas et al. 2020). Scientists have discovered that attempting to apply microalgae to industrial wastewater with such a membrane-bound biopolymer matrix helps to remove cadmium. Membrane biopolymer structure can bind and capture of toxic compounds. Hazardous waste infrastructure may enhance by diverse oxidizing agents when applying it to sewage by effectively managing the Membrane Binder Biopolymer matrix (Duque et al. 2019). The MBBM secrete enzymes include oxidoreductase and hydrolase that are capable of dissolving gas, oil, and lubricant (Goel et al. 2020). The capacity of polycyclic sweet-scented hydrocarbon degradation controlled by the consistency of the membrane-bound biopolymer network of the complementary and unclean habitats. The unhygienic habitat contains polynuclear sweet-smelling hydrocarbons from partial burning of carbon-based products such as lubricating oil, manure, industrial debris, and tobacco. *Aspergillus niger* is naturally involved in the potential removal of such toxic compounds polycyclic aromatic hydrocarbons (PAHs) (Balaji et al. 2014).

This effective technique sufficiently demonstrates the comparative comfort of potential application, very successful, and very environmentally friendly (Zhou and Gao 2019; Storey et al. 2018). Over the last few years, biopolymer matrixes of marine bacteria discovered to progressive accelerate the level of remediation of waste oil materials. MBBM produces beneficial bacteria, developed, designed, and implemented, were able to scale up and propagate rapidly during the British Petroleum deep-water horizon explosion. It was investigated and found to dissolve the oil and form oil aggregates in their membrane-binding biopolymers on the surface of the ocean, thus enhancing the performance of cleaning. (Alejandra 2020; White et al. 2020). Many such petroleum products admixtures have offered numerous different aquacultures with a potentially useful source of bioactive compounds. It encourages analysts to identify and facilitate better being used in this environment to evaluate and accelerate the use of the membrane biopolymer matrix for eutrophication, oil slicks, and marine pollution (Alejandra 2020; White et al. 2020).

23.14 Conclusion

Many microorganisms that exist in an unfavorable polluted biosphere may encompass probiotics biofilms-intermediated bioremediation "PBIB" for strengthening sustainability. Many pathogens throughout the infected biosphere can require the intermediate "PBIB," biofilm probiotics, for ecology enhancement. Now become a potential outlet for the solution of numerous biological toxins that they have shown due to dynamic architecture. Suppose it depends mostly on observational data of numerous researches, in situ, and ex situ biological treatment successfully applied to simple or combination microorganisms in specific biosphere. This critique has encouraged development, improvement of different types of microbial probiotic attack in contaminated biosphere by innovating and improving throughout microbial populations' scientific knowledge all over the biosphere. The ecological modernization of sustainable and environmentally friendly technologies in the potential field of environmental parameters developed even further. The macro-ecosystem epigenetic alteration is adequately investigated for the preparation of bio-engineered probiotic attacks and helping better study aquatic habitats and land-residential plans. The role and function of the "Membrane-Bound -Biopolymer Matrix" MBBM in the bionetworks should not be overlooked or over-reported. Their constructiveness and their cognitive ability enabled them to pursue an unconventional and impactful approach. The role of microbial polysaccharides is very important in ecology. While possible problem in microbiology shown. They have not applied omnipresent. In a short period, microbial polysaccharides proved that they make such a dynamic process competitive. In reality, waste management systems are expensive and effective methods worldwide. MBBM has shown the excellent technique to counter biosphere contamination by dyes and heavy metals, one of the most complicated and challenging pollutants to manage, as a consequence rather than the possible effects of successful application of both dyestuff and heavy metals. Based on our historiography evaluated, methodologies with development strategies identified to continue serving as an alternative for the removal of hazardous and material recovery from highly contaminated industrial sites. Therefore, we conclude that probiotics processes and phytoremediation showed astonishing results of a significant reduction in metal levels and toxicity, with minimal disturbance to the biosphere. We almost always suspect that these integration services can be through in situ processes in both industrialized and developing economies where rapid population growth, agricultural development, and industrial development are leaving a legacy of biodiversity loss.

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