Microorganisms for Sustainability 26
Series Editor: Naveen Kumar Arora

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Yogeshvari K. Jhala *Editors*

Microbial Rejuvenation of Polluted Environment

Volume 2

Springer

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Volume 26

Series Editor

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ISSN 2512-1901 ISSN 2512-1898 (electronic)
Microorganisms for Sustainability
ISBN 978-981-15-7454-2 ISBN 978-981-15-7455-9 (eBook)
https://doi.org/10.1007/978-981-15-7455-9

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Preface

Rapid industrialization and to fulfill the increasing demand for essential commodities result in an increase in environmental pollution. Environmental pollution has been a major concern over the past few decades influencing the quality of life. Bioremediation involves degrading, removing, altering, immobilizing, or detoxifying various chemicals and physical wastes from the environment through the action of microorganisms and plants. Microorganisms are widely distributed on the biosphere and due to their metabolic potentiality can survive in a variety of environments. Microorganisms convert, modify, and utilize toxic pollutants to obtain energy and biomass production, thereby restoring the environment and preventing further pollution. Microorganisms act as a catalyst and facilitate enzyme-powered bioprocess technology that degrades the desired pollutant. The process of bioremediation mainly depends on microorganisms which enzymatically attack the pollutants and convert them to inoffensive products. Bioremediation is recognized as an alternative to traditional physico-chemical methods to restore contaminated sites, being a cost-effective, less labor intensive, safe, and environment friendly technique. Microbial bioremediation technology is still less efficiently utilized despite its potential for environmental restoration.

The book entitled *Microbial Rejuvenation of Polluted Environment Volume 2* comprises chapters from distinguished experts and dedicated researchers with methodical and firm outlooks based on their own experiences during their carrier in the field. Efforts have been made to compile the latest information on the present status of microorganisms-based key bioremediation strategies for sustainable environment. The book also provides in-depth insights and scientific linkages as well as evidence, thereby assisting researchers in planning their future line of research. This book will serve as a treasure of knowledge for students, academicians, and researchers as the scholarly chapters help to enrich readers' understanding on the issues related to environmental pollution mitigation strategies keeping microbial life in focus. Each chapter emphasizes on the mechanism of action and recent advances in the techniques for improvement of bioremediation of pollutants. I hope this book will be extremely useful for researchers and serve as a source of information for academicians to develop novel technologies for lab to land to reduce environmental pollution challenges.

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About the Series Editor

Naveen Kumar Arora, PhD in Microbiology Fellow of International Society of Environmental Botanists (FISEB), is Professor and Head, Department of Environmental Science at Babasaheb Bhimrao Ambedkar University (A Central University), Lucknow, Uttar Pradesh, India. He is a renowned researcher in the field of environmental microbiology and biotechnology. His specific area of research is plant-microbe interactions, particularly plant growth promoting rhizobacteria. He has more than 75 research articles published in premium international journals and several articles published in magazines and dailies. He is an editor of 25 books, published by Springer. He is a member of several national and international societies, Secretary General of Society for Environmental Sustainability, in editorial board of 4 journals, and reviewer of several international journals. He is also the editor in chief of the journal "Environmental Sustainability" published by Springer Nature. He has delivered lectures in conferences and seminars around the globe. He has a long-standing interest in teaching at the PG level and is involved in taking courses in bacteriology, microbial physiology, environmental microbiology, agriculture microbiology, and industrial microbiology. He has been advisor to 134 postgraduate and 11 doctoral students. He has been awarded for excellence in research by several societies and national and international bodies/ organizations. Although an academician and researcher by profession he has a huge obsession for the wildlife and its conservation and has authored a book, *Splendid Wilds*. He is the President of Society for Conservation of Wildlife and has a dedicated website www.naveenarora.co.in for the cause of wildlife and environment conservation.

About the Editors

Deepak G. Panpatte has been working as a research scholar for the past 9 years. His main research interest is in agriculturally beneficial microorganisms, such as biofertilizers, biopesticides, and biodegraders. He has also pioneered the development of fortified biocontrol bacterial consortiums with phyto-extracts for the management of phytopathogenic nematodes and fungi. He has received 5 international conference awards for his research, 1 award for Best Ph.D., and the Rashtriya Gaurav Award for outstanding contributions to agriculture. He has published 14 research papers, 5 books and 16 book chapters with Springer, 1 practical manual, 33 popular articles, and 2 editorials. He is also an editorial board member for several respected national and international journals.

Yogeshvari K. Jhala is an Assistant Professor with 11 years of teaching and research experience. Her main research interest is in agriculturally beneficial microorganisms such as biofertilizers, biopesticides, and biodegraders. She was the first researcher worldwide to report on 5 unique strains of methanotrophic bacteria. She has received the All India Best Research Award and Young Faculty Award for her outstanding research on methanotrophic bacteria. Her publications include 17 research papers, 5 books, 12 book chapters, 2 teaching manuals, 24 popular articles, and 2 editorials.

Chapter 1
Bioremediation of Industrial Pollutants

Juhi Sharma, Jyoti Goutam, Yogesh Kumar Dhuriya, and Divakar Sharma

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Abstract Contemporary scientific progress in applying biotechnological tools for environmental management is the emerging field of bioremediation (assisted with microbes) to mitigate the hazardous effluents from the world. The detrimental marvels have resulted in serious environmental and social problems around the world; these problems must be looked after for solutions elsewhere than the

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D. G. Panpatte, Y. K. Jhala (eds.), *Microbial Rejuvenation of Polluted Environment*,
Microorganisms for Sustainability 26, https://doi.org/10.1007/978-981-15-7455-9_1

established physical and chemical technologies. The highly effective microorganisms are cultured for a variety of applications, but still the valuable probable of these microorganisms is vast and untapped in the field of bioremediation and phytoremediation. Microbes act as significant pollutant eradication tools in soil, water, and sediments, chiefly due to their advantage over other remediation procedural protocols. Microorganisms re-establish the original usual surroundings and encumber further pollution.

Keywords Bio-augmentation · Microbes · Obliteration · Effluents

1.1 Introduction

Most environmental oil pollutants such as polycyclic aromatic hydrocarbons (PHAs), petroleum hydrocarbons, heavy metals, and nutrient-rich organics cause deleterious effects due to their inertness and toxicity (UNCST 2009). To address these drawbacks, the best method which suits the complete removal of pollutants is using the bioremediation approach which uses natural biological activities to destroy various contaminants. This is a safer, cleaner, cost-effective, and environmentally friendly technology with a high public acceptance and easily done at any site (Bbosa et al. 2012). Industrial and crude oil contaminants can be degraded with the use of microorganisms and plants in bioremediation processes. Commonly used modern technologies are very expensive, and oftentimes, there is an incomplete degradation of contaminants (Das and Chandran 2011). The term biodegradation has been used to describe the conversion of every type including those that yield products more complex than the starting material as well as those responsible for the complete oxidation of compounds to CO_2, H_2O, NO_3, and other inorganic compounds (Atlas and Bartha 2003). Microorganisms are widely distributed in the biosphere because their metabolic ability is very impressive, and they can easily grow in a wide range of environmental conditions. The nutritional versatility of microorganisms can also be exploited for the biodegradation of pollutants. This kind of process is termed as bioremediation. It is continued through based on the ability of certain microorganisms to convert, modify, and utilize toxic pollutants to obtaining energy and biomass production in the process (Tang et al. 2007).

The past two decades have seen an incredible upsurge in the pursuit of cost-effective and ecologically sound substitutions to the conventional techniques for dealing with wastes (Fig. 1.1). The technologies that have appeared as most capable are those that thoroughly mimics the time tested, natural system that has re-established atmospheres to their original status succeeding unwanted perturbations. The self-restoring procedure in the environment is what has truly given birth to the notion that the self-cleansing capability of the environment is boundless. Of all

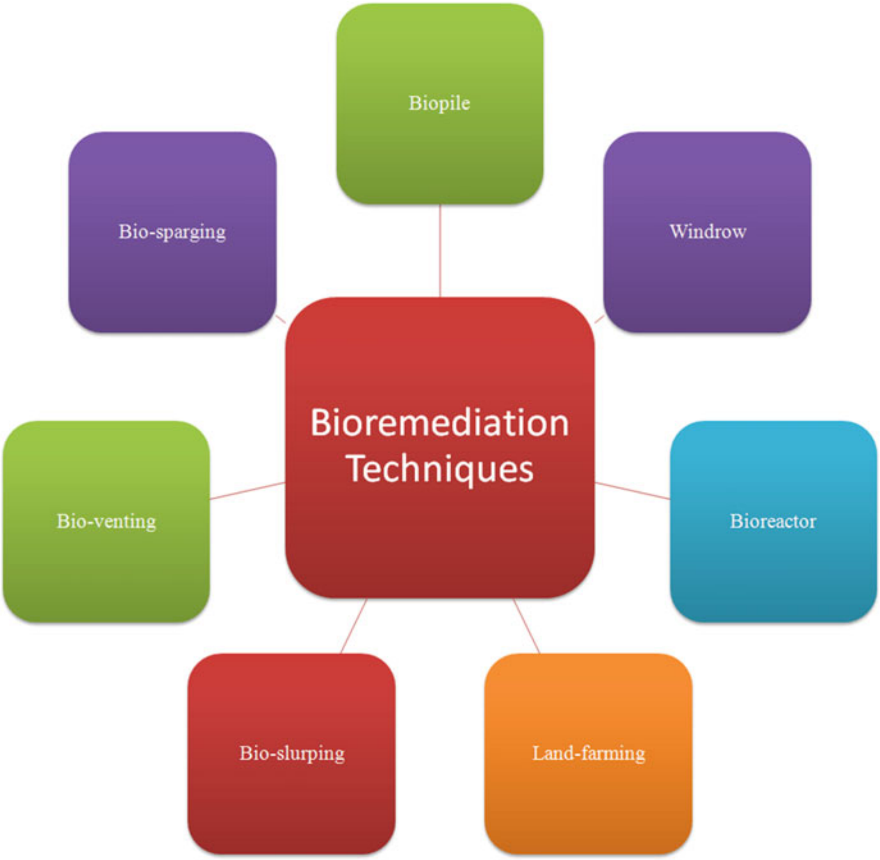


Fig. 1.1 Various methods involved in bioremediation based on microbes or their products

the technologies that have been studied, bioremediation has appeared as the most appropriate method for cleaning up many ecological contaminants in effluents.

1.2 Ecosystem and Acquisitive Pollution

The first and exceedingly affected ecosystems in any nation are the aquatic ecosystems, influenced by either point or non-point cause of pollution. Point sources of pollution transpire when the polluting substance is discharged straight into the waterway. The traditional point sources of pollution are municipal and industrial wastewater effluents, run-off and leachate from solid disposal sites, run-off from industrial sites, run-off and drainage from industrial sites, and discharge from vessels. The non-point sources cover the course of water from agricultural fields and orchards, urban run-off from underwired areas, etc. The consequences of water pollution are devastating to not only the aquatic organisms but also the terrestrial animals and birds. More seriously, contaminated water damages aquatic life and diminishes their reproductive capability. Eventually, the water grows unfit for human consumption or domestic usage, in severe circumstances even a danger to human well-being. Waste disposal has an environmental cost and a financial cost too, which can be lessened by the application of bioremediating agents (Pillay 1992). To speed up the bioremediation process, seeding of contaminated wastewater with competent microflora that signifies the capability of degrading precarious waste is ordinarily practiced in most treatments. The inoculated and injected microorganisms may be either spontaneously occurring varieties or prepared in the laboratory to engage the target waste.

1.3 Apprehensions of Bioremediation

One of the major concerns of bioremediation is its compatibility amidst the principal natural biogeochemical cycles and recycling routes of the earth and marine ecosystems, which make bioremediation a sustainable and environmentally eco-friendly strategy for cleaning up the polluted environments (El Fantroussi and Agathos 2005). This biotechnology employ living organisms or biological elements to achieve the biodegradation of complex organic contaminants over other more simplistic organic compounds into carbon dioxide, water, inorganic compounds, and cell protein (Das and Chandran 2011) (Kumar et al. 2011).

Most of the organic substances and several inorganic ones are subject to enzymatic attack through the activities of living organisms. Most of the modern society's environmental pollutants are incorporated among these chemicals, and the effects of enzymes in them are ordinarily lumped beneath the term biodegradation. The prolific use of biodegradative methods to exclude or detoxify pollutants that have obtained their access within the environment and imperil public well-being, frequently as contaminants of soil, water, or sediments is bioremediation. Bioremediation can occur naturally or can be encouraged with the addition of microbes and fertilizers (Thapa et al. 2012).

Pollutants can be transformed into biodegradable forms through bioremediation process. This acts as an option to clean the environment and its resources by destroying various contaminants using natural biological activity. It is considered as safer, cleaner, cost-effective, and environment-friendly technology which generally has high public acceptance and can often be carried out at any site. Pollution and deterioration of the environment keep on progressing at an alarming rate due to the activities of humans such as urbanization, technological advancement, hazardous agricultural practices, and accelerated industrialization which deprive the environment. Heavy metals liberated into the environment are persistent due to their toxicity which postures a critical threat to organisms revealed to soaring levels of such pollutants. Metals are necessary for the biological purposes of plants and animals, but at raised levels, they intervene with metabolic reactions in systems of organisms.

Environmental pollution created the need to search for new environmentally friendly, low-cost, and more efficient environmental clean-up techniques for its removal or reduction (Hlihor et al. 2017).

India is the second-largest exporter of dyestuffs, where ~80,000 tons of dyes and orpiment are produced yearly (Saraswathi and Balakumar 2009). There are beyond 100,000 varieties of dyes such as acidic, basic, reactive azo dyes, etc. available in the market (Daneshwar et al. 2007). The textile dye effluent contains heavy metals such as cadmium, lead, and zinc either in free ionic metals or complex metals (Hill et al. 1993). There exist numerous traditional physicochemical processes like precipitation, ion exchange, electrowinning, electrocoagulation, cementation, and reverse osmosis for the elimination of heavy metals from the industrial effluents. But all these techniques are very expensive and require skilled professionals. Hence, bioremediation, especially microbial bioremediation, is established as an efficient, eco-friendly, and affordable technology for the elimination of heavy metals from the textile dye effluents.

1.4 Microbial Communities and Toxic Waste

Biogeochemical cycles are guided by the metabolic activity of microbial communities capable to counter toxic wastes from entering the biosphere (Li et al. 2013). Scientists are dealing with a consent to reduce the release of toxins and to alleviate their effects resolved by living organisms such as plants, an approach known as phytoremediation (Conesa et al. 2012), or by microbes which are amalgamated under the generic term bioremediation. Further characterization and strategic biosafety appraisal of various harmful ecosystems like sewage sludge, nuclear waste, land mines, surface wastewater, sub-surface groundwater, and agricultural soils must be taken into account (Wang et al. 2012). At the same time, genetic pollution of the aforesaid ecosystem through transgenic bacteria must not be ignored (Singh et al. 2011). Toxicity of metals to an organism can be defined as the peculiar capability or ability of a metal to cause adverse effects on living organisms and depends on the bioavailability of the metals (Rasmussen et al. 2000). Lead, one of the most persistent metals, has a soil retention time of 150–5000 years. The moderate biological half-life of lead has been predicted to be 18 years, and 10 years once in the human body (Gisbert et al. 2003). Some redundant elements (e.g., As, F, Cd, Hg, and Pb) are highly toxic to biota even at very small concentrations (MoEF 2011). Once a pollutant is introduced into a living organism and attains its target site, it may exhibit a pernicious action. The effect of the pollutant is accordingly a function of its concentration at the locus of its response. Metal toxicity turns into more severe in the acidic medium, nutrient-deficient ecosystem, and poor physical surroundings (Mukhopadhyay and Maiti 2010). Mukherjee et al. (2008) reported industrial emissions of mercury from coal combustion, iron and steel industry, nonferrous metallurgical plants and chlor-alkali plants in India. Industrial effluents without treatment are sometimes directly drained into wetlands water lands and estuaries. Additionally, mercury can accrue in animals as methyl mercury, dimethyl mercury, or other organo-mercury salts. A high level of arsenic in water affects a great risk to animals, plants, and human health (Yin et al. 2012). The flooded paddy fields initiate a reducing environment or oxidative stress and acquire high levels of As III (Meharg et al. 2009). Arsenic contaminated groundwater is distributed for drinking water, domestic water supplies and irrigation of many crop fields, particularly rice (*Oryza sativa L*), in Indian. The World Health Organization (WHO) has observed that arsenic contamination from over 70 countries affect the health of approximately 150 million people across the globe. This situation is causing fear in Bangladesh and the eastern states of India, and the WHO has called this situation as the "worst mass poisoning" event in human history (Hassan, 2005).

1.5 Assets of Toxin and Human Health

Plasticizers are broadly used industrial chemicals, serving as additives in polyvinyl chloride, polyvinyl acetate, cellulosic, and polyurethane resins and convey flexibility and workability (Brown et al. 1996). These compounds are released to the environment through production, manufacturing, use, and final clearance, and, as a result of extravagant use of plastics, plasticizers are one of the powerful sources of environmental toxins (Zeng et al. 2009). Phthalates and adipates, the most exploited plasticizers, are chemicals that display hydrophobic and lipophilic aspects and influence to accumulate in soils. The higher phthalates such as di-ethylhexyl phthalate (DEHP) intrude with the progress of reproductive organs by acting as a resemblance of the sex hormone estrogen (Swan 2008). Pollution by uranium from mining activities is expanded in surface and ground waters across the world, and the ramification of this is not only detrimental to the health of the natural surroundings, considering they also have a burden on human health (Romero-González et al. 2016).

In the past, it was reported that the water-soluble portion of the aromatics and polyaromatics was the most adverse, and therefore, these compounds were the molecules for considering in toxicological studies. They are presumed to be mutagenic, teratogenic, and carcinogenic (Keith and Telliard 1979). More than ever the polyaromatic hydrocarbons with four or five rings are known carcinogens (Cerniglia 1992). The non-aromatic substances in the petroleum were not studied very noxious, and alkanes and cycloalkanes are now also taken into consideration (Peterson, 1994). Hydrophobic hydrocarbons are poisonous for microorganisms by accretion in the membrane, which creates the trouble of membrane integrity (Sikkema et al. 1995).

1.6 Role of Microbes

Microalgae are used in wastewater bio-treatments (Oswald 1992), as food for humans and animals (Becker 1992), as feed in aquacultures (Lora-Vilchis et al. 2004), for the production of pigments (Johnson 1995), and in agriculture. Some bacterial strains such as *Bacillus cereus, Pseudomonas putida, Pseudomonas fluorescence* (Khehra et al. 2005) *Pseudomonas desmolyticum* (Kalme et al. 2009) and *Bacillus* species (Gomaa 2012) have been used in the biodegradation of azo dyes. These microbial consortia were suggested for environmental remediation to disgrace different types of pollutants (Gomaa 2012). Different types of microorganisms can be used for bioremediation including bacteria, archaebacteria, yeasts, fungi, algae, and plants. The microorganism can clean the oil-polluted environment because of their potential to degrade, and such active microorganisms can be recommended in high numbers for treatment (Singh et al. 2013).

Genetically modified microorganisms have also been used as a remediation technique (Poirier et al. 2013). Genetic engineering and chemical modification could modify the components of cells surface and can expertly enhance the adsorption capacity and selectivity to target metal species. Several environmental factors that influence and reduce bioremediation efficiency include temperature, pH, redox potential, nutritional status, moisture, and chemical composition of heavy metals (Shukla et al. 2013). The function of microorganisms has completely shown limited efficiency owing to many factors including less competitiveness as well as excessive heavy metal concentrations. Effectiveness can be improved by various alterations with inorganic nutrients, biosurfactants, bulking agents, and compost as well as biochar (Wiszniewska et al. 2016). These modifications have been comprehensively revised in the latest study (Truu et al. 2015).

1.7 Microbial Solution

Numerous enzymes linked with the treatment of PPME are lignin peroxidase, manganese peroxidase, and laccase (Malaviya and Rathore 2007). Microorganisms exhibiting good production of these enzymes possess the strength to treat the toxicants (Demnerova et al. 2005). Fungal systems feature to be most similar in the treatment of dyed and metallic effluents (Ezeronye and Okerentugba 1999). In this domain of fungi, *Phanerochaete chrysosporium* has arisen as a basic system in textile, polycyclic aromatic hydrocarbon (PAH), and pulp and paper mill effluent remediation. *P. chrysosporium* is a basidiomycete fungus capable of degrading complex compounds such as starch, cellulose, pectin, lignin, and lignocelluloses, which are components of textile effluent. It is also viable to decolorize azo-triphenyl methane dyes by its lignin peroxidase enzyme. *P. chrysosporium* is also adequate of generating extracellular enzymes like manganese peroxidase. It is very powerful in the de-colorization of textile effluent.

Generally known microorganism such as *Achromobacter, Alcaligenes, Arthrobacter, Bacillus, Acinetobacter, Corynebacterium, Flavobacterium, Micrococcus, Mycobacterium, Nocardia, Pseudomonas, Vibrio, Rhodococcus*, and *Sphingomonas* species are involved in the process of remediation (Gupta et al. 2001). The prime species associated with persuasive wastewater treatment constitutes lactic acid bacteria, *Lactobacillus plantarum*, *L. casei*, and *Streptococcus lactis*, and photosynthetic bacteria, *Rhodopseudomonas palustris, Rhodobacter sphaeroides*, etc. (Narmadha and Kavitha 2012). *Arthrobacter* sp. was first isolated from the natural habitat which can degrade nitrogen by heterotrophic nitrification process (Verstrae and Alexande 1972). There is a growing interest in anaerobic bacteria utilized for bioremediation of polychlorinated biphenyls (PCBs) in river sediments, dechlorination of the solvent trichloroethylene (TCE) and chloroform (Derek 1995). *Enterobacter cloacae* utilized the TNT as a nitrogen source for its growth. The pentaerythritol tetranitrate reductase, an enzyme interpreted to be included in the degeneration of nitrate esters is convenient to abate the aromatic ring of TNT and induce the liberation of nitrite (French et al. 1999). Endosulfan, a pesticide residual, is extremely noxious to fish and aquatic invertebrates. It can comply with soil particles and furthermore remains for a comparatively longer duration, with a half-life of 60–800 days. Bacteria such as *Pseudomonas* sp. and *Arthrobacter* sp. can degrade up to 57–90% of α-endosulfan and 74–94% of β-endosulfan in 7 days.

1.8 Registered Microbial Remediation

The first patent for a biological remediation agent recorded in 1974 is a strain of *Pseudomonas putida* that was capable of degrading petroleum. Various studies reveal 42 diverse pollutants including black liquor from a kraft pulp and paper mill effluent, tannery effluent, steel industrial effluent, etc., can be biodegraded by employing *Pseudomonas* sp. (Prescott et al. 2005). In the presence of oxygen, aerobic bacteria such as *Pseudomonas, Alcaligenes, Sphingomonas, Rhodococcus,* and *Mycobacterium* are competent in degrading pollutants. These microorganisms deteriorate pesticides and hydrocarbons, both alkanes and polyaromatic compounds (Fig. 1.2). Several of these bacteria employ contaminants as the only source of carbon and energy (Boricha and Fulekar 2009). Pure culture of *Exiguobacterium aurantiacum* holds the ability of phenol degradation and PAHs in batch culture when presented with pure compounds as a source of carbon and energy (Jeswani and Mukherji 2012). Different researches reveal that *Pseudomonas* sp. acts as fuel-consuming bacteria which can degrade the hydrocarbons (Jayashree et al. 2012). Biological phosphate elimination in the activated sludge method was first reported by Levin et al. (1972). *Acinetobacter* sp. was the first bacterium that has held responsible for phosphate elimination. *Microlunatus* sp., *Lampropedia* sp., *Tetraphaera* sp., *Aeromonas* sp., *Vibrio* sp., and *Pseudomonas* sp. also play a crucial part in the phosphate removal method. Mayer (1991) compared aerobic with

Fig. 1.2 Potential of various microbes involved in bioremediation of xenobiotics

anaerobic treatment of wastewaters in German brewery and reported that anaerobic treatment accomplished 91% COD reduction at loading rates up to 20 g COD/l/day, whereas the aerobic treatment resulted in a 76% reduction at a loading rate of 69 g COD/l/ day. *Pseudomonas* sp. and *Brevibacillus* sp. were nitrate-reducing bacterial strains isolated from petroleum-contaminated soil (Grishchenkov et al. 2000). The most frequent bacteria that carry out ammonia oxidation is *Nitrosomonas* sp., while nitrite oxidation is carried out by *Nitrospina*, *Nitrococcus*, and *Nitrocystis*. Biological treatment by autotrophic nitrogen removal is favored for concentrated wastewater streams with high ammonia concentrations in the range of 100–5000 mg N/L (Mulder et al. 2003). The oxidized nitrogenous compounds (nitrite to nitrate) are reduced to gaseous nitrogen by heterotrophic microorganisms that utilize nitrite or nitrate rather than oxygen as an electron acceptor and organic matter as carbon and energy source. Denitrification is common amid Gram-negative bacteria such as *Pseudomonas, Alcaligenes, Paracoccus*, and *Thiobacillus*. Denitrification is the slow method especially for industrial wastewaters that comprises high concentrations of nitrate. Microorganisms with diverse catabolic versatility use organic pollutants as their energy source and tear down those pollutants into non-toxic intermediate compounds. Bioremediation strategy obtains further consideration due to its cost-effectiveness and diverse metabolic versatility of microorganisms associated (Pandey et al. 2007).

Microorganisms (bacteria/fungi) are the most prominent eco-friendly agents for the degeneration and detoxification of industrial toxic wastes throughout the biological processing of industrial wastewaters. Therefore, bioremediation is an alternative to traditional chemical and physical techniques for wastewater treatment. A fungus is recognized to endure heavy metals. They are a versatile group, as they can adjust and develop under several extreme conditions of pH, temperature, and nutrient availability, as well as high metal concentrations. They extend the benefit of possessing cell wall material which exhibits excellent metal-binding attributes. Chromium toxicity is also one of the principal causes of environmental hazards created by tannery effluents. Chromium exists in numerous oxidation states (I–VI), more stable as Cr (III) and Cr (VI). Cr (VI) is the toxic form of the element 6 which causes severe diarrhea, ulcers, eye and skin irritation, kidney dysfunction, and probably lung carcinoma. Traditional techniques for eliminating toxic Cr (VI) involve chemical reduction accompanied by the precipitation under alkaline circumstances, ion exchange, and adsorption on activated coal, alum, kaolinite, and ash (Sharma and Malaviya 2014).

Utilizing the heterotrophic bacteria revealed the tremendous potential of wastewater and industrial wastewater, bioremediation of soil and water, detoxification of chemical waste, biofertilizers, and food, feed, and fuel industries. The combination of the activated sludge treatment of municipal wastewater is comprised chiefly of microbes like *Pseudomonas, Flavobacterium, Alcaligenes, Acinetobacter*, and *Zooglea* sp. This association of bacteria is fundamentally involved in the biological treatment of municipal wastewater, and the presence of organic constituents in the aerobic system promotes the growth of heterotrophic in the interference of the oxidation of ammonia.

Heterotrophic microorganisms encounter favorably oxygen because of a lower growth rate and exchange of nitrifying microorganisms. *Pseudomonas pseudoalcaligenes*, when introduced in contaminated regions may unfavorably influence more elevated concentrations of tributyl phosphate, practice it as the exclusive carbon source. *Pseudomonas* is accountable for the efficient elimination of chemical oxygen demand, biochemical oxygen demand, and at some degree also ammoniacal nitrogen removal activated sludge. Throughout the nitrification process, chemical consumption of oxygen is eliminated from 95% to 60%, and nitrification varied from 65% to 25%. *Bacillus, Achromobacter, Pseudomonas stutzeri, Pseudomonas putida, Pseudomonas mendocina, Zooglea remigera, Arthrobacter, Alcaligenes faecalis, Flavobacterium, Micrococcus,* and *Rhodococcus* species are some of the common microorganisms utilized in the decontamination process (Shah 2016).

Hydrocarbons degrading microorganisms are widely disseminated in soil habitats. Numerous researchers consider that several bacteria isolates are proficient in degrading PAHs of particular note. *Escherichia coli*, *Alcaligenes* spp., and *Thiobacter subterraneus* were effective isolates for degrading anthracene and phenanthrene. Few microbes of genera *Pseudomonas* and *Mycobacterium* have been observed to be capable of transforming and degrading PAHs under aerobic circumstances (Mrozik et al. 2003).

Bioremediation, the use of microorganisms or microbial procedures to destroy ecological pollutants, is amid these fresh technologies (Fig. 1.2). Bioremediation has various applications, including clean-up of groundwater, soils, lagoons, and sludges and process waste streams (Rajasulochana et al. 2009). Bioremediation, the application of microorganisms or microbial processes, is one of the modern technologies. It has been proven flourishing in various applications, mainly treating petroleum-contaminated soils. Bioremediation tactics for typical hazardous wastes are presented in Brar et al. (2006).

1.9 Bioremediation as Economical Substitute

Bioremediation is a general concept that involves all those processes and activities that take place to biotransform an ecosystem, already altered by contaminants, to its initial state (Thassitou and Arvanitoyannis 2001). Although the processes that can be applied to obtain the aspired outcomes vary (Iwamoto and Nasu 2001), they still possess the same principles, i.e., the application of microorganisms or their enzymes that are either indigenous (stimulated by the addition of nutrients or optimization of conditions) or scattered within the soil. For this purpose, bioremediation signifies a significant environmental remediation strategy because it:

- Harnesses naturally occurring biological processes.
- Terminates or immobilizes pollutants rather than transports them from one environmental medium to another.
- Preserves financial resources due to reduced clean-up times and/or cheaper capital expenditures contrasted to several other remediation technologies.

A crucial factor in any biotransformation application is the procurement and improvement of a suitable biological catalyst. This might necessitate the utilization of several microbiological and biochemical engineering and, especially, molecular technologies. Thus, the investigations of biodiversity and/or molecular engineering are essential measures in the procurement of novel enzyme activities. The majority of enzymes currently being implemented or developed for biotransformation are microbial in origin and the field of molecular genetics has contributed considerable scope for the isolation and manipulation of enzymes to produce biocatalysts with predetermined characteristics (Chiacchierini et al. 2004).

Several procedures are used to treat textile discharges, which consist of physicochemical approaches, such as filtration, coagulation, activated carbon, and chemical flocculation (Gogate and Pandit 2004). These methods are costly and produce a secondary discarding problem; however, microbial degradation is an ecofriendly and economical substitute for chemical treatment (Verma and Madamwar 2003).

Bioremediation denotes the optimization of naturally happening remediation processes carried out by living organisms that destroy, modify, or eliminate toxic biological compounds (Van Hamme et al. 2003). This biological approach depends on the catabolic activities of organisms and on their capability to contribute to the degradation of pollutants of organic origin when using them as a source of food and energy (Pilon-Smits 2005). The application of bioremediation techniques is an alternative for the removal of non-treated wastewater during crop irrigation; the proficiency of bioremediation techniques depends on several aspects that should be well thought out when selecting a treatment that renders the water quality that satisfies the requirements of crops.

Bioremediation is practiced for the recovery of environmental contamination through the optimization of several living organisms (plants, fungi, and bacteria, for instance) which are capable to exclude, degrade, or transform toxic organic compounds into harmless or less poisonous metabolic products (Van Hamme et al. 2003). Phytoremediation, electro bioremediation, leaching, chelation, methylation, and precipitation are some of the usual bioremediation procedures (Martínez-Prado et al. 2011). Phytoremediation consists of the application of plants and associated rhizosphere microorganisms that may support the recovering contaminated water, soil, and sludge. This biotechnology can be practiced in situ which neither are expensive nor has secondary consequences and consequently is an environmentally and ecologically friendly technology (Delgadillo-López et al. 2011). Phytoremediation includes mechanisms that reduce, in situ or ex situ, the concentration of certain poisonous compounds through physiological and biochemical processes performed by plants and microorganisms that eliminate (phytoextraction, phytodegradation, or phytovolatilization) or immobilize (phytostabilization and rhizofiltration) pollutants from soil or water (Bernal et al. 2007). It should be noted that not all of these mechanisms are adopted in the phytoremediation of wastewater (Delgadillo-López et al. 2011).

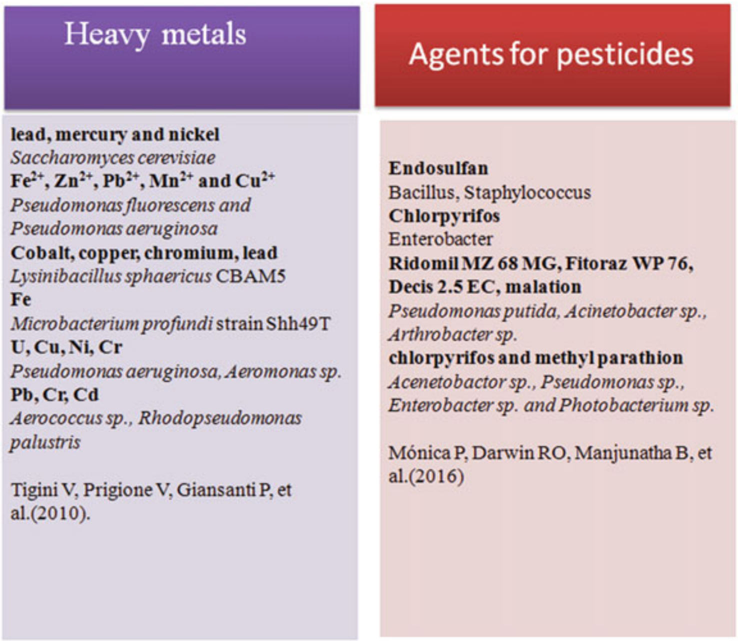
The bioremediation process utilizes multiple agents such as bacteria, yeast, fungi, algae, and higher plants to treat oil spills and heavy metals recognized in the environment. It is extremely essential to employ biological sources because of their capacity to multiply and increase in terms of initial inoculum as compared to physical and chemical treatment means (Bhatnagar and Kumari 2013). The inoculums can be a mixture of non-indigenous microorganisms from different contaminated environments especially selected and cultured for their various pollutant deteriorating characteristics or a composite of microorganisms selected from a site in need of cleaning or can be mass cultured in the laboratory (Bhatnagar and Kumari 2013). Two or more remediation techniques can be practiced to increase the effectiveness of bioremediation in a harshly polluted environment (Gao et al. 2014). The addition of nutrients simultaneously with the seeding process has revealed enhanced outcomes for bioremediation (Boopathy 2000). Many researchers have developed several technologies to treat pollution from the lessons learned from successive studies and practices of the bioremediation process. The most appropriate example is the research performed by (Warr et al. 2013), which is based upon the previous limitations of using direct application of nutrients to the oil spills to fertilize hydrocarbon oxidizing bacteria where nutrients could immediately dissolve in open marine waters.

Bioremediation technology is categorized as ex situ or in situ, whereby in situ bioremediation includes direct utilization of the bioremediating agents (microorganisms or plants) on contaminants at the site of pollution. Ex situ bioremediation is where a poisonous substance (pollutant) is obtained from the contaminated site, and the selected series of microorganisms carry out the biodegradation at the appointed point. This is an enhanced method over in situ since the bioremediating agents that clean up polluted sites are examined for their natural ability to competently biodegrade compounds.

The use of bioremediation to clean oil contaminants was started after the realization of its accomplishment with oil transporter Exxon Valdez oil spill (Atlas and Hazen 2012). Oil spill bioremediation can be completed with the use of microbes with high metabolic rates and simply adjust to the exposed atmosphere to guarantee extraordinary oil biodegradation rates. Significant ecological factors are suitable nutrient concentration, for instance, nitrogen is one of the biodegradation inhibitors of hydrocarbons in soil, the manifestation of oxygen and optimal pH. There are diverse techniques of performing oil spill bioremediation, which consist of bio-augmentation. It is a procedure where the microbial population is enhanced by the oil-degrading bacteria, whereas biostimulation is where nutrients or other growing stimulating constituents are supplemented when growing the original degraders (Whang et al. 2008). Bioaugmentation decreases the adaptation time of microorganisms but significantly escalates the biodegradation rates (Szulc et al. 2014). Phytoremediation is similarly a significant technique in bioremediation procedures where rhizospheric microorganisms are used generally in the hyper-accumulating plants. A microalga has a benefit that it comprises greater biomass production than terrestrial plants. Still compared to terrestrial plants, microalgae need a lower amount of water elimination and can be cultured in brackish water, microalgae require only sunlight and few simple nutrients such as nitrogen, phosphorus, and carbon (Aslan and Kapdan 2006).

Bioremediation is employed to convert poisonous heavy metals into a less injurious state using microorganisms (Ndeddy Aka and Babalola 2016) or its enzymes to clean up contaminated environment (Okoduwa et al. 2017). The method is ecologically friendly and economically effective in the replenishment of the environment. The bioremediation of heavy metals has some restrictions. Among these are the production of poisonous metabolites by microorganisms and the non-biodegradability of heavy metals (Fig. 1.3). The direct use of microorganisms with unique characteristics of catabolic potential and their products such as enzymes and biosurfactant is a fresh approach to improve and boost their remediation effectiveness (Le et al. 2017). Diverse substitutes have also been estimated to expand the applications of microbiological methods toward the remediation of heavy metals. For example, the use of microbial fuel cell (MFC) to degrade intractable heavy metals has been discovered. Biofilm-mediated bioremediation can be applied for cleaning up of the heavy metal-polluted environment.

Bioremediation is the process in which biological wastes are organically degraded under controlled settings to a harmless state or levels underneath concentration limits recognized by supervisory establishments. The term mineralization is the ultimate degradation and reprocessing of the organic molecule to its mineral of the preferred microorganism, loss of hereditary potential in adversative ecological



Heavy metals

lead, mercury and nickel
Saccharomyces cerevisiae
Fe^{2+}, Zn^{2+}, Pb^{2+}, Mn^{2+} and Cu^{2+}
Pseudomonas fluorescens and Pseudomonas aeruginosa
Cobalt, copper, chromium, lead
Lysinibacillus sphaericus CBAM5
Fe
Microbacterium profundi strain Shh49T
U, Cu, Ni, Cr
Pseudomonas aeruginosa, Aeromonas sp.
Pb, Cr, Cd
Aerococcus sp., Rhodopseudomonas palustris

Tigini V, Prigione V, Giansanti P, et al.(2010).

Agents for pesticides

Endosulfan
Bacillus, Staphylococcus
Chlorpyrifos
Enterobacter
Ridomil MZ 68 MG, Fitoraz WP 76, Decis 2.5 EC, malation
Pseudomonas putida, Acinetobacter sp., Arthrobacter sp.
chlorpyrifos and methyl parathion
Acenetobactor sp., Pseudomonas sp., Enterobacter sp. and Photobacterium sp.

Mónica P, Darwin RO, Manjunatha B, et al.(2016)

Fig. 1.3 Representative flowchart of microorganisms used for heavy metal and pesticides degradation

circumstances, the formation of intractable complexes and poor process optimization for treatment at large scale. Even though the physical and chemical procedures are applied for the treatment, they are not superior to organic treatment because of reasons like cost-ineffectiveness and residual effects.

Bioremediation is the metabolic capability of microbes to convert or mineralize organic pollutants to less damaging, nonhazardous materials, which are then incorporated into natural biogeochemical cycles. The intensity of biodegradation is prejudiced by numerous factors, such as nutrients, oxygen, pH value, composition, concentration and bioavailability of the pollutants, chemical and physical features, and the history of pollution of the polluted environment (Zchendir and Bouwer 1993).

As an alternative of merely gathering the contaminant and storing it, bioremediation is a microbiological well-systematized procedural activity that is useful to breakdown or convert pollutes to less toxic or nontoxic elemental and compound forms. The bioremediators are organic agents used for bioremediation to clean up polluted locations. Bacteria, archaea, and fungi are typical leading bioremediators (Strong and Burgess 2008). Bioremediation is a biotechnological procedure concerning microorganisms for resolving and eliminating risk of several impurities through biodegradation from the environment. Both the terms, bioremediation and biodegradation are interchangeable.

Microbes are suitable for the task of pollutant demolition since they possess enzymes that let them use ecological pollutants as a portion of food. The purpose of bioremediation is inspiring them to work by providing optimal levels of nutrients and other chemicals vital for their metabolism to degrade/detoxify elements that are harmful to the environment and living things. All metabolic reactions are assisted by enzymes. These belong to the groups of oxidoreductases, hydrolases, lyases, transferases, isomerases, and ligases. Several enzymes have an extraordinarily wide degradation capability due to their non-specific and specific substrate affinity. For bioremediation to be effective, microorganisms must enzymatically attack the contaminants and transform them into innocuous products. As bioremediation can be effective only where ecological circumstances authorize microbial growth and activity, its application frequently includes the manipulation of ecological factors to permit microbial growth and degradation to advance at a faster rate (Kumar et al. 2011). Bioremediation occurs spontaneously and sustained within the addition of living beings and fertilizers. Bioremediation technology is generally based on biodegradation. It refers to accomplish the removal of organic poisonous contaminants into harmless or spontaneously occurring compounds like carbon dioxide, water, inorganic compounds that are safe for human, animal, plant, and aquatic life (Jain and Bajpai 2012). Numerous ways and pathways have been illustrated for the biodegradation of a wide variety of organic compounds; for instance, it is achieved in the presence and absence of oxygen.

1.10 Microbes as Pollutant Annihilation

Bioremediation uses living systems specifically microbes to catalyze the degradation of wastes without disrupting the atmosphere. “Remediate” means to resolve a problem, and “bioremediate” means the utilization of biological organisms to resolve ecological complications such as polluted soil or groundwater. In a pollution-free environment, bacteria, fungi, parasites, and other microorganisms are continuously at work breaking down organic matter. Some of the microorganisms would perish, while others capable of consumption of the organic effluence would survive. Bioremediation works by providing pollution-eating organisms with fertilizer (dairy residues like proteins, salts, fatty substances, and lactose), oxygen, and other circumstances that inspire their rapid growth. These organisms would then be able to break down the organic contaminant at a correspondingly quicker rate. Bioremediation is frequently used to assistance clean up oil spills. Bioremediation of a polluted site typically works in one of two ways. In the situation described above, ways are found to improve the growth of any kind of pollution-eating microorganisms that might already be existing at the polluted site. In the second, a less common, case, specific microorganisms are supplemented to reduce the pollutants. Bioremediation provides a good clean-up tactic for several kinds of pollution, but as you might assume, it will not work for all. Nevertheless, bioremediation offers a technique for cleaning up contamination by enhancing the same biodegradation procedures that transpire in nature. Depending on the location and its pollutants, bioremediation may be innocuous and less expensive than alternative solutions such as incineration of the polluted elements. It also holds the advantage of treating the pollution in place, so that huge quantities of soil, sediment, or water do not have to be dug up or pumped out of the ground for treatment. The bioremediation is classified into two general classifications that include in situ bioremediation and ex situ bioremediation (Punnagaiarasi et al. 2017).

Bioremediation is the method in which valuable microbiological agents, such as yeast, fungi, or bacteria are used to clean up polluted soil and water. It is defined as the eradication, reduction, or transformation of contaminating or polluting materials by the application of biotic methods.

Microbial bioremediation can economically and expeditiously terminate or immobilize pollutants in a way that shields human well-being and the environment (Gadd 2000). Research using exogenous, specialized microorganisms, or genetically engineered microbes to enhance bioremediation (Hassan et al. 2003). A successful, cost-effective, microbial bioremediation program is reliant on hydrogeologic circumstances, the contaminant, microbial ecology, and other spatial and temporal aspects that differ extensively. In any bioremediation process, the introduced microorganisms use the pollutants as nutrients or energy sources (Tang et al. 2007). Bioremediation activities through microorganisms are enthused by complementing nutrients (nitrogen and phosphorus), electron acceptor (oxygen), and substrates (methane, phenol, and toluene) or by introducing microorganisms with anticipated catalytic abilities.

According to Van Dillewijn et al. (2007), "bioremediation" is described as the process employing multiple biological agents, primarily microorganisms to degrade the ecological pollutants into less virulent forms. The first patent for a biological remediation agent was registered in 1974, using a strain of *Pseudomonas putida* to degrade petroleum (Prescott et al. 2005).

Low cost, high efficiency, minimization of chemical and biological sludge, selectivity to specific metals, no additional nutrient requirement, regeneration of biosorbent, and the possibility of metal recovery are some of the chief benefits of bioremediation over traditional treatment (Kratochvil and Volesky 1998). Bioremediation can transpire on its own in the environment (natural attenuation or intrinsic bioremediation) or can be encouraged via the enhancement of fertilizers for the improvement of bioavailability within the medium (biostimulation). Bioventing, bioleaching, bioreactor, bioaugmentation, composting, biostimulation, land farming, phytoremediation, and rhizofiltration are all examples of bioremediation technologies (Li and Li 2011).

Bioremediation is a broad concept that encompasses all those processes and activities that take place to biotransform an environment, already changed by pollutants, to its original status (Adhikari et al. 2004). It is the process of cleaning up perilous wastes with microorganisms or plants and is the most trustworthy process of clearing soil of contaminants. Bioremediation uses primarily microorganisms or microbial processes to degrade and transform environmental pollutants into harmless or less virulent forms (Garbisu and Alkorta 2003). Bioremediation is a method used to eliminate ecological pollutants from the ecosystem. It uses the biological mechanisms inherent in microorganisms and plants to eliminate perilous pollutants and re-establish the environment to its original condition (Ayangbenro and Babalola 2017). The elementary principles of bioremediation include reducing the solubility of these environmental pollutants by changing pH, the redox reactions, and adsorption of pollutants from the contaminated environment (Jain and Arnepalli 2016).

Bioremediation, a branch of environmental biotechnology, is nowadays regarded as one of the most assuring alternatives. This technology utilizes the astonishing capability of microorganisms or plants to accumulate, detoxify, deteriorate, or exclude environmental pollutants. Bioremediation provides the transformation and/or even elimination of organic and inorganic contaminants, even when they are present at low concentrations. Constant efforts are still made to understand the mechanisms by which microorganisms and plants eliminate or transform ecological pollutants. Thus, the objective of this specific concern was to explore different conceptions on bioremediation, while addressing recent advancements and new concepts from the perspective of effective process scale-up because of application at larger scales (Hlihor et al. 2017).

A wide variety of plants are used for the accumulation of heavy metals categorized under the section of phytoremediation. This method is encouraging because it is an innovative tool with greater potential and also to phytoremediate metal contamination from soil and water (Wenzel et al. 1999). Hyperaccumulator plants are normally described as the species which can accumulate the heavy metals at 100-fold greater levels than non-accumulator plants (Reeves and Baker 2000).

Given the sustainability concerns and ecological ethics, bioremediation, the exploitation of biological methods for the clean-up of polluted sites, is a promising, favorable, and ecologically stable alternative to chemical technologies (Gillespie and Philp 2013). Phytoextraction (a type of phytoremediation) is one of the most cost-effective techniques to remediate the metal-polluted soils (Padmavathiamma and Li 2007). Phytoremediation occurs only at minimal cost, which is due to harvesting and field management, e.g., weed control. Besides, the resulting biomass of phytoremediating plants can be utilized for heat and energy generation in specialized facilities (Peuke and Rennenberg 2005). Unlike physicochemical methods, phytoremediation is an environment-friendly and comprehensive approach, having no side effects on soil texture and health (Suresh and Ravishankar 2004).

1.11 In Situ and Ex Situ Bioremediation

In situ bioremediation projects have characteristically depended on water to transfer the essential electron acceptors, nitrogen, phosphorus, and trace minerals to the native microbial population and improve the amount of biodegradation of biological pollutants (Lee et al. 1988). For this purpose, the importance of orthodox in situ bioremediation projects has been on treating impurities in the saturated region, with comparatively little effort, directed toward bioremediation of the unsaturated zone and capillary fringe where a major portion of the subsurface pollution may take place. Bioremediation of the unsaturated zone with the conservative water-based transfer methods have shown to be challenging and frequently unproductive because the infiltration galleries or spray irrigation practices adopted to distribute water through this zone are inadequate to provide sufficient amounts of oxygen for convenient biodegradation of the organics. Wilson and Ward (1986) promoted utilizing air as the oxygen source for in situ aquifer bioremediation because air comprises more than 20% oxygen. It has been determined that the mass transfer of oxygen through the subsurface using air should be 1000 times more efficient and productive than using water. This increased mass transfer of oxygen could be implemented in the saturated zone by dewatering the aquifer and then inserting air or pulling air through the formation or injecting air under pressure into the subsurface to displace the groundwater.

Bioventing combines soil venting, which eliminates unstable constituents from the soil, with bioremediation which utilizes the oxygen from the vented air for biodegradation of the remaining organic pollutants. The volatilization of low molecular weight, high vapor pressure compounds can be maximized using a greater volume of air or short transportable distances among injection and extraction wells (Dupont et al. 1991). The bioventing procedure can be maximized by utilizing lower airflow rates, lengthier flow paths, and optimizing circumstances for microbial growth through the accumulation of moisture and inorganic nutrients.

A major concern for petroleum hydrocarbon bioremediation is the presence of complex compounds such as polycyclic aromatic hydrocarbons (PAHs), asphaltenes, and many-branched mixtures with 20 or more carbon atoms. These heavy hydrocarbon elements are not easily metabolized by microorganisms and are recognized potential health risks due to their probable carcinogenic and mutagenic effects (Baheri and Meysami 2002). Information on kinetics is very crucial because it describes the concentration of the chemical residing at any time.

Bioremediation is concerned with the biological re-establishment and rehabilitation of traditionally polluted sites and with the clean-up of regions polluted in more recent times, either unintentionally or incidentally, as a result of the manufacture, storage, transportation, and use of organic and inorganic compounds (Baker and Herson 1994). Bioremediation offers the likelihood of degrading, eliminating, altering, restraining, or otherwise decontaminating several chemicals from the atmosphere through the action of microorganisms like bacteria (Singh 2006), fungi, and plants (Eapen et al. 2007). The assistance of the scientific areas of microbiology, biochemistry, molecular biology, analytical chemistry, chemical, and environmental engineering, among others, has played a major role in the recognition of most of the developments in bioremediation. Contemporary environmental biotechnology uses techniques that employ ordinarily natural strains of microbes to mobilize and eliminate organic or restrain inorganic contaminants from the environment. The significant benefit of bioremediation methods as compared to other biological technologies is that they can employ enzymatic metabolic pathways that have been evolved in nature over very long periods, therefore becoming very precise. Many books are specialized in particular purposes of bioremediation such as bioremediation of MTBE (Jacobs et al. 2001), perchlorate (Stroo and Ward 2009), oil spills, hydrocarbons pollution (Pichtel 2007), chlorinated solvents (EPA 2000), metal ions (Wang et al. 2009), radionuclides (Voigt and Fesenko 2009), explosives (Noyes 1996) in many environments, e.g., marine harbors cold areas (Van Stempvoort and Biggar 2008), etc. The economic features of bioremediation is also very significant and recognized (Hardisty and Özdemiroglu 2005). Lastly, a fresh section such as phytoremediation has gained consideration in recent years (Pichtel 2007).

Bioremediation of wastewater by hydroponic techniques is recommended as decentralized wastewater treatment and reuse (López-Chuken 2012). Hydroponic systems, which utilize plants which are grown in a nutrient solution without soil, are expanding and raising a great interest in the commercial and scientific community (López-Chuken 2012). They are engineered systems designed and constructed to utilize the natural processes involving macrophytes, media, and the associated microbial assemblages to assist in treating wastewaters. This is a relatively new approach in wastewater treatment by which a variety of emergent macrophytes are grown hydroponically on top of a floating platform with their roots developing freely into the flowing wastewater (Osem et al. 2007). The roots provide a support medium for attached microbial growth which participates in the treatment process. Breweries produce a substantial effluent stream, rich in organic matter and nutrients originating from the brewing process (Simate 2015). Despite significant technological improvements, water consumption, wastewater, solid waste, and by-products and emissions to air remain major environmental challenges for the brewing industry (Alayu and Yirgu 2017). Bioremediation is the use of biological interventions for mitigation of the noxious effects caused by pollutants in the environment. It is a very useful approach for a variety of applications in the area of environmental protection. It has become an attractive alternative to the conventional clean-up technologies that employ plants and their associated microorganisms to remove, contain, or render harmless environmental contaminants (Ojoawo et al. 2015). It is noted that the application of bioremediation for wastewater treatment has been expanded, but knowledge of bioremedial potential using hydroponics is still not well exploited, so it is necessary to better understand for getting more insight into the bioremediation potentials of vetiver grass using hydroponic techniques in the context of Ethiopia. The performance under different environmental conditions imposed by wastewater is not well known.

Deaden the use of microorganisms or condense the concentration of the hazardous waste contaminated plant is called biodegradation. Biological cleaning systems have a variety of applications such as decontamination of contaminated areas such as water, soil, sludge, and flows. Rapid industrialization, urbanization, intensive agriculture, and other human activities have led to land degradation, pollution, and decrease in crop productivity in all sectors of agriculture. Human activity has increased pressure on natural resources and has become a source of countless impurities. Several methods were designed and developed, but more often, the process again produces secondary contamination, which again stood environment (Shah 2016). Bioremediation through its first successful application on the Exxon

Valdez oil spill (Zhu et al. 2001) has motivated many researchers to investigate physical, chemical, and biological factors that could produce favorable conditions for in situ and ex situ remediation of contaminants.

Land farming has successfully been used for over 100 years for the treatment of hydrocarbon contaminated soils. Lighter petroleum hydrocarbons are mainly removed from soils by volatilization and, to a lesser extent, by microbial degradation. In contrast, heavier petroleum hydrocarbons like lubricating oils and diesel fuel do not evaporate, and their removal is predominantly due to microbial degradation (Khan et al. 2004). Land farming can be performed in situ or ex situ; if contaminated soils are shallow (i.e., <1 m below ground surface), microbial activity may be stimulated without excavating the soils. If petroleum contaminated soils lie deeper than 1.7 m, the soils need to be translocated to the ground surface (Anon 1994). Biosurfactants, which are more effective and environmentally friendlier than chemical surfactants, consist of a hydrophilic moiety and a hydrophobic moiety, which allows them to enhance water solubility of hydrocarbons and increase the displacement of oil molecules from soil particles (Ron and Rosenberg 2010). Therefore, the application of biosurfactants in bioremediation treatments of hydrocarbon polluted environments might be advantageous. Bioremediation aims to accelerate the rate of natural attenuation of petroleum hydrocarbons by optimizing environmental conditions for microbial activity (Greer et al. 2010).

Effluent organic soap can be used to effectively treat cassava effluent effects in the soil. The process requires a very less effort and cost-effective process when compared to other conventional methods that are used for clean-up of cyanide and other heavy metals infested soils. This method not only degrades the cyanide plus heavy metal level but improves soil nutrient content. As a result of bioaugmentation treatment of soil, available potassium, sodium, and phosphorus increased significantly, which are essential elements required by plants for growth. The significant degrading of the cyanide and other heavy metals in the soil is an indication that organic soil solution could be used effectively in soil bioremediation (Eboibi et al. 2018). It may be concluded that microbes can tolerate heavy metals, and they are armed with various resistance and catabolic potentials. This catabolic potential of microbes is enormous and is advantageous to mankind. It is essential to conduct more studies on the gene level to know the biosorption potential and the heavy metal resistance of the microorganism (Basha and Rajaganesh 2014).

1.12 Pertinent Tactics

The recent approaches of bioremediation such as microbial-induced calcite precipitation (MICP) through urease hydrolyzing bacteria, the formation of soluble nanoparticles as end products by bacteria, bacterial signaling systems for biosensors, biomineralization of radionuclides and other toxic heavy metals, synthesis of biomaterial or functionalized polymer silica hybrid nano particles, genomics, and proteomics of biological treatments to the contaminants, root–microbe interaction, and detoxification of heavy metals have been proven as promising techniques to remediate the contaminated ecosystems. Microbe-assisted phytoremediation can be best applied at sites having relatively shallow contamination of pollutants that are amendable to the processes such as biomineralization, biostimulation, mycoremediation, cyanoremediation, phytodegradation, phytostabilization, hyperaccumulation, dendroremediation, and rhizofiltration, for a sustainable period (Mani and Kumar 2014).

Despite these obstacles, a range of potential techniques for the management of petroleum hydrocarbon–contaminated sites in cold regions are available. No contaminated site is without its unique challenges, and site-specific factors typically require multiple technologies for effective, long-term management. This is particularly so at sites co-contaminated with heavy metals and petroleum hydrocarbons and at heterogeneous contaminated sites. Selecting the most appropriate treatment strategy requires consideration of the contaminants present and their distribution, climate, soil characteristics, financial expenses, legislative considerations, logistics, equipment, required energy, and infrastructure.

Camenzuli and Freidman (2015) used immobilized microbiological preparation comprising a mixed culture of bacteria capable of removing the toxic components of textile industrial effluent within a few periods, under laboratory conditions. Bioremediation of textile industrial effluents by bacteria is an effective method for treating textile effluent and can be a good substitute for conventional remediation processes. For improved commercial use of microorganisms, immobilization, or pellet preparations in suitable carriers will prove economical for their use. However, if this can be developed in large scale, it will be useful for the treatment of not only the textile effluent but industrial effluent of any kind (Ajao et al. 2011). The comparison of treatment by different methods showed that native microbes isolated from the site of pulp and paper mill can use lignin, as a carbon source, and reduce the COD, BOD, and other contaminants. With the increased demand for paper, the treatment of effluents emerges as a most pressing problem in environmental protection (Madan et al. 2018).

The emerging science and technology of bioremediation offers an alternative method to detoxify contaminants. Apart from bacteria, white-rot fungi also play a significant role in the biodegradation of PAHs. They have key enzymes lignin peroxidase and manganese which can convert these PAHs into less harmful substances. Several algae have also the capability to degrade a wide range of PAHs (Jimoh et al. 2018). Although protozoa is not directly involved in the process of biodegradation, it can influence the rate of biodegradation (Pandey et al. 2016). In comparison to other microbial treatment, algal soil bioremediation overcomes the necessity of carbon and other nutrients. It may provide the additional benefits of renewable energy generation by algal CO_2 fixation. Algal–bacterial consortia have been shown to be more efficient for the treatment of hazardous pollutants (Pengcheng and Secundo 2016). Different plants and microorganisms can be used to treat any polluted site. Bacteria species most suited to the removal of toxic oil pollutants are *pseudomonas* and *bacillus* since they use these compounds as the source of carbon to generate energy for cell development. *Aspergillus* species are the major fungi used in the treatment of contaminated sites from the petroleum hydrocarbons or untreated industrial effluents. Fungi species are more adaptable as compared to bacterial species since they can thrive in environmentally stressed conditions. Other advantages with fungi include ease of production in large quantities, transportation, and genetic engineering. White-rot fungi (*Phanerochaete chrysosporium*) are the most efficient in biodegradation of toxic and insoluble compounds as compared to microorganisms. They secrete extracellular enzymes that help in the oxidation of complex aromatic compounds and other hazardous pollutants. Aquatic plants such as the macrophytes and pteridophytes as well as other different grass species can also be used as bioremediation agents, but duckweed is more recommended. The most used aquatic plant in wastewater treatment is duckweed, importantly in the removal of heavy metals because it is more tolerant of environmental conditions and produce biomass faster. Interestingly, the water hyacinth can also be used in the removal of heavy metals and petroleum hydrocarbons which has been one of the plants that populated Lake Victoria due to high eutrophication levels. From the literature data analysis, bacteria are most suitable for treating oil pollution in a water body. *Pseudomonas* sp. can biodegrade organic matter, hydrocarbons, and also remove heavy metals. *Phragmites australis* which is an aquatic plant is also suited for cleaning up oil pollution in both water and soil. Duckweed is the best in treating water polluted with industrial effluents. Thus, phytoremediation is more applicable for heavy metals removal, whereas biodegradation by using bacterial species can be used for the breakdown of organic and inorganic compounds from industries or oil and gas production (Kabenge et al. 2017). The fungal and bacterial isolates having appropriate enzyme activity with optimized proper physical conditions are playing a significant role in the bioremediation process. Further research is needed to develop fast biodegradation processes which are likely to provide an economically feasible process (Madan et al. 2018).

The bioremediation of the pollution load of the oil refinery effluent with *Scenedesmus obliquus* can be used as an effective technology in the reduction of pollutants like inorganic and organic compounds (Rajasulochana et al. 2009). Bioremediation constitutes a “good technique” for solving environmental contamination due to the food industry waste. In particular, wastewater treatment by free or immobilized polyphenol oxidases (laccase and tyrosinase) appears to be very promising for both decolorization and dephenolization of the effluent stream. Investigation of several sectors of the food industry confirmed its potential usefulness (Chiacchierini et al. 2004).

Bioremediation is a low-cost technology that does not require complex infrastructure and can be used to treat large volumes of wastewater. In developed countries, bioremediation is highly efficient for removing, transforming, or degrading different types of contaminants found in wastewater, particularly using the mechanisms of phytoextraction and rhizofiltration (Mora-Ravelo et al. 2017). Bioremediation is a proven alternative treatment technique that is sustainable and ecofriendly for the removal of petroleum and industrial waste compounds from the contaminated sites. It is a very efficient and cost-effective method in comparison to other methods used commercially for pollutant removal (Kabenge et al. 2017).

The peptidoglycan and polysaccharide component of the cell wall of the biosorbents is an active binding site for higher metal uptake. This technique is cost-effective and a green technology that has advantages such as faster kinetics, high metal-binding over a broad range of pH, and temperature. Further research area needs to be extended on the focus of gene transfer within biofilms for heavy metal remediation. These would facilitate the development of improved techniques for the bioremediation of heavy metals in the ecosystem.

Presently, bioremediation is taken to be an attractive option for reducing pollution load from contaminated water because of its high efficiency and economic impact than the chemical remediation (Madan et al. 2018).

Biodegradation is a very fruitful and attractive option to remediating, cleaning, managing, and recovering techniques for solving the polluted environment through microbial activity. In the future, in the area, researchers should explore novel species that have great potential. The speed of unwanted waste substance degradation is determined in competition within biological agents, inadequate supply with essential nutrient, uncomfortable external abiotic conditions (aeration, moisture, pH, temperature), and low bioavailability of the pollutant. Due to these factors, biodegradation in the natural condition is not more successful and leads to be less favorable. Bioremediation can be effective only where environmental conditions permit microbial growth and activity. Bioremediation has been used in different sites globally within varying degrees of success. Mainly, the advantages are greater than that of disadvantages which are evident by the number of sites that choose to use this technology and its increasing popularity over time. Generally, different species are explored from different sites, and they are effective in control way (Abatenh et al. 2017).

1.13 Natural Biodegradation Processes

Bioremediation is an efficient process for such organic pollution of soils. It is possible to humiliate about 50% of the initial pollution load in 200 days by simply aerating the soil layer. Importantly, it has been shown that pollutant biodegradation could be valuable followed by an appraisal of carbon dioxide evolution during the process which provides a simple way for characterizing the kinetics of degradation. Bioremediation has been used for biological treatment in several locations around the world, including Europe, with varying degrees of success. Techniques have been improved and gained more knowledge and experience. There is no doubt that the biological treatment has great potential to deal with many types of pollution including soil pollution (Punnagaiarasi et al. 2017).

Bioremediation provides a technique for cleaning up pollution by enhancing the natural biodegradation processes. Thus, by developing an understanding of microbial communities and their response to the natural environment and pollutants, expanding the knowledge of the genetics of the microbes, it is possible to improve on our capabilities to biodegrade pollutants. Identifying the right microbe from the waste to be biodegraded and conducting field trials with these identified microbes for bioremediation techniques would provide cost-effectively technologies and offer potential for significant advances in the field. Every microbe has different growth requirements (temperature, pH, and nutrients); hence, there arises the need to isolate those forms, which can be cultured easily in the lab, with minimal requirement and can be utilized in treating a variety of pollutants. The use of genetically engineered microorganisms is not necessary as in most cases there is a wide diversity of naturally occurring microbial strains. As natural resources are major assets to humans, bioremediation of contaminated sites and ecosystems will be the best eco-friendly approach to preserve scarce resources and also ensure efficient recycling of wastes. Bioremediation is an emerging field, with many players already in the field producing a myriad of products to overcome the nutrient deficiency in fish farms and improve nutrient release in agricultural land, improving in composting of industrial waste, removal of toxic chemicals, and the list is growing. Still, there is scope for developing new products that could assist in our goal of cleaning-up our environment (Divya 2015). Bioremediation is a multidisciplinary technology, and successful application requires a deep understanding of all the relevant scientific fields and attenuation processes. It seems that nowadays we have entered in the most interesting and intense phase of process development (Hatzikioseyian 2010).

1.14 Conclusion

Bioremediation makes use of microorganisms and higher plants to treat precarious organic and metallic debris or by-products that penetrate within the soil and sediments from several processes associated with residential, municipal, agricultural, industrial, and military activities. Bioremediation appears to be an effective and attractive tool to treat and recycle the environment in an environmentally friendly manner. Bioremediation was used in many places around the world, with varying degrees of success. Bioremediation, both in situ and ex situ also had strong scientific growth, partly due to increased use of natural suppression, because of the most natural attenuation due to biodegradation. Bioremediation technology leads to the degradation of pollutants can be lucrative and environmentally friendly alternatives. Industrial emissions are a major source of toxic contaminants in all environments.

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Chapter 2
Bioremediation of Metals, Metalloids, and Nonmetals

Darshan M. Rudakiya and Yogesh Patel

Contents

Abstract On earth, all elements are divided into three categories which are metals, metalloids, and nonmetals. Among all elements, some are essential while some metals, metalloids, or nonmetals are hazardous. Lethal or toxic heavy metals like arsenic, mercury, lead, selenium, etc. should be treated to reduce the toxicity of metals. Bioremediation is an environmental friendly and green approach to remediate the metals using biological agents such as bacteria, yeast, fungi, and plants. This

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Microorganisms for Sustainability 26, https://doi.org/10.1007/978-981-15-7455-9_2

approach is an effective alternate to costly and hazardous physical and chemical treatments. This chapter provides a detailed discussion on the metals, metalloids, and nonmetals with their toxicity in the organisms. It also provides the bioremediation of metals, metalloids, and nonmetals using various biological agents. Lastly, this chapter concludes by providing future aspects of the bioremediation.

Keywords Bioremediation · Heavy metals · Bacteria · Fungi · Plants

2.1 Introduction

According to the International Union of Pure and Applied Chemistry (IUPAC), a pure chemical substance is composed of atoms with the same number of protons in the atomic nucleus (McNaught 1997). Based on this definition, a substance with same number of protons in the atomic nucleus is called as element. In the periodic table, a total of 118 elements have been identified, wherein 94 elements occurs naturally on the Earth while rest of the elements are chemically synthesized or synthetic elements. Of the 94 elements, 83 are primitive and mostly are stable. Some of these elements are weakly radioactive. Other 11 natural elements possess short half-life, and they convert into transient elements. Thorium and uranium have five transient element products which are radium, radon, polonium, actinium, and protactinium. The other six transient elements such as neptunium, technetium, astatine, francium, promethium, and plutonium occur only rarely because of the rare decay of uranium and other heavy elements into these transient elements. Almost 80 elements have their own stable isotopes while 38 elements are radionuclides which decay over the time and convert into other elements after specific time (Burbidge et al. 1957).

Since the civilization, human societies found some native elements such as carbon, sulfur, copper, gold, and silver. Later, modern civilization extracted the elements such as copper, silver, lead, and iron for various application. By 1950, majority of the elements that occurred naturally were discovered. After discovery of the periodic table, all elements have been categorized into a total of 18 groups with lanthanide and actinide families. Furthermore, scientist further classified the chemical elements as metals, nonmetals, and metalloids largely based on the elements' abilities to conduct electricity at normal temperatures and pressures, and there are other distinctions considered when classifying the elements in the periodic table (Walker 1995; McNaught 1997).

2.2 Metals, Metalloids, and Nonmetals

Based on the physical, chemical, and electrical properties, all elements have been divided into six major groups which are alkali metals, alkaline earth metals, transition metals, post-transition metals, metalloids, and nonmetals. In the left side of the periodic table, metallic elements are present while semimetals and nonmetals are present on the right part of the periodic table. Transition metals are the metallic elements that makes a bridge between metals and nonmetals. Inner transition metals are the elements which are presented below the periodic table which are lanthanides and actinides because they have atomic numbers that fall between the first and second elements in the last two rows of the transition metals (Ćirić-Marjanović, 2013).

2.2.1 *Alkali Metals*

Lithium (Li), sodium (Na), potassium (K), rubidium (Rb), caesium (Cs), and francium (Fr) are the alkali metals which lie in the s-block of the periodic table. All alkali metals are mainly followed by hydrogen (H) on the left side of the periodic table. Density of element increases by going down in the periodic table, wherein Li is the lightest metal of alkalis. Reaction with water becomes more violent as atomic weight of this group increases. The chemistry of this group is primarily determined by the anion that is attached with it. Mostly inorganic compounds synthesize using alkali metals such as hydrides, oxides, hydroxides, pentoxides, nitrides, phosphates, and silicates. Additionally, organo-alkali compounds synthesize commonly wherein Na or K combine with different hydrocarbons (Coghill and Garson 2006).

2.2.2 *Alkaline Earth Metals*

After alkali metals, next group is the alkaline earth group which stands between transition and alkali metals. The metals are beryllium (Be), magnesium (Mg), calcium (Ca), strontium (Sr), barium (Ba), and radium (Ra). They have metallic properties like all metals. It shows some specific contrast to transition metals and post-transition metals. Comparison of metals, metalloids and nonmetals have been shown in Table 2.1.

Alkaline earth metals have low density, melting point, and boiling point as compared to the transition metals. These group of metals cannot form the insoluble precipitates with sulfide ions. These metals form sulfates which are water soluble like magnesium sulfate, calcium sulfate, and strontium sulfate. These metals react with the halides and form the chlorides, bromides, and iodides. Among alkaline earth

Table 2.1 Comparison of metals, metalloids, and nonmetals

Characteristics	Metals	Metalloids	Nonmetals
Elements	88	11	22
Appearance	Lustrous	Lustrous	Submetallic (except S) if solids
Form	Solid (except Ga, Hg, Rb, Cs, Fr are liquid)	Solid	Solid (10), liquid (1), gaseous (11)
Heat conductivity	Good	Moderate	Poor
Electric conductivity	Good to high	Moderate to good	Poor to moderate
Luster	Shiny	Shiny or dull	Dull
Ductile and malleable	Yes (thin wire and sheets	Sometimes but mostly brittle	Brittle
Melting and boiling points	High (except Hg)	Lower than metals	Low
Density	High	Lower than metals	Low
Ionization energy	Low	Moderate	High
Electronegativity	Low	Moderate	High
When mixed with metals	Alloys	Alloys	Interstitial or ionic compounds
Oxides	Lower oxides basic, higher oxides acidic	Amphoteric or weakly acidic	Acidic and compounds

metals, Ba, Be, Ca, and Ra have at least one naturally occurring radioisotope except Mg and Sr (Wieser and Berglund 2009).

2.2.3 *Transition Metals*

Transition metals are a group of metals that have balance electron in the shells. These groups occupy the middle long periods and groups of the periodic tables of elements from group 3 to 12. Almost 24 metals show the similarity as all transitional metals are hard, strong, and lustrous. They have higher boiling and melting points with good conductors of heat and electricity. In this group, the included elements are Fe, Ti, Ag, Au, Ni, Co, Cu, Zn, Ni, Cd, etc. Many elements are industrially and technologically important as majority elements are used to synthesize different alloys with other metallic elements. All transition metals dissolve in the mineral acids; however, some metals like Pt, Au, and Ag are exception. These metals are divided into first, second, third, and two inner transition series called lanthanoids and actinoids (Zweig et al. 2017).

2.2.4 Post-Transition Metals

These metals are a set of metallic elements which are situated between transition metals and metalloids in the periodic table. In post-transition metals, gallium (Ga), indium (In), tin (Sn), thallium (Tl), lead (Pb), and bismuth (Bi). These metals are physically soft (or brittle) and have poor mechanical strength with lower melting points as compared to those of transition metals. Being close to the metal–nonmetal border, their crystalline structures tend to show covalent or directional bonding effects, having generally greater complexity or fewer nearest neighbors than other metallic elements. Basically, they form anionic species like stannate, aluminates, and bismuthates (Gagné and Hawthorne 2018).

2.2.5 Metalloids or Semi-Metals

Semi-metals or metalloid is a group of elements that comprises the intermediate properties of metals and nonmetals. Mainly six metalloids are boron (B), silicon (Si), germanium (Ge), arsenic (As), antimony (Sb), and tellurium (Te). Other than these six metalloids, five elements are less classified frequently in the metalloids such as carbon, aluminum, selenium, polonium, and astatine. Generally, metalloids have a metallic appearance; however, they are brittle and moderate conductors of electricity. Mostly they behave as nonmetals during all chemical reactions. These elements make alloys with the metals. Physical and chemical properties of metalloids are shown in Table 2.1. Applications of the metalloids and their compounds are in alloys, catalysts, flame retardants, optoelectronics, semiconductors, electronics, and optical storage (Mosa et al. 2016).

2.2.6 Nonmetals

Nonmetal is a group of chemical elements that mostly lack the characteristics of metals. They have relatively lower melting and boiling points and density with poor conduction of electricity. They are generally brittle when they are solid and poor conductor of thermal. Nonmetals have high ionization energy, electron affinity, and electronegativity. Twenty-two elements have been classified as nonmetals. They are divided into two categories, reflecting their relative properties to form chemical compounds which are reactive nonmetals and noble gases. Most of the nonmetals are gases such as hydrogen, helium, nitrogen, oxygen, fluorine, neon, chlorine, argon, krypton, xenon, and radon. Carbon and sulfur are the less electronegative nonmetals wherein they have weak to moderately strong nonmetallic properties and tend to form covalent compounds with metals. Oxygen and fluorine are strong nonmetallic properties as they have more electronegativity (Steudel 2011).

2.3 Heavy Metals and Pollution

Heavy metals are a group of metals and metalloids that comprises of an atomic density more prominent than 4000 kg/m^3. Majority of heavy metals are toxic at lower, moderate, or higher concentration, which mainly include Cu, Zn, Sn, Sr, Ni, Mo, Pb, Ti, Cr, Co, V, and Hg (Shah et al. 2018; Satyanarayana et al. 2019). Some metals are essential for the growth of cells such as Zn, Cu, Mo, Co, and Ni; however, higher concentration or above permissible limit of the metal cause harmful effects. Some heavy metals are not essential for the growth of cells (As, Cd, and Pb), but they hamper the cellular activities while interaction (Rudakiya et al. 2018). The soil and water get polluted because the industrial wastewater, sewage sludge, and other untreated wastewater directly discharge into soil and water. Heavy metals do not create only pollution but also influence food chain, so each stage of organisms comprises of certain level of metal contamination within the cells. This may affect the cellular activities (Rudakiya and Pawar 2013; Vardhan et al. 2019). For instance, humans are exposed to all forms of mercury through accidents, environmental pollution, food contamination, dental care, preventive medical practices, industrial and agricultural operations, and occupational operations. When Hg is absorbed by body, then it affects kidneys, neurological tissue, and the liver (Sarkar 2005).

2.4 Metal Sources

2.4.1 Natural Sources

In nature, high metal concentration also occurs in nature because of weathering of parent metals. For instance, various sites have been checked where some specific metals are increased by 10% in Canada, the USA, and China (Roane et al. 2015).

2.4.2 Anthropogenic Sources

Metal pollution is caused when human activity hampers the biogeochemical activities or results in the disposal of concentrated metal wastes. In some cases, single metal is involved while sometimes more than one metals are disposed on the dumping sites. Various organic contaminants also comprise of different metal contaminants. For instance, As, Cu, and Zn are presented in the pesticides and other endocrine disrupting chemicals. Some metals are extensively used in the production of pigments, alloys, and batteries. Extreme utilization and disposal of these metals cause the metal pollution that leads to harmful effects to plants, animals, and human (Roane et al. 2015).

2.5 Heavy Metal Toxicity

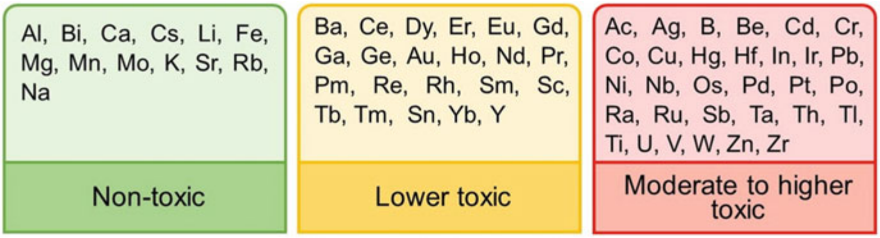
According to the World Health Organization (WHO), a total of 13 metals are considered as toxic heavy metals, which include arsenic, cadmium, cobalt, chromium, copper, mercury, manganese, nickel, lead, tin, and titanium (Index 2018). Lead, cadmium, arsenic, and mercury are well known for showing a toxicity profile upon exposure. Although numerous cellular, intracellular, and molecular mechanisms have been reported to underpin heavy metal toxicity, Fig. 2.1 shows the list of nontoxic to highly toxic metals.

Cadmium: Cd has been classified as a human carcinogen by the US National Toxicology Program and International Agency for Research. It causes genomic instability in humans, which induces carcinogenesis. Major target organs of Cd carcinogenesis are pancreas, pituitary, liver, adrenal, prostate, and hematopoietic system. Cd interferes with major DNA repair pathways wherein Cd interacts with DNA nucleotide excision base pair, double-strand break repair, DNA mismatch repair, DNA base excision repair, and cell cycle checkpoints (Fig. 2.2) (Filipič 2012).

Lead: Pb is also toxic and xenobiotic heavy metal with its unique properties such as high ductility, highly malleability, low melting point. When it exposes to human body, it affects many organs like the nervous system, renal system, hematopoietic system, reproductive system, and cardiovascular system and shows some effects on bone. Major target of Pb is nervous system wherein lead induces toxicity and successively performs paralysis. Higher exposure to Pb contamination led to fatal consequences (Pirkle et al. 1994; Flora et al. 2006).

Chromium: Cr(VI) is highly toxic and Cr-containing compounds is known to cause multiorgan toxicity such as renal damage, allergy, asthma, and cancer of the respiratory tract in humans (Goyer 2001). It causes the problems in breathing as well as irritation to the lining of the nose and nose ulcers. The main health problems seen in animals are as follows: ulcers, irritation, disruption in stomach and small intestine, anemia, sperm damage, and male reproductive system damage.

As compared to Cr(VI), Cr(III) compounds are less toxic and do not cause problems. However, some compounds show allergic reactions and increasing risk



Al, Bi, Ca, Cs, Li, Fe, Mg, Mn, Mo, K, Sr, Rb, Na	Ba, Ce, Dy, Er, Eu, Gd, Ga, Ge, Au, Ho, Nd, Pr, Pm, Re, Rh, Sm, Sc, Tb, Tm, Sn, Yb, Y	Ac, Ag, B, Be, Cd, Cr, Co, Cu, Hg, Hf, In, Ir, Pb, Ni, Nb, Os, Pd, Pt, Po, Ra, Ru, Sb, Ta, Th, Tl, Ti, U, V, W, Zn, Zr
Non-toxic	Lower toxic	Moderate to higher toxic

Fig. 2.1 List of the metals from higher toxicity to nontoxicity for humans and environment

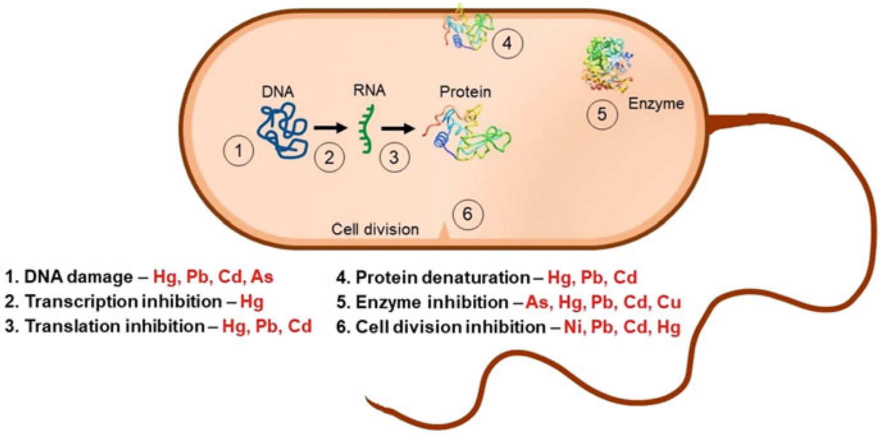


Fig. 2.2 Summary of various toxic influences of metals on the microbial cell, demonstrating the ubiquity of metal toxicity. Metal toxicity generally inhibits cell division and metabolism. As a result of this ubiquity, microorganisms have to develop "global" mechanisms of resistance that protect the entire cell from metal toxicity

of stomach tumors. Accidental or intentional ingestion of extremely high doses of Cr(VI) compounds by humans has resulted in severe respiratory, cardiovascular, gastrointestinal, hematological, hepatic, renal, and neurological effects as part of the sequelae, leading to death or in patients who survived because of medical treatment (ATSDR 2008).

Arsenic: Like all heavy metals, As also show carcinogenesis and other diseases. Mainly, clinical manifestation of As is referred to as arsenicosis, which is mainly the prolonged exposure of arsenic in humans. As toxicity in human causes various respiratory diseases like reduced pulmonary function, lung cancer, chronic cough, or chronic bronchitis. Various other diseases are also observed like black foot disease, peripheral neuritis, and gastroenteritis when As is absorbed by the intestine wall. Unlike Pb and Cd, the molecular mechanism underlying arsenic toxicity is multifactorial. It involves generation of oxidative stress, suppression of DNA repair, inhibition of cell cycle check points, and induction of apoptosis (Tchounwou et al. 2002, 2003).

2.6 Bioremediation

Conventionally, various approaches have been used to remediate the metal contaminants wherein physical, chemical, biological, and electrical methods are the major techniques (Table 2.2). Physical, chemical, and electrical methods include chemical precipitation, reverse osmosis, oxidation-reduction solvent precipitation, lime coagulation, electrodialysis, evaporation, and incineration have been utilized to remediate

Table 2.2 Comparison of physical, chemical, and biological methods for remediation

Physical methods	Chemical methods	Biological methods
Adsorption	Hydrogen sulfide	Biotransformation
Ion exchange	Sodium dithionite	Bioaccumulation
Membrane filtration	Photocatalysis	Biomineralization
Reverse osmosis	Sodium metabisulfite	Biosorption
Granular activated carbon	Calcium metabisulfite	Metal chelation
Electrokinetics	Calcium polysulfide	
Electrodialysis	Ferrous sulfate	

the metals, metalloids, and nonmetals (Alhuwalia and Goyal 2007; Zahoor and Rehman 2009). These techniques have several disadvantages such as high cost, higher usage of chemicals, incomplete removal, high electricity, and toxic sludge (Bishnoi et al. 2004; Pandey et al. 2013). So, various attempts have been made for bioremediation of heavy metals using microbial systems as an attractive method because such techniques are cost-effective and environmentally compatible (Yin et al. 2008).

Till date, various types of bioremediation have been developed to remediate the hazardous contaminants including heavy metals which is shown in Fig. 2.3.

Bioremediation is a complex process which requires mainly microorganisms, plants, or microbial or plant enzymes to detoxify or degrade contaminants in the environments. In bioremediation, it also includes biodegradation, biotransformation, and biodeterioration (Fig. 2.4). By supplementing the bacteria and fungi, the process of bioremediation can be enhanced. Furthermore, this process can be enhanced by adding various nutrients such as carbon source, nitrogen source, surfactants, and other enriched co-cultures (Rudakiya et al. 2019a, b; Zaki et al. 2014). The goal of bioremediation is to at least reduce pollutant levels to undetectable, nontoxic, or acceptable levels, that is, to within limits set by regulatory agencies or, ideally, to completely mineralize organopollutants to carbon dioxide (Pointing 2001).

Bioremediation is a natural process and is therefore perceived by the public as having a reduced impact on natural ecosystems. It is typically less expensive than the equivalent physical-chemical methods. Complete destruction of target pollutants is possible on site without the need of excavation or the transport of large quantities of waste off site (Vidali 2001). Finally, it requires little energy input and preserves the soil structure (Höhener et al. 1998). Perhaps the most attractive feature of bioremediation is the reduced impact on natural ecosystems, which should make it more acceptable to the public (Zhang and Qiao 2002). For fungal systems, this does require the soil to be aerobic, with the provision of enough oxygen to enable effective colonization to occur. However, bioremediation possess several disadvantages which comprises the process that is limited to those compounds that are biodegradable. Furthermore, there are some concerns that the products of bioremediation may be more persistent or toxic than the parent compounds. Furthermore, it is difficult to extrapolate the results from bench and pilot-scale studies to full-scale

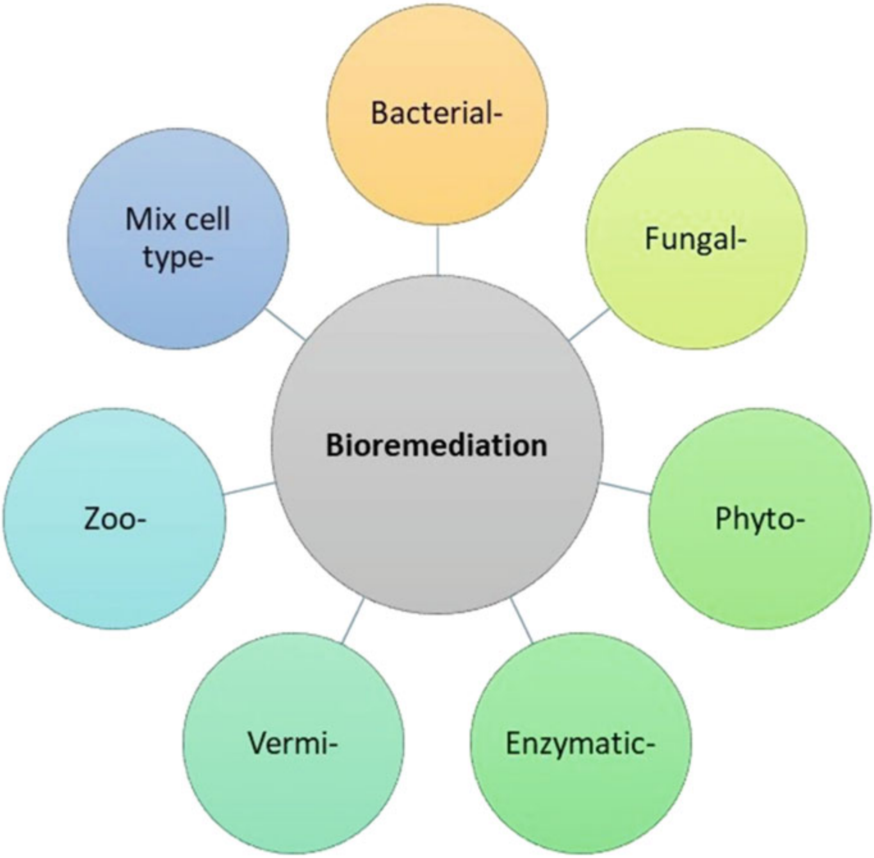


Fig. 2.3 Types of bioremediation employed to treat the hazardous contaminants including heavy metals

field operations. All biological processes, such as this, are often highly specific and complex and take longer than other treatment options (Vidali 2001).

In case of heavy metals, bioremediation of heavy metals has been conducted using bioleaching, biomineralization, biosorption, bioaccumulation, biodegradation, and biotransformation. In case of biodegradation, partial, and sometimes total, transformation or detoxification of contaminants by microorganisms and plants. Bio-mineralization is a more specific term wherein mostly fungus, bacteria, and plants excrete various organic acids and mineralize it into insoluble form of metal (Rudakiya et al. 2019b; Gouma et al. 2014).

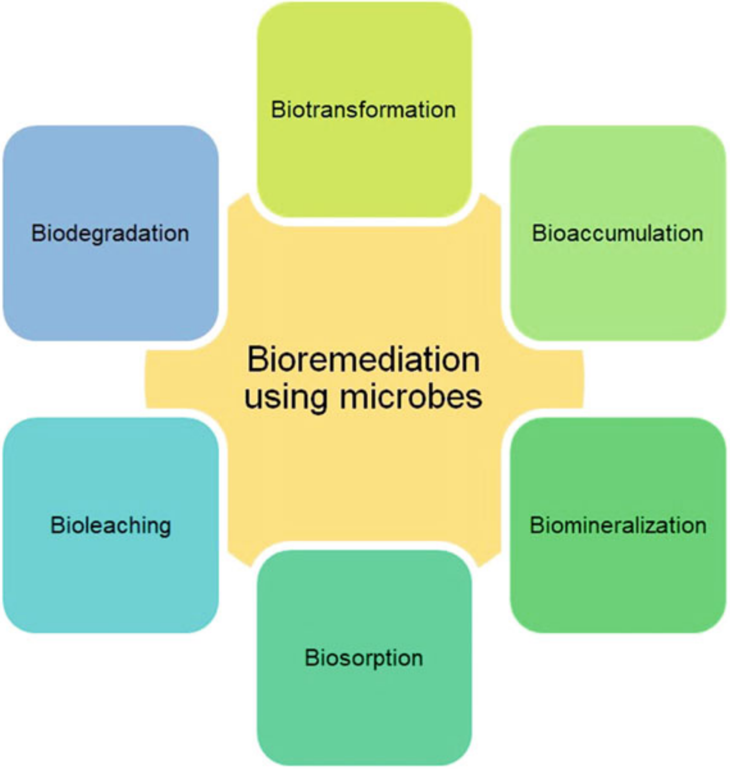


Fig. 2.4 Different mechanisms of bioremediation of metals using microbes

2.6.1 Bacteria

Bacteria use various pathways to resist and/or tolerate the metals. Bioremediation of metals in bacteria mainly conducted by biotransformation, metal efflux, metal binding, biosorption, and metal chelation pathways (Rudakiya and Pawar 2017; Rudakiya 2018). In case of biotransformation, metal is reduced and/or oxidized to be converted into the nontoxic form. Within metal biotransformation, oxidation, reduction, methylation, and dealkylation processes also occur outside the cell. Various efflux and receptor are more efficient to remediate different enzymes wherein CDF, CBA, and p-type ATPase types of transporters allow the metal outside. In biosorption, ion exchange, reduction, methylation, and dealkylation processes are involved. Sometimes, chemical modification of metals also occurs when certain chemicals involve reducing the toxic metals (Fig. 2.5). Bacteria comprises proteins, carbohydrates, and fatty acids which are important for metal binding mechanisms. In addition, certain metal transformation also occurs using enzymes, e.g., chromate

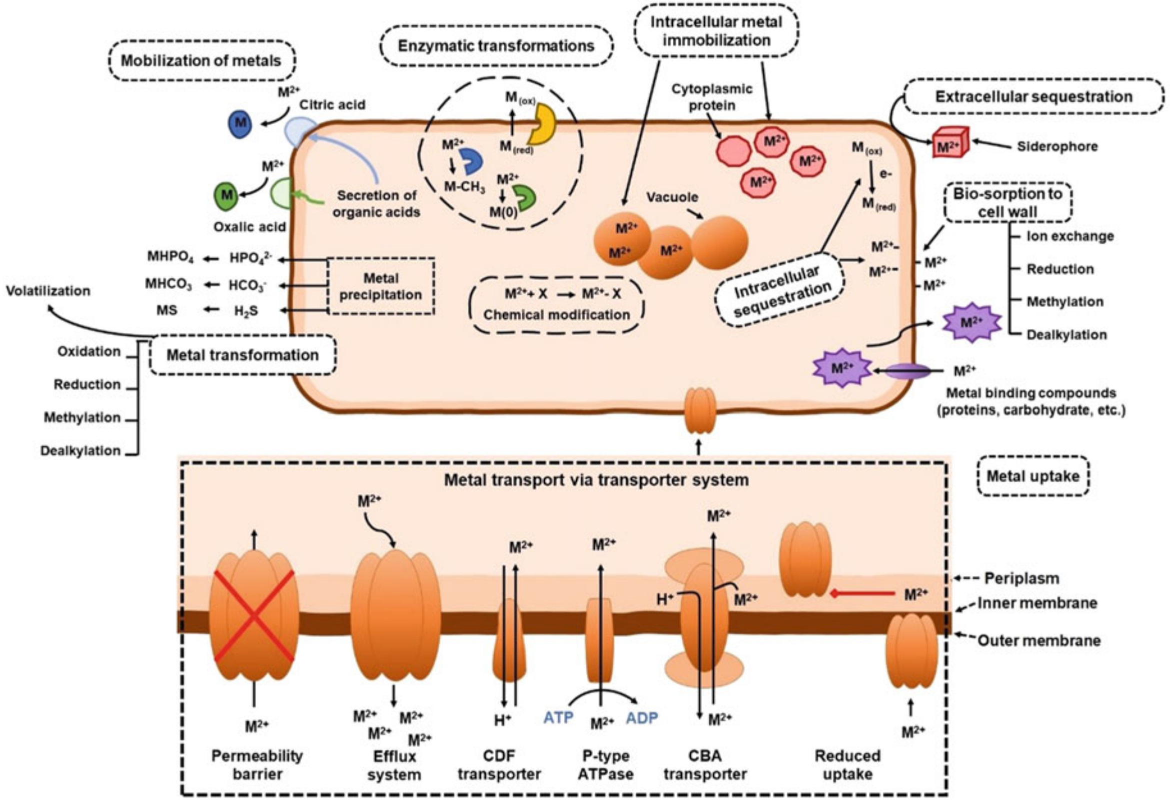


Fig. 2.5 Various bioremediation mechanisms are conducted by bacteria and fungi. These mechanisms include biotransformation, metal efflux, metal binding, biosorption, etc.

reductase. Mobilization of metals occurs when organic acid interacts with the metals and forms the insoluble metal species (Rudakiya et al. 2020).

2.6.2 Fungi

Fungi are the effective organisms to remediate the metals, metalloids, and radionuclides on the basis of morphological, ecological, and biochemical properties. Majority of fungi can remediate the metals during the different stages of the life cycle using various pathways. Fungal cell wall contains a large quantity of polysaccharides and proteins, which contain many functional groups such as carboxyl, amine, hydroxyl, and phosphate groups, which are known to be involved in the metal chelation (Rudakiya and Gupte 2017; Baldrian 2003; Couto et al. 2004). Moreover, most of the microorganisms produce extracellular polymeric substances (EPS) in natural environment for attachment, tolerance, and reduction of heavy metals. Anionic property of EPS imparts the electrostatic interactions with heavy metals (Guibaud et al. 2005). The acidic property of EPS is mainly contributed by several functional groups such as hydroxyl, carboxyl, uronic acids, amino acids, phenolic, and sulfhydryl groups, which interact with positively charged metal ions (Gutnick and Bach 2000). *A. niger* has been found to be capable of removing heavy metals like Pb, Cd, and Cu (Kapoor et al. 1999).

2.7 Bioremediation of Some Heavy Metals

Among various heavy metals, arsenic, lead, mercury, chromium, selenium, cadmium, and nickel are the priority class toxic metals/metalloids/nonmetals. So, environmental occurrence and bioremediation of some heavy metals have been discussed in the further sections.

Chromium: Cr(VI) is generally reduced to Cr(III) by bacteria and fungi. Sometimes biosorbants have been used to remove Cr from the solution (Shah et al. 2018). Mrudula et al. (2012) used Plackett-Burman design, central composite design, etc. to optimize physical and chemical factors for Cr biosorption and biotransformation through *Acinetobacter junii* VITSUKMW2. It was observed that maximum 99.95% removal of Cr(VI) was achieved in 12 h through *A. junii* VITSUKMW2 under optimized parameters, i.e., 14.85 g L1 molasses, 4.72 g L1 yeast extract, and 54 mg L1 initial Cr(VI). Jeyasingh and Philip (2005) operated a bioreactor under optimized conditions for chromium reduction and achieved complete reduction of Cr (5.6 mg Cr(VI) g1 of soil) in 20 days.

Cadmium: Normally, Cd forms complex oxides with Pb, Zn, and Cu ores and further converts into different sulfides and carbonates because it does not exist in pure form in the environment (Monachese et al. 2012). Bioremediation of Cd is mainly carried out by bacteria, fungi, yeast, and plants. In eukaryotic microorganisms, binding with polythiols is the main mechanism for the detoxification of Cd. However, various mechanisms have been developed to remediate Cd by bacteria which are efflux, precipitation, vitalization, oxidation/reduction, intracellular accumulation, cell wall binding, etc. Bacterial species like *Staphylococcus, Bacillus, Pseudomonas, Escherichia, Proteus, Klebsiella, Citrobacter, Lactobacillus*, and *Bifidobacterium* are very well reported to remediate Cd via the above mechanisms (Kermani et al. 2010; Kalkan et al. 2013; Jang 2016).

Nickel: Nickel is the 24th most abundant and ubiquitous element which causes certain toxicity on soil, water, microbial communities, eukaryotes, and human beings. Most of the reports are related to the carcinogenic, mutagenic, genotoxic, and immunosuppressive. Annually, 120,000 tons of Ni is deposited using human activities, and annually 50,000 tons of airborne Ni is deposited on earth. Biological approach to remediate Ni is effective wherein various bacteria, fungi, algae, and plants have been utilized. Biosorption is also an effective route to remediate Ni metal (Gadd 2000). Various microorganism such are *Candida tropicalis* (20 mg/g), *Bacillus subtilis* (6 mg/g), *Rhizopus arrhizus* (18 mg/g), *Pseudomonas stutzeri* (10 mg/g) and *Anacystis nidulans* (18 mg/g) are reported to remediate the Ni metal at higher scale (Bhusan and Hoondal 1997; Ramteke 2000; Kardel and Torabi 2019). Typical uptake of metal is pH dependent wherein acidic carboxyl groups R-COOH attaches with Ni ions and uptake the Ni (Fosso-Kankeu et al. 2016).

2.8 Conclusion and Future Aspects

Nowadays, potential risk of water and soil contamination with heavy metals to environment and human health has been concerned so much. So many methods have been developed to minimize this risk involving various biological agents which are mentioned in earlier sections. Bioremediation is a green approach to remediate the heavy metals as well as hazardous contaminants, which may also provide some other by-products that are industrially important molecules. In forthcoming years, attempts should be made to develop certain strategies to improve the tolerance and uptake of heavy metals/metalloids using genomic and metabolic engineering approaches (Mosa et al. 2016). Future research should be more focused on the by-products as well as increasing the efficacy with wider range of metal remediation. Detailed future research points are shown as below:

(a) *Meta"omics" study*: More research should focus on the metagenomics, metatranscriptomics, metaproteomics, and metabolomics of environmental samples such as contaminated water bodies and soil sites, so more bacterial and fungal isolates will identify which can be helpful for further metal bioremediation research work.

(b) *Gene identification and expression*: Identification and expression of metal tolerance and reducing genes will be effective for organisms to improve metal remediation efficacy.
(c) *Gene modification*: Future research work should focus on the genetic modification in organisms to remediate more than one metals, metalloids, and/or nonmetals.
(d) *Consortia development*: Development of consortia such as bacteria/bacteria, bacteria/fungi, and bacteria/yeast should be carried out for large-scale field-level application.
(e) *Pilot and large-scale research*: Large-scale research study should focus to remediate the heavy metals using various biological agents such as bacteria, fungi, yeast, or plants.
(f) *By-product importance*: After remediation, byproducts such as biomass or other compounds extracted from biomass should be utilized for various biotechnological applications.

Collectively, these potential efforts may enhance the bioremediation of heavy metals with lower cost and in lesser time.

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Chapter 3
Fungal-Mediated Bioremediation of Heavy Metal–Polluted Environment

Jyoti Goutam, Juhi Sharma, Ranjana Singh, and Divakar Sharma

Contents

Abstract The inexorable flow of heavy metals such as (Pb), mercury (Hg), chromium (Cr), zinc (Zn), uranium (Ur), selenium (Se), silver (Ag), gold (Au), cadmium (Cd), nickel (Ni), and arsenic created unhinge in the ecosystem and become recalcitrant pollutants. Due to anthropogenic interference in the natural system, heavy metals are incorporated in the food chain of the organism, which leads to deleterious effects in the growth of plants and animals. Anthropogenic sources such as industry effluent, agricultural land, and wastewater sludge are continuous sources of heavy metal induction in soil water and the environment. Looking toward hazardous ongoing deleterious effects of heavy metals, there is a need of an efficient,

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D. G. Panpatte, Y. K. Jhala (eds.), *Microbial Rejuvenation of Polluted Environment*, Microorganisms for Sustainability 26, https://doi.org/10.1007/978-981-15-7455-9_3

eco-friendly, and cost-effective approach to safeguard the entire ecosystem. Heavy metal is not destroyed by microbes but can be transformed into an innocuous state. Ecosystem possesses a plethora of diverse microorganism which exists, survives, and completes its lifecycle in the extreme environment. Microbes such as fungus can change the structure of the contaminant to make it harmless to humans and animals or change the solubility of the contaminant so that it can no longer mix into and mobilize. Among them, fungi inherit robust features and distinguished mechanisms to tolerate heavy metal stress. Fungi possess complex oxidative and hydrolytic enzymatic (such as cytochrome P450 monooxygenases and glutathione transferases) systems for detoxifying toxic compounds in the environment. Therefore, fungi can effectively sequester the contaminant, thus limiting recalcitrant pollutants to the living organism. In this chapter, we have discussed the role of heavy metals on the environment and mechanism used by fungi to remedying the environment. This study highlighted multiple modes employed by fungi to detoxify heavy metals from the environment. Herein heavy metals taken via different forms of fungi were also discussed such as endophytic fungi and quantum dots.

Keywords Heavy metals · Recalcitrant · Fungi · Sequester

3.1 Introduction

Metals are essential to the biological functions of plants and animals, but at elevated levels (more than the required amount), they contribute to the deleterious effect to organisms. Metals whose density exceeds 5 g/cm^3 are considered heavy metal. Heavy metals such lead (Pb), mercury (Hg), chromium (Cr), zinc (Zn), uranium (Ur), selenium (Se), silver (Ag), gold (Au), nickel (Ni), and arsenic (As) do not have a biological role but become toxic at low concentrations. With the pace of time, heavy metals are being continuously assimilated in land-water and soil. The wide-scale occurrence of these heavy metals leads to adverse health effects such as multiple organ failure and carcinogenic. Looking over the ever-increasing flow of heavy metal in the environment and its adverse health effect to living organisms leads to search an alternative way for metal removal. Bioremediation refers to waste management techniques which employ natural source to convert hazardous substance to innocuous substances. It is mediated by various bacteria, fungi, algae, and plants. Fungi bear indestructible morphology with a specific mechanism that captivates heavy metal into the surface, later on, accumulated inside the fungal cell. Fungi absorb the metal ions into the cell and also chelate on the cell, so that they tolerant heavy metal compounds (Gadd and White 1993; Anahid et al. 2011). Generally, detoxifications of heavy metals are possible by compartmentalization and biotransformation into an inactive form of the element (Nies et al. 1989; Nies 1991). Safe sustainable management of metals is required to restore the ecosystem. This chapter is primarily based on fungal-mediated bioremediation, which is further elaborated by other modes of fungi that detoxify heavy metals. Fungal-mediated decontamination of environments deals with multiple strategies to decontaminate the environment with heavy metals such as biosorption, bioaccumulation, bioleaching, and bio-immobilization.

3.2 Heavy Metals

Heavy metals generally exist in the form of carbonates, hydroxides, oxides, sulfides, sulfates, phosphates, silicates, and organic compounds (Singh et al. 2011). They also exist in their metallic, elemental form, but they are mobilized by the action of human (anthropogenic activity extraction, smelting) or natural phenomenon (weathering and leaching) (Salem et al. 2000) (Fig. 3.1). Toxic heavy metals cannot be biodegraded when their concentration is elevated, and their accumulation is found to cause serious diseases and disorders (Jackson et al. 2001). In humans, the toxicity of metal has been linked with birth defects, cancer, skin lesions, retardation leading to disability, liver and kidney damage, and host of other maladies (ATSDR 2001). In plants, they reduce plant growth by affecting mineral nutrition and essential enzyme which are necessary to maintain physiological activities (Fig. 3.1). In 2011, World Health Organization (WHO) listed deleterious 11 heavy metals, namely arsenic, cadmium, cobalt, chromium, copper, mercury, manganese, nickel, lead, tin, and titanium. The distribution and concentration of heavy metals in the environments are driven by anthropogenic activities, which ultimately deplete the minerals from naturally confined reservoirs represented in Fig. 3.1 (Albert 2015). In 2012, WHO listed arsenic, cadmium, lead, and mercury as challenges for public concern. The United States Environmental Protection Agency (US EPA) and the International Agency for Research on Cancer (IARC) have classified them as either “known” or “probable” human carcinogens (Tchounwou et al. 2012). A comprehensive review has been widely elaborated on the toxicity of heavy metal and its detrimental effect on humans (Vardhan et al. 2019).

3.3 Microbes Involved in Bioremediation

Bioremediation refers to the cleaning of the ecosystem via natural sources, which comprises plants, bacteria, algae, fungi, etc. (Fig. 3.2). About 35% of biological remediation is assisted by microbes and 16% is based on plants (EA 2015). In the very beginning, Tausz and Donath (1930) presented the idea of using microorganisms to clean the petroleum derivative–contaminated soil, which was the origin of the biodegradation processes. Among microbes, prokaryotes and eukaryotic organisms are capable of detoxifying heavy metals (Fig. 3.2) (Beveridge and Doyle 1989). But now with the involvement of advanced biotechnologies such as biofilm algae,

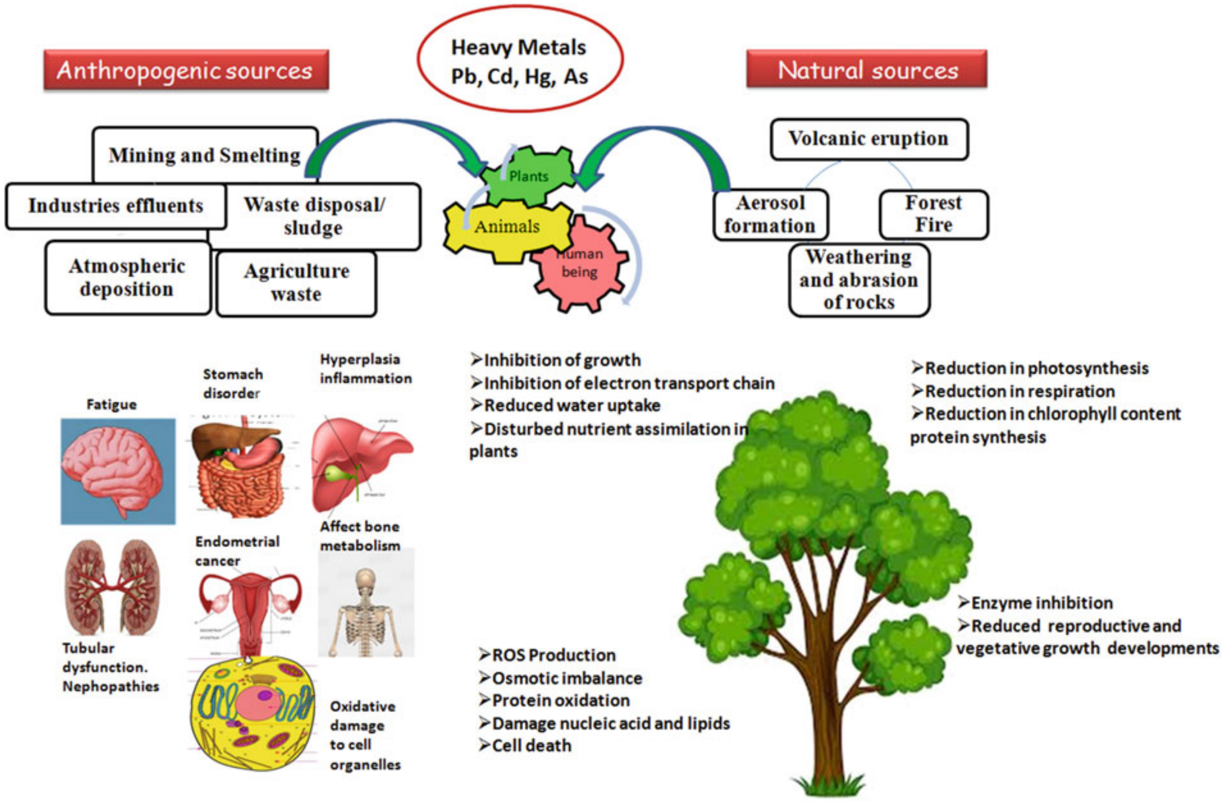

Fig. 3.1 Sources of heavy metals and their hazardous effect on human being and plants

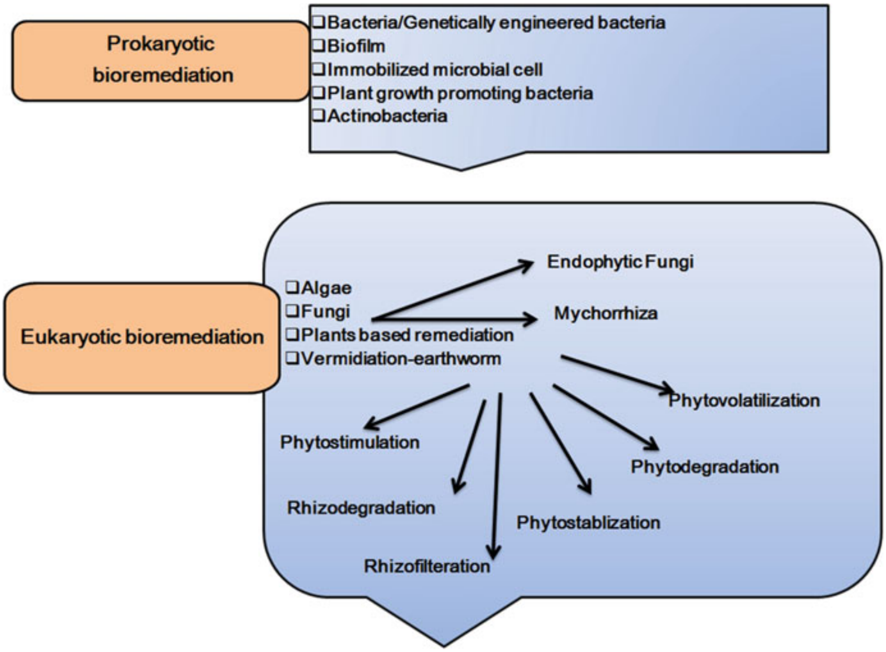

Fig. 3.2 Dendrogram showing different types of prokaryotic and eukaryotic bioremediation of heavy metals

genetically engineered microbes, and immobilized microbial cells, it has enhanced the approach of bioremediating heavy metals. In addition to this, our plant system is endowed with the various mechanisms at the cellular level to detoxify heavy metals which are termed as phytoremediation (Fig. 3.2). Moreover, the symbiotic associations between plants and rhizobacteria efficiently improve plant growth by increasing mineral nutrition and alleviating heavy metal toxicity on target plants (Titah et al. 2013). These rhizobacteria possess a variety of natural mechanisms to endure the toxicity of heavy metals. Microbes are capable of accumulating metals by binding them as cations to the cell surface in a passive process.

3.3.1 Advantages of Biological Methods Over Conventional Methods

Nowadays, industrial effluents are pre-treated through several conventional technologies before their discharge into the environment. Methods such as chemical precipitation, ion exchange, electro-deposition, biosorption, liquid–liquid extraction, adsorption, membrane separation, reverse osmosis, and coagulation are being used (Kratochvil and Volesky 1998). But due to several disadvantages, these methods become less effective in treating pollution. For example, conventional methods become unsuccessful at a higher concentration of heavy metals (100). These are expensive and produce large quantities of secondary pollutants (sludge) (Igwe and Abia 2006; Onyancha et al. 2008). Hence, these conventional physical and chemical methods become noneconomical as they generate large volumes of chemical waste ultimately. Therefore, an endeavor is made to develop effective alternative techniques which are applicable to the local conditions and must be able to meet with the established permissible limits.

3.3.2 Bioremediation of Heavy Metals by Different Interaction Between Fungi and Metals

3.3.2.1 Biosorption and Bioaccumulation

Fungi become a better choice of bioremediating heavy metals due to immense growth and admirable binding properties. They can easily and economically culture in mass quantities because of their short multiplication cycle and can be easily modified morphologically and genetically (Dhankhar and Hooda 2011).

First, the term “mycoremediation” was coined by Paul Stamets which expresses the meaning “removal of toxic materials by fungi.” Fungi detoxify the heavy metal through different strategies as other microorganisms. Biosorption is considered one of the significant processes involved in heavy metal bioremediations. The biosorption process was carried by both living and dead cells as the dead biomass of fungi has greater ability to remediate heavy metals as compared to living fungi, since it includes physical process and later includes a physiological process (Volesky 2007).

Generally a fungus adopts two basic methods of metal detoxification, the primary method involves the binding of metal to the surface known as biosorption and secondly involves intracellular uptake of metals via cellular metabolism known as bioaccumulation (Veglio and Beolchini 1997; Kadukova and Vircikova 2005). Biosorption is the ability of biological materials to accumulate heavy metals from wastewater through metabolically mediated or physico-chemical pathways of uptake (Fourest and Roux 1992). Hitherto a number of in vitro studies (between heavy metals and fungus) have been conducted which is based on the basic biosorption process. A long list have been illustrated (Table 3.1). Biosorption of metal ion usually occurs by ion exchange reaction, surface binding, and complexion with functional groups which are present in cell surface such as carboxyl, amine, hydroxyl, phosphate, and sulfahydryl group (Strandberg et al. 1981; Wang and Chen 2009; Nilanjana et al. 2008) (Fig. 3.3). Element chromium has been adsorbing by living and dead biomass of fungi *Aspergillus* followed by sequestration of above functional groups. Other than this, the uptake mechanism is felicitated by nonspecific sulfate transporters, inside the cell, such as glutathione, which plays an important role in the intracellular reduction of Cr(VI) (García-Hernández et al.

Table 3.1 List of potential fungi involved in the bioremediations of different heavy metals

S. No	Metal	Fungi	References
1	Cr	*A. flavus*	Bennett et al. (2013)
		Rhizopus arrhizus	Tobin et al. (1984)
		Aspergillus foetidus	Prasenjit and Sumathi (2005)
		Aspergillus ochraceous, *Dactylosporium* sp. *Drechslera rostrata*	Seshikala and Charya (2012)
		Rhizopus nigricans	Bai and Abraham (2001)
		Candida utilis	Pattanapipitpaisal et al. (2001)
		Trichosporon cutaneum	Bajgai et al. (2012)
		Aspergillus niger	Acosta-Rodríguez et al. (2018)
		Fusarium Solani	Sen and Dastidar (2011)
2	Pb	*A. foetidus*	Chakraborty et al. (2013)
		Penicillium chrysogenum	Niu et al. (1993)
		A. niger	Kapoora et al. (1999)
		Trichoderma asperellum, *Penicillium simplicissimum*	Iskandar et al. (2011)
		Cunninghamella	El-Morsy El-Sayed (2004)
		Phanerochaete chrysosporium	Fu et al. (2012)
		Rhizopus arrhizus	Fourest and Roux (1992)
		Penicillium sp.	Siegel et al. (1983)
		Penicillium chrysogenum	Alothman et al. (2020)
		Botrytis cinereal	Akar et al. (2005)
3	Hg	*A. flavus*	Kurniati et al. (2014)
		Rhizopus arrhizus	Tobin et al. (1984)
		Penicillium canescens	Say et al. (2004)
		Aspergillus niger	Rodríguez et al. (2018)
4	U	*Aspergillus niger, Cryptococcus,* *Penicillium* sp., *Curvularia*	Mumtaz et al. (2013)
		Aspergillus niger	Horikoshi et al. (1981)
		S. cerevisiae *A. terreus*	Horikoshi et al. (1981), Strandberg et al. (1981)
		Penicillium chrysogenum, Aspergillus ustus	Tsezos and Velosky (1981) Alothman et al. (2020)
5	Cd	*Aspergillus niger*	Das et al. (2013), Kapoora et al. (1999)
		Aspergillus oryzae	Kiff and Little (1986)
		Penicillium spinulosum	Townsley and Ross (1986)
		Penicillium notatum	Siegel et al. (1983)
		Rhizopus stolonifer	Fawzy et al. (2017)
		Penicillium chrysogenum *Aspergillus ustus*	Alothman et al. (2020)

(continued)

Table 3.1 (continued)

S. No	Metal	Fungi	References
		Aspergillus versicolor, Aspergillus fumigatus, Paecilomyces sp., *Paecilomyces* sp. G, *Terichoderma* sp., *Microsporum* sp., *Cladosporium*	Mohammadian Fazli et al. (2015)
6	Cu	*Rhizopus arrhizus*	Tobin et al. (1984)
		Phanerochaete chrysosporium	Fu et al. (2012)
		Aspergillus Niger	Rao et al. (1993), Kapoora et al. (1999)
		Aspergillus awamori	Rose and Devi (2018)
		Aspergillus fumigates	Rao et al. (2005)
		Aspergillus awamori	Rose and Devi (2018)
		Trichoderma atroviride	López and Vázquez (2003)
		T. virens (PDR-28)	Tahir (2012)
		Penicillium chrysogenum, Aspergillus ustus	Alothman et al. (2020)
7	Ni	*A. niger,* *Aspergillus flavus*	Kapoora et al. (1999) Rose and Devi (2018)
		Aspergillus niger, *Circinella* sp., *Aspergillus fumigates.* *Alternaria alternate,* *Saccharomyces cerevisiae*	Alpat et al. (2010) Rao et al. (2005) Levinskaite (2001), Nguyen and Ruey-Shin (2015)
		Phanerochaete chrysosporium, *Aspergillus awamori, Aspergillus flavus,* *Trichoderma viride*	Joshi et al. (2011)
8	Zn	*Aspergillus niger* *Rhizopus stolonifer*	Rodríguez et al. (2018) Fawzy et al. (2017)
9	As	*A. nidulans* *Aspergillus niger*	Maheshwari and Murugesan (2009) Rodríguez et al. (2018)
10	Co	*Trichoderma, Aspergillus, Mortierella, Apecilomyces,*	Townsley and Ross (1986)
		Penicillium, Pythium, and Rhizopus *Aspergillus Niger*	Rodríguez et al. (2018)
11		*Trichoderma atroviride, Mortierella exigua*	Karcprzak and Malina (2005)
		Aspergillus, Penicillium, *Alternaria, Geotrichum, Fusarium*	Ezzouhri et al. (2009)

2017). The cell wall of fungi was found to come into contact with the metal ion in a solution where the metal can be deposited on the surface or within the cell wall structure before interacting with cytoplasmic materials (Gadd 1990). Extracellular mechanism deals with chelation, precipitation, and cell wall binding (Bellion et al. 2006). Bioaccumulation is the intracellular mechanism of fungi that involves binding to sulfur compounds, organic acids, peptides, polyphosphates, and transport into intracellular compartments. Here intracellular uptake occurs due to increased permeability preceded by cell wall ruptures which leads to subsequent exposure of metal-binding sites (Gadd 1990). Additionally, fungi have an internal cellular system of detoxification assisted by the generation of antioxidant compounds (Bellion et al. 2006).

Fungal cell wall also contains chitin and chitosan which have shown to sequester the metal ion (Treen-Sears 1986). Proteins also interact with metals during the biosorption process (Spiro 1981). Plants, algae, bacteria, yeasts, and fungi have proved to be the potential metal biosorbents. They are found sufficient to remove heavy metals in substantial quantities (Mcclean et al. 1995; Volesky and Holan 1995; Volesky and May 1995).

In bioremediation process, recycling of fungi has been proven to be very cost-effective (Galun et al. 1983; Tsezos 1984). In industries, dead biomass can be procured directly from industrial sources. The live cell can be killed by physical treatment such as autoclaving, vacuum drying, chemical drying, or mechanical drying. It is also seen that alkali pretreatment is very effective, as a chitin cell wall to form a chitosan–glucan complex which offers higher affinity for metal ions (Muzzarelli et al. 1980). Various eluants were also screened for the recovery process. H_2SO_4 and HCl are found to be efficient in the recovery of absorbed uranium from Rhizopus and Penicillium biomass. Penicillium biomass loaded with Ni, Cu, Zn, and Cd can be eluted using NaOH (Galun et al. 1987). Vennkobakar (1990) and Muraleedharan reported in *Ganoderma lucidium* for Cu(II) removal. Cu, Zn, and Mn are the major metal that absorbed by fungi and yeasts along with some non-nutrient metals like Hg, Ni, Sn, and U. Apart from the absorption approach, fungi also used immobilization, plasma membrane exclusion, and chelation approaches to bioremediate the heavy metals. Sharma and Dietz (2009) reported various mechanisms to remediate the heavy metals such as sequestration of heavy metals by ligands, restriction of heavy metal uptake, and transport ROS effects like upregulation of antioxidants, synthesis of heavy metal transporters, and biosynthesis of proline and other signal molecules like salicylic acid and nitric oxide. Additionally, microbes develop different strategies such as bioaccumulation, bio-mineralization, bio-immobilization, and biotransformation for continued existence in heavy metal–polluted environments (Fig. 3.3). The ubiquitous presence of fungi has allowed acclimation to most types of wastes. Fungi perform completely different techniques to detoxify the environment loaded with heavy metals.

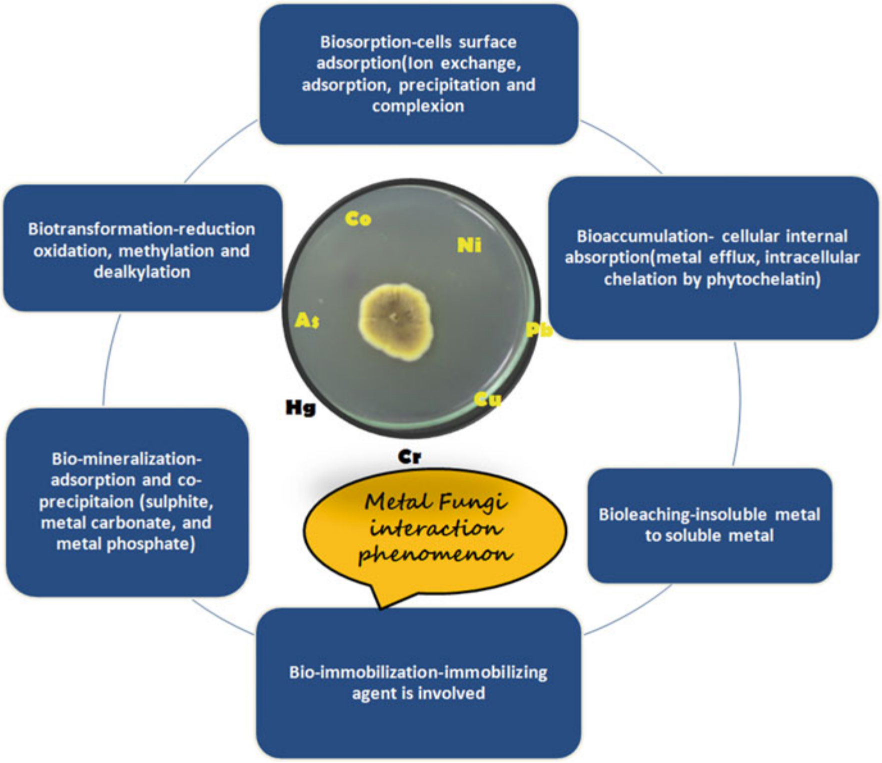

Fig. 3.3 The basic phenomenon involves metal fungal interaction which mediates heavy metal bioremediation

3.3.2.2 Parameters that Affect the Biosorption

The elimination of heavy metals via microorganisms depends upon the genetics of microfauna, type of metals, and environmental factors (Hassen et al. 1998). But in vitro experiments revealed that metal uptake by fungi cells are affected by different parameters. Initially, researchers found that glucose, oxygen level, and concentration of cells in aqueous solutions affect metal uptakes (Kurek et al. 1982; Galun et al. 1987; Kiff and Little 1986). Later, the biosorption process was seen to be affected by different abiotic parameters such as temperature, pH, biomass, concentration, contact time, and initial metal ion concentration. Fungal biosorption also depends on physical or chemical pretreatment of biomass, presence of various ligands in solution, and a limited extent on temperature (Kapoor and Viraraghavan 1995). Metabolites secreted by fungus also interfere with the pH; hence, it affects the biosorption capacity of fungi. The researcher suggested that the role of parameters varies in each fungus with respect to accessed heavy metals. For example, removal of copper, gold, zinc, cadmium, and manganese by *Penicillium spinulosum* found maximum in the lag phase of growth and declines as the culture reaches the stationary phase (Townslcy et al. 1986; Townsley and Ross 1986) (Table 3.1). It has been hypothesized that the pH declines in lag phase which is due to cell wall differences or metabolite secretion. pH is significant on biosorption since it has a substantial effect on the solubility, speciation, dissociation of functional groups, and solution chemistry of heavy metals (Javaid et al. 2011).

Second, time also affects biosorption since it influences the chemistry of fungal extract, which is further associated with other reaction of biosorption such as hydrolysis, complexation by inorganic/organic ligands, precipitations, redox reactions, speciation, biosorption availability of heavy metals, and the site dissociation of the functional groups (Ozer and Ozer 2003). Kumar and co-workers also revealed that the removal efficiency of heavy metals (Cu, Ni, and Zn) increases as the contact time increases.

Temperature is one of the significant factors which alters the magnitude of other factors. Some of the factors include (a) initial stability of metal ion species, (b) the stability of microorganism–metal complex depending on biosorption sites; (c) cell wall configuration; and (d) the ionization of chemical moieties on the cell wall (Sag and Kutsal 2000). Similarly, initial metal ion concentration also affects the biosorption process; this acts as driving energy to overcome mass transfer resistance of metal between the aqueous and solid phases. All of these collectively influence the metal uptake by living microorganisms.

3.3.2.3 Bioleaching

In mining industries, mining and smelting operation mobilize heavy metals in land and water, thus leading to heavy metal contamination; such types of contaminations are handled by the bioleaching process. The bioleaching process is the extraction of metal from low-grade ores and with the help of microorganisms. Microbial leaching has potential in mining sites and treating of metal-containing waste products (Bosecker 2001). Fungi are found helpful in sorting the metal from carbonaceous low-grade ore. Microbes convert metal compounds into their water-soluble forms and act as biocatalysts of leaching processes. Bioleaching processes are mediated by the metabolites produced from the microbial metabolic process. Interaction of fungi with metals and minerals occurs both synthetically and naturally, which further change their chemical and physical properties. Thus bioleaching process creates metal speciation mobility, thus effecting mineral dissolution and formation through a variety of metal mobilization or immobilization mechanisms (Gadd 2007, 2010). Fungi may interact with metal-containing ores depending on their metal tolerance and ability to influence the metal mobilization (Fomina et al. 2005). Several examples quoted have shown the bioleaching process by fungi. *Aspergillus* and *Penicillium verruculosum* were found to solubilize iron from iron ore (Chaudhary et al. 2014). Bioleaching of heavy metals from red mud by using the fungus *Aspergillus niger* showed that toxicity of red mud (bauxite residue) decreased (Qu et al. 2013). In another study, *Aspergillus* and *Penicillium* leached Ni, Co, Fe from saprolite, weathered saprolite, limonite, and nontronite (Valix et al. 2001). A new fungal isolate, *Penidiella* sp. strain T9, accumulates the rare earth element dysprosium that is found in an acidic condition that grows in heavy metal (Horiike and Yamashita 2015). In a separate study, metals (68% of Cu 46% of Zn of 34% nickel) were solubilized during low-grade mining ore using *Aspergillus niger* (Mulligan et al. 2004). Bioleaching is essential for the recovery of copper, uranium, and gold. Even though bioleaching with fungi has been successfully achieved in a laboratory scale (there are no reports of industrial operations that would utilize fungi).

3.3.2.4 Bio-immobilization

Bio-immobilization reduces the mobility of metals, by transforming soluble metal ions to insoluble solids via microorganisms. It is generally achieved by biosorption, bioaccumulation, bioprecipitation, and bioreduction/bio-oxidation. It is an advanced biosorption process. The only difference is that biosorption is immobilized by the different immobilizing agents. Lewis (1998) reported the removal of Cd^{2+}, Cu^{2+}, Fe^{3+}, Mn^{2+}, Pb^{2+}, and Zn^{2+} from solution by immobilized biomass of the filamentous fungus *Rhizopus arrhizus.*

Prakasham (1999) found that the elevated absorption pattern of chromium (IV) at pH 2 while using non-living free biomass over the immobilized biomass of *Rhizopus arrhizus*. Bio-immobilization is a technique that surpasses the disadvantages of biosorption methods. *Pycnoporus sanguineus* (white rot fungi) were immobilized into Ca-alginate gel. The immobilized cells of *P. sanguineus* were capable of removing Cu(II) ions from aqueous solutions (Yahaya et al. 2009). Biosorption of uranium(VI) ions by immobilized *Aspergillus fumigatus* beads was also investigated in a batch system (Wang et al. 2010). In a study, *A. terreus* UFMG-F01 was immobilized in polyurethane foam which leads to the uptake of 16.5 mg g(-1) iron, 96.5 mg g(-1) chromium, and 19.6 nickel mg g(-1) (Dias et al. 2012). Similarly in a natural matrix biosorption of lead, mercury, and cadmium were removed by *Aspergillus terreus* (Sun et al. 2010).

In 2016 Cai and other researchers immobilized the living conidia of the heavy metal–resistant *Penicillium janthinellum* strain GXCR by polyvinyl alcohol (PVA)-sodium alginate (SA) beads to remove heavy metals (Cu, Pb, and Cd) from an aqueous solution containing a low concentration (Cai et al. 2016).

3.3.2.5 Biomineralization

Biomineralization is a biological method of detoxifying heavy metal along with the bio-recovery process. Microorganisms immobilize heavy metals and convert into insoluble minerals through metabolism to mineralize heavy metal ions, thereby reducing their mobility and bioavailability. Biomineralization fall into two categories: biologically induced mineralization (BIM) and biologically controlled mineralization (BCM). In biologically controlled mineralization (BCM), the physiology of

Table 3.2 List of fungi involved in the bioremediations of different heavy metals via bio-mineralization process

S. No.	Fungi	Metals	References
1	*Neurospora crassa*	Cd was precipitated as ($CdCO_3$)	Li et al. (2014)
2	Yeasts	Pb precipitated as ($Pb_3(PO_4)_2$), pyromorphite ($Pb_5(PO_4)3Cl$), anglesite ($PbSO_4$), and the lead oxides	Liang et al. (2016)
3	*Aspergillus* sp. *Fusarium oxysporum*	Precipitation of calcite, vaterite, aragonite carbonates, and hydroxides of lead and strontium	Dhami et al. (2017)
4	*Pestalotiopsis* sp. and *Myrothecium gramineum*	$CaCO_3$ and $SrCO_3$ biomineralization	Li et al. (2015)

microorganisms controls the nucleation, growth, and morphologies of the biominerals. Whereas in biologically induced mineralization, it depends on the organism modifying its local microenvironment to create appropriate physicochemical conditions for the precipitation of minerals (Gadd 2010). Few fungal-mediated biomineralizations are discussed in Table 3.2. It is generally found that an ureolytic microorganism is effective in immobilizing toxic metal pollutants via calcium carbonate precipitation (Table 3.2). The ureolytic organisms can immobilize toxic metals efficiently by precipitation or co-precipitation, independent of metal valence state and toxicity and the redox potential.

3.3.2.6 Endophytic Fungi-Assisted Bioremediation

In the twentieth century, endophytic fungi are widely studied to their existent, distribution and applications in medicine relevance. Besides this, the researcher has drawn attention to the role of endophytic fungi as heavy metal bioremediators. Endophytic fungi possess structure as extended mycelia networks that have the biological ecological capacity to reduce the risk related to the heavy metal via chemical modification or by changing the chemical availability.

Endophytic microorganism lives in mutual association inside the plant that ranges from symbiotic, commensalism and neutral or as latent pathogen. They occur as versatile microorganism to the development stage, nutritional status, and other environmental factors (Schulz et al. 2002). Endophytic fungi especially dark septate endophytes (DSEs) have been reported to be promising biosorbent for heavy metal treatment. In addition to drought, heat, low pH, and high salinity, they also showed metal tolerance (Waller et al. 2005; Rodriguez et al. 2004). Simultaneously metal tolerance was found to promote the plant growth under the higher concentration of metals (Li et al. 2011; Xiao et al. 2010; Deng et al. 2014). Several in vitro studies revealed that endophytic fungi can tolerate heavy metals (Table 3.3).

Table 3.3 List of potential endophytic fungi involved in the bioremediations of different heavy metals

S. No	Fungal endophytes	Host plant	Metals	References
1	*Aspergillus fumigatus, Rhizopus* sp., *Penicillium radicum, Fusarium*	Healthy plants	Cr +6, strains were able to carry out intra- and extra-mycelial reduction of Cr-VI to Cr-III	Bibi et al. (2018)
2	*Fusarium* sp. *Colletotrichum* sp.	*Shorea robusta* *Terminalia bellirica*	Lead, chromium, copper, and zinc	Mahish et al. (2017)
3	*Pestalotiopsis* sp.	*Nypa fruticans*	Copper, lead, zinc, and chromium	Choo et al. (2015)
4	*Cryptococcus* (yeast)	*Brassica chinensis*	Cd, Pb, Zn, Cu	Deng et al. (2012)
5	*Lasiodiplodia* sp.	*Portulaca oleracea*	Cd, Pb, Zn	Deng et al. (2014)
6	*Piriformospora indica*	Rice (paddy), *Oryza sativa*	As	Mohd et al. (2017)
7	*P. fortinii, R. veluwensis, Rhizoscyphus* sp.	*C. barbinervis*	Cu, Ni, Zn, Cd, and Pb in roots These metals reduced the K uptake in plants and promote chlorosis	Yamaji et al. (2016)
8	*Chaetomium cupreum*	*Miscanthus sinensis* Andersson	Al tolerance via inducing chlorogenic acid production and producing oosporein	Haruma et al. (2019)
9	*Pyrenochaeta* sp. SR35, *Paraphaeosphaeria* sp. SR46, *R. vagum* SR37, and *R. vagum* SR44 (DSE)	*S. variegate*	Cd	An et al. (2015)
10	*Mucor* sp. CBRF59	*Brassica chinensis*	Cd and Pb	Deng et al. (2011)
11		*D. ambrosioides*		Parmar et al. (2018)

3.3.3 Mycorrhizal-Based Bioremediation

Naturally, fungi make symbiotic associations with the roots of the higher plants to combat heavy metal pollution in the environment. This symbiotic association is known as mycorrhiza. Mycorrhiza facilitates host plants to uptake and transport phosphorus (P), and other relatively immobile soil nutrients promote plant growth and enhance their stress tolerance (Smith and Read 2008). Fungi, such as *Trichoderma, Aspergillus, Rhizopus*, and arbuscular mycorrhizal fungi (AMF) have shown the potential to remove soil contaminants by enhancing phytoremediation (Adams et al. 2007; Jiang et al. 2007; Lebeau et al. 2008). Plants having AMF is known as hyperaccumulator. In an in vivo study, it has been suggested that mycorrhizal inoculation enhances Pb uptake and accumulation in the root system compared to non-mycorrhizal plants. Hence *R. intraradices* plays a significant role sequestering and metal detoxification (Yang et al. 2016). Similarly, olive plants associated with AMF were able to grow in the high-level manganese concentration. Their symbiosis reduced Mn concentrations from 43% to 83% (Briccoli et al. 2015). Interaction of fungi with lead-contaminated plants was studied by Yang et al. (2016); they found that arbuscular mycorrhizal fungi alleviate the heavy metal toxicity by inhibiting their uptake and translocation in plant parts (Yang et al. 2016). Arbuscular mycorrhizal fungi not only comprehend the physiology of symbiotic association with the plant but also restore the degraded ecosystem. It is a cost-effective process for the contamination of land remediation methods.

3.3.4 Fungal Nanoparticle–Mediated Heavy Metal Remediation

The emergence of nanotechnology contributes to its special role in heavy metal detection by fungal nanoparticles (less than a micron to that of individual atoms). Although different physical and chemical methods have been used to synthesize nanoparticles, they offer many disadvantages. Therefore, there is a need to develop an eco-friendly method for nanoparticle synthesis. Among microbes, fungi have special features that attribute to the most efficient tools to synthesize metal nanoparticles. As compared to bacteria, fungal mycelia offer a large surface area (Taherzadeh et al. 2003) and secrete much amount of enzymes (Mohanpuria et al. 2008; Chen et al. 2009; Pantidos and Horsfall 2014). It is hypothesized that the two enzymes such as NADH (nicotinamide adenine dinucleotide) and NADH-dependent nitrate reductase play an important role in the synthesis of nanoparticles from metal ions (Kalishwaralal et al. 2008). During the biological process, the rate of particle synthesis is affected by the size and shape of the nanoparticles, which are manipulated by controlling parameters such as pH, temperature, metal concentration, and exposure time to metal (Gericke and Pinches 2006). The increased surface and shape of nanoparticles are responsible for their different chemical, optical, mechanical, and magnetic properties, thus making fruitful for industries like food, medicine, pharmaceutical, and agriculture fields. A large number of silver and gold nanoparticles have been synthesized via a different type of fungi (Siddiqi and Husen 2016). In addition to gold and silver, other metal nanoparticles synthesized by fungi were also discussed. These extra small nanoparticles also felicitate the uptake of hazardous heavy metal, thereby bio-remediating the environment and promote them as biosensors. Their detection process can act as tools in ecological detection (heavy metal ion sensing) and bio-monitoring services (Shan et al. 2009). A list of fungi are illustrated in Table 3.4; they have been suggested as efficient, cost-effective, and environmentally friendly alternatives to other treatment in the view of resource

Table 3.4 Fungi that synthesize nanoparticle and remove heavy metal

S. No	Fungus	Nanoparticles	References
1	*Fusarium oxysporum*	Pb^{2+} and Cd^{2+} react with CO_2 to form $PbCO_3$ and $CdCO_3$ crystals	Sanyal et al. (2005)
2	*Schizosaccharomyces pombe* and *Candida glabrata*	CdS nanoparticles from cadmium salt in solution	Dameron et al. (1989)
3	*Rhodotorula mucilaginosa*	Cu nanoparticles	Salvadori et al. (2014)
4	*Aspergillus aculeatus*	Nickel oxide nanoparticles	Salvadori et al. (2015)
5	*Penicillium aurantiogriseum* *Penicillium citrinum* *Penicillium waksmanii*	Cooper oxide nanoparticles	Honary et al. (2012)
6	Endophytic fungi	Zinc oxide nanoparticles	Uddandarao and Balakrishnan (2017)
7	*Phanerochaete chrysosporium*	Cd sulfide nanoparticles	Chen et al. (2014)

conservation and environmental remediation, leading to nanobioremediation (Friedrich et al. 1998; Dastjerdi and Montazer 2010). Sometimes toxic metals/metalloids may even be mixed with recalcitrant Cu and biphenyl (Romero et al. 2006). Recently fungal sporangiospores of three Mucor species (EH8, EH10, and EH11) were found to overcome multimetal toxicity (Hoque and Fritscher 2019). Therefore, fungal nanoparticles serve as efficient tools to detect heavy metal ion, thus remediating the ecosystem (Fig. 3.4).

3.4 Fungal-Mediated Synthesis of Quantum Dots that Sense Heavy Metal

Quantum dots are generally semiconductors whose excitons are confined in all three dimensions. The diameter of the dot is less than the Bohr radius (0.52 Å). Heavy metal semiconductors consist of elements of groups II–IV, III–V, or IV–VI (such as Cd, Te, Se, Zn, In, and As) (Kershaw et al. 2013). These semiconductor nanocrystals can transport electrons and create valence band and conduction band. The gap of valence band and conduction band develops quantum confinement effect, a discrete quantized energy spectrum that contributes to varied optical properties and thermal properties. Hence, quantum nanocrystal found various applications in biology and pharmaceutical drug delivery systems (optical probes for biologically important molecules, biosensors, and medical imaging). It is referred to as low-cost nanotechnological transformations that serve many purposes of scientific applications. Besides the above application, synthesis of quantum dots is accompanied by heavy metal detection.

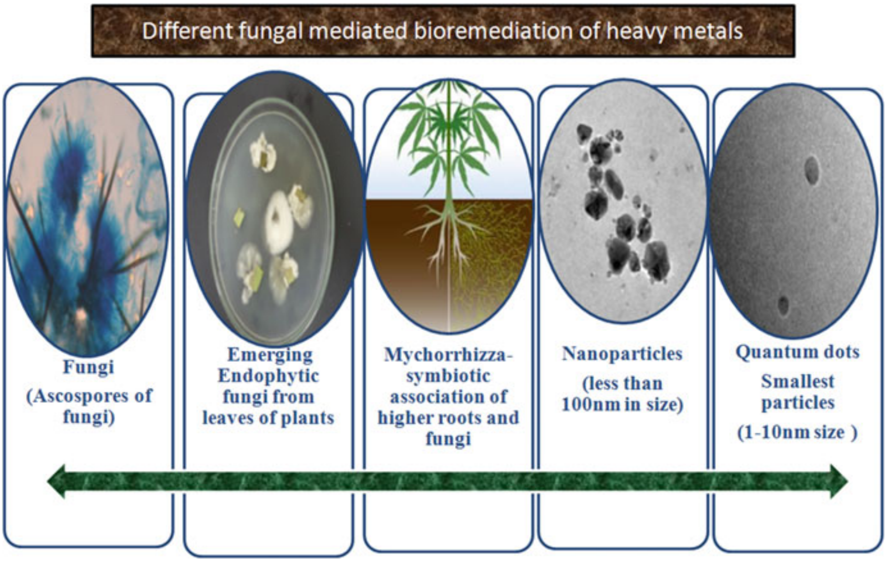

Fig. 3.4 Different ways by which fungi remediate the heavy metals

In general, carbon quantum dots (CDs) and nitrogen-doped carbon quantum dots (NCQDs) are formed which have a size of the order of ~10 nm, exhibit broader photoluminescence profile, and are superior to the traditional semiconductor quantum dots. These dots can be derived from natural sources such as banana, orange, leaf, and curcumin (Singh et al. 2017, 2019). Due to the larger surface area and plenty of functional groups available with these dots, a large amount of selective heavy metal ions binding with these dots can greatly affect the targeted biosorption capacity of fungi. They have good aqueous solubility, less toxicity, biocompatibility, facilitation to functionalize, and good resistance to photobleaching (Singh et al. 2017, 2019). Highly fluorescent CDs and NCQDs have a strong ability to bind selectively with toxic heavy metal ions. Hence, with growing demand for semiconductor nanoparticles, biosynthesis of microbe-mediated quantum dots witnessed the highly stable, water-dispersible nanoparticle formation. Extracellular biosynthesis of CdTe quantum dots has been reported, when fungus fusarium oxysporum reacted with a mixture of $CdCl_2$ and $TeCl_4$ (Syed and Ahmad 2013). Conjugated quantum dots having amino groups of glycine, arginine, and chitosan incubated with penicillium fungi (a saprotroph) and annual bluegrass (*Poa annua*) (Whiteside et al. 2009). Nitrogen-doped carbon quantum dots (NCQDs) are also found to have efficient charge delocalization and enhanced fluorescence quantum yield that are useful in bio-imaging and catalysis (Singh et al. 2017, 2019). Nitrogen-doped carbon dot–derived lotus roots have been utilized to Hg(II) ion detection. In this way, more heavy metal ions can be consumed by fungi which may play a very important role in

Table 3.5 Fungal-mediated syntheses of quantum dots that sense heavy metal ion

S. no	Quantum dot	Fungi	Significance	References
1	CdTe quantum dots	*Fusarium oxysporum*	Antibacterial properties	Syed and Ahmad (2013)
2	Cadmium sulfide	*Pleurotus ostreatus*	Used in fluorescence microscopy	Borovaya et al. (2015)
3	CdSe QD CdSe QDs	*Fusarium oxysporum* *Saccharomyces cerevisiae*	Bacterial detection and killing	Kumar et al. (2007)
4	ZnS quantum dots	*Aspergillus flavus*	Cu^{2+} and Mn^{2+} Colorimetric probe	Uddandarao (2016)
5	Gd-doped ZnS	*Aspergillus flavus*	Pb(II), Cd (II), Hg (II), Cu (II), and Ni(II)	Uddandarao et al. (2019)
6	Carbon nanodots	*Pleurotus* spp.	Hg(II)	Venkateswarlua et al. (2018)

bioremediation (Fig. 3.4). Table 3.5 lists fungal-mediated QDs that are found to be significant in heavy metal detection.

3.5 Conclusion and Future Perspective

The continuous increase in anthropogenic interference leads to the uneven distribution of heavy metals in the ecosystem. Microbes can significantly control the distribution of heavy metals. Although physical and chemical methods are being used, they infer lots of disadvantages such as high-cost treatment and production of sludge which is toxic and difficult to handle. Therefore, biological treatments are alternative methods that are eco-friendly, best removal, and low-cost methods. In the current chapter, significance of fungi has been described for the removal of heavy metals. Fungal microorganisms endowed with robust morphology which makes them suitable to bear the harsh environment imbedded with toxic metals. Fungi utilized biosorption, bioaccumulation, biotransformation, and biomineralization techniques for their continued existence in metal-polluted environments. These strategies have been exploited for remediation procedures (Gadd 2000; Lin and Lin 2005). In this chapter, biosorption appears as an eco-friendly and cost-effective process. Despite the occurrence of bioremediating fungi, it is important to modify the techniques based on the biosorption process, since all the remediating processes are based on biosorption. Therefore, researchers are required to work on parameters affecting the biosorption processes such as surface morphology, area, zeta potential, functional groups, and particle size.

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Chapter 4
Biological Decolorization and Degradation of Synthetic Dyes: A Green Step Toward Sustainable Environment

Yogesh Patel, Urvish Chhaya, Darshan M. Rudakiya, and Sanket Joshi

Contents

Abstract Synthetic dyes are extensively used in a variety of industrial applications. The release of dye containing wastewater leads to severe water pollution. The synthetic origin and recalcitrant property of dyes are responsible for superior self-life and difficulties in their degradation. Majority of dyes and their intermediate products are harmful to flora and fauna due to toxic, carcinogenic, and mutagenic characteristics. Consequently, the treatment of the dye-containing environment has become an important concern for researchers as well as regulatory authorities. A number of techniques mainly based on physical and/or chemical treatment are

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D. G. Panpatte, Y. K. Jhala (eds.), *Microbial Rejuvenation of Polluted Environment*, Microorganisms for Sustainability 26, https://doi.org/10.1007/978-981-15-7455-9_4

available for decolorization of synthetic dyes; the application of such techniques has some limitations. Removal of dyes by biological method has received special interest with respect to its eco-friendly nature and cost-competency. Bacteria, yeast, filamentous fungi, algae, actinomycetes, and plants are key players of the biological system. The metabolic diversity in various groups of biological system and ability to work under different environmental conditions provides better advantages for making strategies of decolorization, transformation, degradation, and mineralization of numerous synthetic dyes.

Keywords Synthetic dye · Biological system · Decolorization · Degradation · Bioremediation

4.1 Dye and Its Eco-Toxicological Impact

Synthetic dye is an organic compound with chromophore and auxochrome groups coupled to benzene ring. The color imparting property of dye is due to chromophore group; the auxochrome group facilitates the electrolytic dissociation and interaction property of dye. Synthetic dyes have potential applications in textile, color photography, paper printing, plastic, cosmetics, food, pharmaceutical, and leather industries (Liu et al. 2004; Khalid et al. 2008). Synthetic dyes are enormously used in textile industry, where huge amount of water is consumed for textile processing. At the time of textile processing, owing to improper binding of the dye to fabrics, a considerable amount of unbound dyestuff is directly discharged in to the effluent. The loss of dye in the wastewater is about 5–10% of total dyes used (Vaidya and Datye 1982). However, this figure reaches to 50% if reactive dyes are used for textile processing (O'Neill et al. 1999). The presence of dye in the receiving water body poses several undesirable effects. In the aquatic system, the dye interferes with photosynthetic activity of plants and algae. It is also responsible for an increased level of turbidity, biological oxygen demand (BOD), and chemical oxygen demand (COD) of water bodies. Moreover, abridged diffusion of oxygen and therefore the depletion of dissolved oxygen (DO) are due to the formation of a thin layer of dye over the water surface.

Irrigation of agricultural crops with dye-containing wastewater leads to diminution in the rate of germination and development of plant biomass. Moreover, it also augments the susceptibility of plants to a variety of pathogens. The negative effect in terms of reduced soil fertility and integrity is the upshot of rigorous use of dye-containing effluent for agricultural land irrigation. The textile wastewater adversely affects plant growth parameters of different cereal, pulse, and vegetable crops (Rehman and Bhatti 2009; Jolly et al. 2012; Ravi et al. 2014). Many times, dyes and their intermediates are detrimental to animals as well as humans. This includes the mutagenic and carcinogenic effects of several dyes, aromatic amines, and other biotransformation products (Freeman 2013; Patel and Gupte 2015). The toxic effect of dye Resacor Blue 2F on animal cell lines has been reported by Hildenbrand et al. (1999). The reports suggest that various dyes even in a very lower amount are lethal to small animals like rats, Chinese hamster, and fishes (Clark and Anliker 1980; Au et al. 1978; Amutha et al. 2002).

4.2 Treatment of the Dye-Containing Environment

The presence of dye in the environment has several consequences. It is accountable for severe coloration of the receiving water body. Due to unpleasant coloration, a lower concentration of 1.0 ppm dye in water is enough to attract public attention. Moreover, the dyes resist decolorization and degradation as these are of synthetic origin and complex aromatic molecular structure. Nowadays, the public concern and governmental directive regarding environmental safety have become very much stringent. Therefore, the treatment of dye-contaminated environments is viewed as one of the primary requirements. Removal of dye is accomplished by a variety of physical, chemical, and biological techniques. Physical methods include adsorption, filtration, ion-exchange, coagulation/flocculation, irradiation, reverse osmosis, and use of activated carbon. Chemical methods are oxidation, ozonation, electrolysis, use of Fenton's reagent and sodium hypochlorite. Biological method relies on the use of either microorganisms or their enzymes for decolorization and degradation of dyes (Patel and Chhaya 2019). The main outcome of the application of various physico-chemical methods is color removal by concentration of dye into sludge or absolute destruction of the dye molecules. These methods are widely used for the removal of dyes from textile wastewaters and have become a part of effluent treatment procedure. However, under certain conditions, the use of physico-chemical methods for dye removal is discouraging. The reasons may possibly be limited selectivity and efficiency, economically unfeasible and labor intensive procedures, the use of a number of toxic chemicals, and generation of a vast amount of sludge which may cause secondary pollution. Therefore, the biological method using microbial bioagents is viewed as an environmentally friendly alternative for decolorization, degradation, transformation, and mineralization of several pollutants, including synthetic dyes (Usha et al. 2012; Patel and Gupte 2015). There are many advantages of the biological technique, such as an effectual and environmentally companionable process, requires less energy and water, relatively cheaper, generates nontoxic end product as well as lesser volume of sludge, and complete degradation and mineralization are achieved (Rai et al. 2005). Bacteria, yeasts, fungi, algae, actinomycetes, and plants are the main biological representatives which are used for decolorization and degradation of dyes (Fig. 4.1).

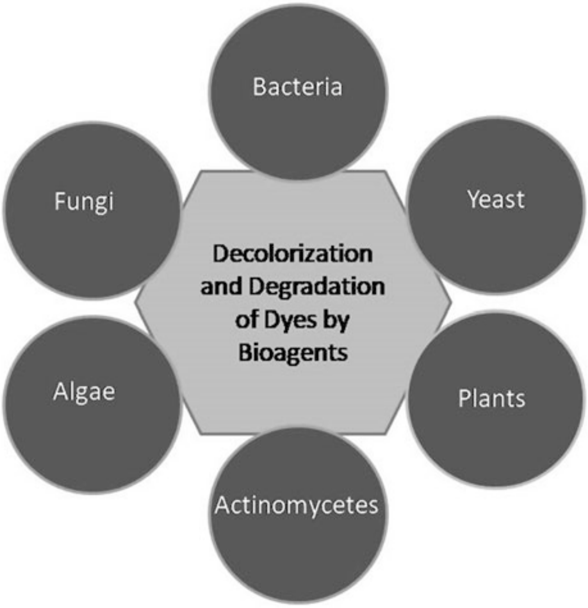

Fig. 4.1 Biological representatives for the treatment of the dye-containing environment

4.3 Removal of Dyes by Bacteria

Bacteria are a group of microorganisms which are vastly explored for their bioremediation prospective. The bacterial decolorization and degradation of dyes is advantageous as these organisms have a relatively faster growth rate ensuing into larger biomass production and rapid decolorization of dyes, can be adopted to a range of nutritional and environmental conditions, removal of dyes can be accomplished by aerobic, anaerobic, and facultative anaerobic mechanisms with a lesser volume of sludge production, and comparatively inexpensive and eco-friendly treatment of the dye-containing environment (Patel et al. 2012). Both pure cultures of bacteria and mixed cultures/consortium including diverse bacterial cultures are used for dye removal intention (Table 4.1). Today different bacteria belonging to *Bacillus, Pseudomonas, Shewanella, Corynebacterium, Aeromonas, Enterococcus, Sphingomonas, Staphylococcus, Citrobacter, Acinetobacter*, and many more genera are used for the treatment of dye-containing environment.

While using pure culture of bacteria, it is likely to generate reproducible research data, and thus, the elucidation of dye decolorization experiments becomes easier. The accurate mechanism of dye degradation and contribution of different enzymes and their regulation for biodegradation can be narrated from pure culture study. Various species of *Pseudomonas* bacteria have competence to decolorize and degrade large number of dyes (Patel and Gupte 2016; Zabłocka-Godlewska et al. 2014; Garg et al. 2012). Brás et al. (2001) have reported the involvement of acidogenic and methanogenic bacteria for decolorization of dyes. Under alkaline

Table 4.1 Selected pure culture and consortium/mix culture of bacteria for decolorization of synthetic dyes

Bacteria	Dye	Concentration (mg/l)	Decolorization (%)	Time (h)	Reference
Pure culture					
Alcaligenes faecalis AZ26	Novacron Super Black G	200	92	96	Hossen et al. (2019)
Enterobacter sp. CV-S1	Crystal Violet	100	81	72	Roy et al. (2018)
Pseudomonas aeruginosa KY284155	Remazol Black B	200	100	32	Hashem et al. (2018)
Brevibacillus laterosporus	Disperse Red 54	50	100	48	Kurade et al. (2016)
Dietzia sp. (DTS26)	Congo Red	100	95	30	Babu et al. 2015
Comamonas acidovorans MTCC 3364	Reactive Orange16 Reactive Black B Reactive Red MEBL6 Reactive Blue 160 Reactive Red 141 Reactive Yellow16	100 100 100 100 100 100	89 90 77 65 70 45	24	Rudakiya and Pawar (2014)
Bacillus lentus BI377	Reactive Red 141 Reactive Red 2	500 500	99 99	06	Oturkar et al. (2013)
Consortium/mix culture					
Lactobacillus acidophilus, *Lactobacillus plantarum*	Remazol Brilliant Orange 3R	750	99	12	Ayed et al. (2019)
Bacillus sp. AK1, *Lysinibacillus* sp. AK2, *Kerstersia* sp. VKY1	Ponceau 4R	800	82	36	Masarbo et al. (2019)
Halomonas desertis G11, *Microbaterium trichothecenolyticum* TL13, *Kocuria rosea* BU22S	Tubantin Brown GGL	100	73	240	Sghaier et al. (2019)
Neisseria sp. (EK5), *Vibrio* sp. (EK6), *Bacillus* sp. (EK7), *Bacillus*	Novacron Orange FN-R	100 100 100	70 80 90	144 144 144	Karim et al. (2018)

(continued)

Table 4.1 (continued)

Bacteria	Dye	Concentration (mg/l)	Decolorization (%)	Time (h)	Reference
sp. (EK9), *Aeromonas* sp. (EK13)	Novacron Brilliant Blue FN-R Novacron Super Black G Bezema Yellow S8-G Bezema Red S2-B	100 100	65 75	144 144	
Bacillus pumilus strain HKG212, *Zobellella taiwanensis* strain AT 1–3	Reactive Green 19	100	93	24	Das and Mishra (2017)
Bacillus subtilis, *Stenotrophomonas* sp., *Pseudomonas stutzeri*, *Pseudomonas aeruginosa*	Reactive Orange M2R	100	93	30	Shah (2016)
Bacillus subtilis, *Bacillus cereus*, *Bacillus mycoides*, *Bacillus* sp., *Micrococcus* sp., *Pseudomonas* sp.	Carmine Red Light Green Erichrome Black T Metanil Yellow	200 200 200 200	84 84 85 85	24 24 24 24	Mahmood et al. (2015)
Pseudomonas sp. ARa, *Bacillus* sp. ARc, *Bacillus* sp. ARd, *Ochrobactrum* sp. ARf	Reactive Red 195	100	100	14	Khan et al. (2014)
Enterobacter dissolvens AGYP1, *Pseudomonas aeruginosa* AGYP2	Acid Maroon V	100	93	20	Patel et al. (2012)

condition, the decolorization of reactive and direct dyes such as Reactive Yellow 84, Reactive Blue 198, Reactive Red 239, Reactive Red 141, Reactive Yellow 160, Reactive Blue 19, Reactive Red 120, Direct Yellow SG, and Direct Brown MR is achievable by pure cultures of *Bacillus* sp. strain CH12 (Guadie et al. 2017) and *Serratia marcescens* JCM 1239 (Kumar and Krishnaswamy 2016). The role of halophilic and halotolerant bacteria like *Halomonas meridian*, *Halomonas aquamarina*, and *Halomonas salina* for decolorization of number of dyes in varied conditions of pH, temperature, and salt concentration is well documented (Asad et al. 2007).

It is a general observation that absolute degradation of dyes by pure bacterial culture is sometimes difficult. Moreover, under reduced oxygen condition, the azo dyes are converted into certain degradation products like aromatic amines which have carcinogenic nature. Therefore, it becomes very imperative to decompose those toxic compounds. The use of mixed cultures/consortium of different bacterial species is found to be a feasible choice for such circumstance. The probability of complete degradation and mineralization of dyes is comparatively superior with the use of bacterial consortium. This is owing to outcome of synergistic metabolic activities of microbial population. During decolorization, the breakdown of dye molecule from different sites by individual bacterial strains leads to quick and complete degradation. Many times, during biodegradation, the dye breakdown intermediate produced by one bacterial strain serves as substrate for another strain, and likewise, the absolute degradation and mineralization of large molecules of dye is achievable (Forgacs et al. 2004; Khehra et al. 2005). Hence, the application of bacterial consortium is advisable as an alternative of individual pure culture to achieve bioremediation of highly polluted environment. Karim et al. (2018) have used bacterial consortium containing *Neisseria* sp. (EK5), *Vibrio* sp. (EK6), *Bacillus* sp. (EK7), *Bacillus* sp. (EK9), and *Aeromonas* sp. (EK13) for decolorization of Novacron Super Black G, Bezema Red S2-B, Bezema Yellow S8-G, Novacron Brilliant Blue FN-R, and Novacron Orange FN-R. It is not always that consortium prepared from different bacterial cultures is effectual; the consortium from bacteria and fungi is also effective for dye decolorization. For instance, the co-culture of *Exiguobacterium* sp. TL (bacteria) and *Penicillium* sp. QQ (fungus) has the potential to decolorize and mineralize Reactive Brilliant Red X-3B via combined anaerobic-aerobic process. The decolorization of dye takes place in anaerobic phase, whereas COD reduction is accomplished in aerobic phase (Shi et al. 2014). In spite of several advantages, the application of consortium has certain limitations. During biodegradation of dye, the precise contribution of individual bacterial strain is poorly understood. The reproducibility of biodegradation data is quite lower, and hence, the systematic elucidation of results finds difficulties.

The mechanisms of dye removal by bacteria are non-enzymatic biosorption, bioaccumulation, and enzymatic degradation. Biosorption is a passive dye uptake mechanism, typically performed by either dead or alive bacterial cell biomass through various physico-chemical interactions. Bioaccumulation is an active dye uptake mechanism which is normally executed by live bacterial biomass (Patel and Chhaya 2019). A number of intra- as well as extracellular oxidoreductive enzymes are found in bacteria which play crucial role in dye degradation. The examples of such enzymes are azoreductase, NADH-DCIP reductase, riboflavin reductase, laccase, lignin peroxidase (LiP), tyrosinase, veratryl alcohol oxidase, and aminopyrine N-demethylase (Maier et al. 2004; Patel and Chhaya 2019). Bacteria are proficient of decolorizing and degrading dyes under both anaerobic and aerobic conditions. Anaerobic decolorization of dyes is quite simple but nonspecific. Bacteria reduce the azo bonds of dye under anaerobic condition and development of colorless aromatic amines takes place. The aromatic amines are sometimes more toxic than original dye compound. Moreover, further degradation and mineralization of such intermediate compounds are difficult under anaerobic condition (Chang et al. 2004; Dos Santos et al. 2007). In aerobic condition, bacterial degradation of dyes is mediated by certain oxidative enzymes. The mono- and di-oxygenase enzymes of bacteria catalyze an incorporation of oxygen into the aromatic ring of organic compounds such as dye under aerobic condition (Sarayu and Sandhya 2010). The biodegradation of aromatic amines produced during anaerobic dye reduction is also attained under aerobic condition. Conversely, a combined anaerobic/aerobic system is more appropriate for complete decolorization and degradation of dyes. Here, the reduction of azo bonds of dye takes place in anaerobic phase; further degradation and decomposition of dye intermediates is carried out in aerobic phase. The bacterial dye decolorization can be accelerated by the supplementation of redox mediators. Examples of such redox mediators are methyl, ethyl, and benzyl viologen, lapachol (2-hydroxy-3-(3-methyl-2-butenyl)-1,4-naphthoquinone), menadione, anthraquinone-2-sulfonate (AQS), anthraquinone 2,6-disulfonate (AQDS), lawsone (2-hydroxy-1,4-naphthoquinone), riboflavin, cyanocobalamin, FMN, FAD, etc. The redox mediator speeds up the transfer of reducing equivalent from electron donor to the terminal electron acceptor like azo dye (Guo et al. 2010). The immobilized bacterial cultures are also used for decolorization of dyes. Various types of natural as well as synthetic materials, like agar-agar, alginate, chitosan, carrageenan, polyacrylamide, poly-vinyl alcohol, and cellulose acetate, are exploited for entrapment of bacterial cultures (Saratale et al. 2011; Patel and Gupte 2015). The management of synthetic and real industrial effluents is achieved by bioreactors containing immobilized bacteria. Patel and Gupte (2015) have immobilized bacterial consortium EDPA containing *Enterobacter dissolvens* AGYP1 and *Pseudomonas aeruginosa* AGYP2 in agar-agar beads. The immobilized consortium is capable of 96% removal of dye Acid Maroon V (100 mg/l) within 6 h; the consortium has displayed dye decolorization performance for 18 successive batches of the dye. The packed bed reactor containing immobilized consortium is also operated in both batch and continuous modes; 2.57 times decolorization is evident when packed bed reactor is operated under continuous mode compared to batch mode. The packed bed reactor is also able to treat synthetic dye wastewater effectively.

4.4 Removal of Dyes by Filamentous Fungi

The application of filamentous fungi for bioremediation of varieties of xenobiotic compounds has attracted scientific attention. Different genera of filamentous fungi are utilized for the removal of dyes in either living or dead form. Being ubiquitous in nature and capability of production of large array of enzymes (intracellular and extracellular) make fungi as potential agent for the biodegradation and biotransformation of varieties of synthetic textile dyes. The possible mechanisms involved in fungal treatment of dye-containing environment are biosorption, enzymatic degradation, adsorption and biodegradation, mineralization, and utilization as carbon source. Table 4.2 illustrates some representative fungal cultures utilized for dye removal purpose.

Table 4.2 Selected filamentous fungi for decolorization of synthetic dyes

Filamentous fungi	Dye and concentration	Decolorization and time	Mechanism of color removal	Reference
Lasiodiplodia sp.	Malachite Green, 50 mg/l	97% in 24 h	Adsorption and mineralization	Arunprasath et al. (2019)
Oudemansiella canarii (EF72)	Congo Red, 50 mg/l	80% in 24 h	Laccase production	Iark et al. (2019)
Consortium of *Daldinia concentrica* and *Xylaria polymorpha*	Cibacron Brilliant Red 3B-A, 50 mg/l	99% in 5 days	Laccase and LiP production	Bankole et al. 2018
Aspergillus tamari	Reactive Black 5, 100 mg/l Reactive Violet 5, 100 mg/l Reactive Orange 16, 100 mg/l	100% in 24 h 100% in 24 h 95% in 24 h	Biosorption	Sharma et al. (2017)
Phanerochaete chrysosporium MTCC 787	Direct Yellow 12, 100 mg/l Golden Yellow HER, 100 mg/l Acid Red 18, 100 mg/l Reactive Violet 5R, 100 mg/l	87% in 7 days 66% in 7 days 59% in 7 days 05% in 7 days	Biosorption and degradation	Dharajiya et al. (2016)
Aspergillus fumigatus A23	Reactive Violet 5R, 100 mg/l Direct Yellow 12, 100 mg/l Acid Black 52, 100 mg/l Reactive T Blue, 100 mg/l	98% in 4 days 96% in 4 days 95% in 4 days 27% in 4 days	Biosorption and degradation	Dharajiya et al. (2016)
Myrothecium Roridum	Malachite Green, 10 mg/l	99% in 24 h	Thermostable Low-molecular-weight factors and laccase production	Jasińska et al. (2015)
Ganoderma sp. En3	Reactive Orange 16, 100 mg/l	95% in 96 h	Laccase production and mediator induced decolorization	Ma et al. (2014)
*Ganoderma cupreum*AG-1	Reactive Violet 1, 100 mg/l	98% in 4 days	Laccase and MnP production	Gahlout et al. (2013)
Pleurotus ostreatus MTCC 142	Crystal Violet, 20 mg/l	92% in 10 days	Laccase, MnP and LiP production	Kunjadia et al. (2012)
Trametes sp. SQ01 and *Chaetomium* sp. R01 consortium	Crystal Violet, 20 mg/l, Cresol Red, 100 mg/l, Coomassie Brilliant Blue G250, 100 mg/l	36–93% in 3 days	Biosorption and MnP production	Yang et al. (2011)

White rot fungi are the most studied and explored for the decolorization and degradation of number of textile dyes. Such fungi produce relatively nonspecific lignin-modifying enzymes (LME) like LiP, manganese peroxidase (MnP), and laccase which produce free radicals during variety of reactions (Pointing 2001; Patel and Gupte 2014). *Phanerochaete chrysosporium*, a white rot fungus has been considered as a model fungus for biodegradation studies. In 1990, Cripps et al. demonstrated the degradation of azo dyes like Orange II, Tropaeolin O, and Congo Red using such fungus. They documented that nitrogen-limiting nutrient medium favors rapid degradation of dyes. Under such condition, the induction of lignin-degrading enzyme system takes place which further leads to the degradation of dyes. The decolorization of synthetic dyes such as Amaranth, Tropaeolin O, Remazol Black B, Remazol Orange, Reactive Blue, Remazol Brilliant Blue, Reactive Orange 16, and Naphthol Blue Black has been carried out by *Phanerochaete chrysosporium* (Swamy and Ramsay 1999; Svobodová et al. 2006). Three white rot *Pleurotus* species namely *Pleurotus florida*, *Pleurotus sapidus*, and *Pleurotus ostreatus* possess decolorizing potential toward Coralene Dark Red, Coralene Navy, and Blue Coralene Golden Yellow; the concomitant stimulation of laccase, MnP, and LiP activities justifies their role in overall decolorization of dyes (Kunjadia et al. 2016). The purified yellow laccase from *Trametes* sp. F1635 exhibits good decolorization of Evans Blue (89%), Remazol Brilliant Blue R (76.1%), Malachite Green (61.9%), and Eriochrome Black T (61%) in 24 h. Moreover, the use of mediators like acetosyringone, 1-hydroxybenzotriazole, (2, 2, 6, 6-tetramethylpiperidin-1-yl)oxidanyl, and violuric acid improves enzymatic decolorization effectiveness with shorter decolorization time (Wang et al. 2018). A successful decolorization of 12 dyes of acid, disperse, and reactive classes (Acid Red 114, Acid Blue 62, Acid orange 7, Acid Black 172, Disperse Red 1, Disperse Blue 79, Disperse Orange 3, Disperse Black 1, Reactive Red 120, Reactive Blue 4, Reactive Orange 16, Reactive Black 5) is feasible with *Trametes versicolor*. In that study, the induction of LiP, MnP, and laccase activities are observed; the LiP and MnP activities amplified with higher concentration of yeast extract, whereas laccase activity is increased with cultivation time, regardless of the concentration of yeast extract (Yang et al. 2017). The dye structure has strong influence on its degradation by fungal enzymes. Dyes with simpler structures are prone to easy degradation, whereas complex dyes are rather difficult to be degraded. In some cases, mineralization of dyes is possible, but the efficiency is solely reliant on chemical structure of dye. The dye structures containing substituted aromatic rings are highly susceptible to fungal mineralization in contrast to unsubstituted ring structures. Moreover, the nitrogen-limiting condition accelerates the mineralization process.

Besides white rot fungi, a number of non-white rot fungi belonging to *Aspergillus*, *Penicillium*, *Rhizopus*, *Xeromyces*, and *Geotrichum* genera have very good potential for the decolorization of several dyes. El-Rahim et al. (2017) have performed decolorization of 20 different dyes, namely Tartrazine, Direct Violet 51, Reactive Blue 4, Methyl Red, Cibacron Brilliant Red 3B-A, Crystal Violet, Direct Blue 71, Alura Red AC, Naphthol Blue Black, Alizarin Yellow R, Janus Green B, Trypan Blue, Evans Blue, Safranin, Ponceau S, Pararosaniline, Brilliant

Green, Direct Red 80, Fast Green, and Reactive Orange by 18 strains of *Aspergillus alabamensis*, *Aspergillus flavus, Aspergillus fumigates, Aspergillus niger, Aspergillus terreus*, and *Aspergillus oryzae* under submerged condition. The transformation of dye Direct Violet is comparatively easier; Fast Green on the other hand is found to be the most resistant for decolorization. The dye decolorization and LiP and laccase production are greatly influenced by carbon and nitrogen source as well as micronutrients. The nonligninolytic fungus *Myrothecium* sp. IMER1 has been found to be an effective decolorizer of Indigo Carmine, Remazol Brilliant Blue R, Congo Red, Malachite Green, and Bromophenol Blue. The study revealed that the Remazol Brilliant Blue R elimination rate by *Myrothecium* sp. IMER1 is 2–5 times higher in alkaline pH (8.0–10.0) compared to white rot fungi tested. The main mechanism involved in dye decolorization is biodegradation and biosorption (Huang et al. 2014). Shah et al. (2013) have obtained decolorization of eight textile dyes, namely Reactive T Blue, Acid Red 18, Direct Yellow 12, Reactive Violet 5R, Direct Orange 39, Acid Black 52, Golden Yellow HER, and Direct Red 31, simulated textile effluent and real textile effluent by white rot fungus *Phanerochaete chrysosporium* MTCC 787 and non-white rot fungi *Aspergillus terreus* A2, *Aspergillus flavus* A6, and *Aspergillus fumigatus* A23.

The utilization of fungal bioreactors for decolorization and degradation of synthetic dyes is an area of research nowadays. Bioreactors are prepared in such a way that both exclusion of color and biodegradation of dye can take place individually or simultaneously. A number of bioreactor systems like packed bed, rotating drum, fluidized bed, immobilized and membrane bioreactors are utilized for the removal of dyes. The immobilization of *Pleurotus ostreatus*-BWPH, *Gleophyllum odoratum*-DCa and *Polyporus picipes*-RWP17 fungal biomass on various solid supports like polypropylene washer, polyethylene foam, tile cross spacers, polystyrene fitting, grid, saw dust, and brush for washing bottles has been performed for the successful removal of the dyes Brilliant Green and Evans Blue (Przystaś et al. 2018). It has been found that immobilization of fungal biomass has many advantages like enhancement in fungal stability, enzyme activity, biomass reuse, resistance against environmental stress and toxic molecules, and liquid–solid separation. Moreover, it avails greater surface area for dye binding with the reduction in mass transfer resistance. Instead of whole fungal biomass, enzymes are also immobilized for dye decolorization. The purified laccase from *Cyathus bulleri* has been immobilized in continuous enzyme membrane reactor (EMR); the combination of alum and enzyme treatment has profound capacity of color removal from textile mill effluent (Chhabra et al. 2015). The bioactive ultrafiltration membrane has been prepared from *Aspergillus carbonarius* M333 fungal biomass; more than 90% decolorization of textile wastewater is achieved by placing it at the dead end of the filtration system (Isik et al. 2019). The air-pulsed bioreactor containing *Trametes versicolor* pellets has the capacity to decolorize 86–89% of the commercial tannery dye Black Dycem TTO during four repeated batches for 14 days. Adsorption and biodegradation are found to be main mechanisms for the removal of dyes by fungi. The laccase along with mediator hydrate 1-hydroxy-benzotriazol (HOBT) is the main enzyme for dye degradation (Baccar et al. 2011). It is possible to treat the textile industry effluent continuously in a rotating biological contactor (RBC) with *Phanerochaete chrysosporium* immobilized on polyurethane foam disks. The active fungal lifetime can be improved by merely reversing the feed inlet of the reactor. This system is capable of removing color and reducing total phenols and COD (Karthikeyan and Sahu 2014). The air-lift bioreactor containing *Bjerkandera adusta* OBR105 is used for the effective decolorization of Acid Red 114, Acid Blue 62, Acid Black 172, and Reactive Blue 4 as well as real textile wastewater (Sodaneath et al. 2017).

4.5 Removal of Dyes by Yeast

The dye decolorization potential of yeast has been investigated by various researchers. The faster growth rate and resiliency against unfavorable environmental conditions of low pH, high salt concentration, and high-strength organic wastewaters are key features of preferring yeasts for the decolorization of selected dyes. The precise mechanism of decolorization of dyes is poorly understood, but mainly focuses on biosorption, bioaccumulation, and biodegradation capacity of yeast. In biosorption mechanism, the key players are nitrogen-containing groups in peptidoglycan, peptidomannan, and protein in yeast biomass. The presence of active groups like acidic polysaccharides, amino acids, lipids, and other cellular components of yeast also have influence on the overall biosorption competence of the yeast (Das and Charumathi 2012). Bioaccumulation is the process of active uptake of dye carried out by living and actively growing yeast cells. In such process, the initial uptake of dye is rapid, which is independent of temperature and yeast cell metabolism. Further step leads to diverse metabolic processes of yeast resulting into accumulation of large amount of dye. Biodegradation of dye involves various enzyme catalyzed metabolic reactions, which eventually result into modification in dye molecular structures and conversion into simpler forms. The overall dye decolorization efficiency of yeast depends on different factors like pH, temperature, initial dye concentration, and cell biomass. The decolorization of synthetic dyes by selected yeast cultures is shown in Table 4.3.

The yeast species belonging to phylum Ascomycota are the most investigated for their color removal ability. *Saccharomyces cerevisiae*, *Candida albicans*, *Issatchenkia occidentalis, Candida tropicalis*, and *Debaryomyces polymorphus* have been used for decolorization and degradation of a variety of azo dyes. However, very few basidiomycetous yeast species, namely *Trichosporon multisporum*, *Pseudozyma rugulosa*, and *Cryptococcus curvatus*, are reported for decolorization purpose. The salt-tolerant yeast *Scheffersomyces spartinae* TLHS-SF1 could decolorize Acid Scarlet 3R, Acid Red B, Acid Orange II, Acid Scarlet GR, Reactive Brilliant Red K-2G, and Reactive Green KE-4BD (Tan et al. 2016). The biosorption of reactive dye Remazol Blue by dried yeast species, *Candida tropicalis*, *Saccharomyces cerevisiae*, *Candida quilliermendii*, *Schizosaccharomyces pombe*, *Candida utilis*, *Kluyveromyces marxianus*, *Candida membranaefaciens*, and *Candida lipolytica* is dependent on a range of factors like yeast morphological structure,

Table 4.3 Selected yeast species for decolorization of synthetic dyes

Yeast	Dye	Concentration (mg/l)	Decolorization (%)	Time (h)	Reference
Pichia kudriavzevii CR-Y103	C.I. Basic Blue 41	50	98	4	Roşu et al. (2019)
Cyberlindnera samutprakarnensis	Acid Red B Reactive Yellow 3RS Reactive Violet KN-4R Acid Scarlet 3R Reactive Brilliant Blue K-R Acid Orange II Reactive Brilliant Red K-2G	50 50 50 50 50 50 50	99 96 96 96 92 97 98	18 24 28 30 32 34 40	Song et al. (2018)
Pichia occidentalis G1	Acid Red B K-2 G 3R GR Reactive Yellow 3RS Acid Orange II KE-4BD K-R KN-4R	20 20 20 20 20 20 20 20 20	98 96 96 94 91 96 95 94 94	6 8 10 12 21 22 10 12 15	Song et al. (2017)
Saccharomyces cerevisiae ATCC 9763	Methyl Red	100	100	12	Vatandoostarani et al. (2017)
Scheffersomyces spartinae TLHS-SF1	Acid Scarlet 3R Acid Red B Acid Orange II Acid Scarlet GR Reactive Brilliant	20 20 20 20 20 20	98 98 97 97 96 96	12 13 16 24 14 18	Tan et al. (2016)

(continued)

Table 4.3 (continued)

Yeast	Dye	Concentration (mg/l)	Decolorization (%)	Time (h)	Reference
	Red K-2G Reactive Green KE-4BD				
Magnusiomyces ingens LH-F1	Acid Red B Acid Red 3 R Acid Brilliant Scarlet GR Acid Orange II Reactive Yellow 3RS Reactive Green KE-4BD	20 20 20 20 20 20	97 97 95 91 97 96	8 18 10 30 14 14	Tan et al. (2014b)
Candida tropicalis TL-F1	Acid Brilliant Scarlet GR Acid Red B Acid Orange II Acid Orange G Reactive Brilliant Red X-3B Reactive Brilliant Red K-2G Reactive Yellow 3RS Reactive Green KE-4BD	20 20 20 20 20 20 20 20	97 90 93 91 61 95 94 83	10 16 14 12 24 16 16 20	Tan et al. (2013)
Saccharomyces cerevisiae MTCC (dead, immobilized)	Malachite Green	100	96	01	Singh et al. (2012)
Candida albicans	Direct Violet 51	100	73	100	Vitor and Corso (2008)
Trichosporon multisporum	Reactive Red 141	200 200	90–95 81–99	72 72	Pajot et al. (2007)

(continued)

Table 4.3 (continued)

Yeast	Dye	Concentration (mg/l)	Decolorization (%)	Time (h)	Reference
	Reactive Blue 221				
Candida oleophila	Reactive Black 5	100	95–100	20–24	Lucas et al. (2006)
Issatchenkia occidentalis	Methyl Orange	0.2 (mmol/l)	>95	20	Ramalho et al. (2004)
Debaryomyces polymorphus	Reactive Black 5 Procion Scharlach H-E3G Procion Marine H-EXL Reactive Brilliant Blue K-NR Reactive Yellow M-3RE Reactive Brilliant Red K-2BP Reactive Red M-3BE	100 100 100 100 100 100 100	100 80 94 69 70 80 85	12 48 48 48 48 48 48	Yang et al. (2005)
Candida tropicalis	Reactive Black 5 Procion Scharlach H-E3G Procion Marine H-EXL Reactive Brilliant Blue K-NR Reactive Yellow M-3RE Reactive Brilliant Red K-2BP Reactive	100 100 100 100 100 100 100	100 70 97 30 40 45 40	12 48 48 48 48 48 48	Yang et al. (2005)

(continued)

Table 4.3 (continued)

Yeast	Dye	Concentration (mg/l)	Decolorization (%)	Time (h)	Reference
	Red M-3BE				
Kluyveromyces marxianus IMB3	Remazol Black B	25–200	94–96	24	Meehan et al. (2000)

surface area, and the presence of functional groups on yeast surface. The yeast cell wall polysaccharides contribute more in dye adsorption. In addition, various proteins and lipids in yeast cell wall provide amino, sulfydryl, thiol, phosphate, and carboxyl functional groups for dye binding. These functional groups have different dye-binding specificity and affinity in different yeast species (Aksu and Dönmez 2003). Das et al. (2010) have demonstrated bioaccumulation of Direct Red 28, Basic Violet 3, and Acid Blue 93 by growing cells of *Pichia fermentas* MTCC 189. The maximum bioaccumulation of all dyes is in acidic pH (5.0). The dye Basic Violet 3 has been accumulated up to 67% at 10 mg/l and 24 g/l concentrations of dye and sugar from sugarcane bagasse, respectively. Rovati et al. (2013) have isolated 61 yeast cultures having capability to decolorize the mixture of Reactive Yellow 84, Reactive Blue 221, Reactive Black 5, and Reactive Red 141; the identification of all isolates by 16S rDNA sequencing revealed four basidiomycetous genera *Rhodotorula*, *Leucosporidiella*, *Bullera*, and *Cryptococcus*. Seven wild yeast strains having C.I. Basic Blue 41 dye decolorization ability have been isolated from soil samples; the color removal performance of *Pichia kudriavzevii* CR-Y108, CR-Y119, and CR-Y112 is 99.89%, 98.88%, and 98.75% respectively. *Candida tropicalis* CR-Y128 has removed the dye 99.51%; *Candida saturnus* CR-Y125 and *Candida solani* CRY124 displayed the ability to decolorize the dye 78.00% and 76.09%, respectively. *Saccharomyces cerevisiae* CR-Y123 on the other hand displayed least decolorization (36.39%) of the dye. The main mechanism of dye removal is an adsorption (Roşu et al. 2019).

Several oxido-reductive enzymes of yeast are implicated in biodegradation of dyes. The reductive cleavage of azo-bond results into formation of aromatic amines, which are further undergo mineralization by yeasts. NADH dependent reductase and azoreductase are such reductive enzymes. *Trichosporon beigelii* NCIM-3326 decolorized Navy Blue HER with the concomitant rise in NADH-DCIP reductase and azoreductase activities after decolorization (Saratale et al. 2009). The oxidative enzymes on the other hand are ligninolytic enzymes like laccase, LiP, and MnP which lead to oxidative cleavage of azo dyes. The stimulation of MnP activity in *Debaryomyces polymorphus* is evident during decolorization of Reactive Black 5. The enzyme activity has been detected after 6 h and reached its maximum value at 24 h cultivation. Further increase in time demonstrated gradual decline in enzyme activity. The rapid drop of residual Reactive Black 5 concentration within 24 h could be correlated with the increase of MnP activity. However, the lower concentration of residual dye is found to be indispensable to the MnP production; cessation of enzyme production by *Debaryomyces polymorphus* is observed when the residual dye concentration reached to a very low level (Yang et al. 2005). The salt-tolerant yeast strain *Pichia occidentalis* G1 decolorized nine azo dyes, including four acid types and another five reactive ones aerobically. During decolorization of Acid Red B, the activity of azoreductase is not detected; the elevated activity of NADH-DCIP reductase on the other hand is detected in cell extracts of *Pichia occidentalis* G1, signifying its role in azo bond cleavage and considered as the first step in biodegradation of dye. Moreover, induction of LiP, MnP, and laccase activities suggested their probable role in oxidative degradation and biotransformation of Acid Red B by the yeast (Song et al. 2017).

The integrated system having a combination of physical, chemical, and biological processes for dye removal is also used nowadays. The removal of Acid Orange G has been performed by *Candida tropicalis* TL-F1 cells immobilized in calcium alginate (Tan et al. 2014a). The use of immobilized yeast cells is advantageous as an easy separation of cells from the liquid medium, prolonger persistence, and protection against unfavorable culture conditions as well as shear damage is possible. The decolorization of Reactive Black 5 has been achieved by advanced oxidation through Fenton's reagent followed by aerobic biodegradation using *Candida oleophila.* With this approach, the decolorization of the dye at 500 mg/l concentration is obtained, wherein Fenton's reagent is used as primary treatment and growing yeast cells are utilized as a secondary treatment (Lucas et al. 2007). The degradation and mineralization of Reactive Black 5 by combined photocatalytic process using UV/TiO_2 and biological process using *Candida tropicalis* JKS2 has been carried out by Jafari et al. (2012). The microbial consortium consisting of *Galactomyces geotrichum* MTCC 1360 and *Brevibacillus laterosporus* NCIM 2298 has been used for complete mineralization of Golden Yellow HER by aerobic/microaerophilic batch process. The consortium decolorized dye 100% with 84% and 63% reduction of COD and TOC, respectively, in microaerophilic/aerobic condition (Waghmode et al. 2011).

4.6 Removal of Dyes by Algae

Algae are large and diverse group of photosynthetic eukaryotic organisms with ubiquitous distribution in numerous habitats around the world. They are considered as feasible choice for the treatment of colored effluents. Three predominantly different mechanisms are involved in color removal by algae. In the first mechanism, the dye chromophores are assimilated into algal biomass, CO_2, and H_2O. The second mechanism deals with the transformation of colored dye molecules to noncolored compounds by various processes. The algal cell surface serves as an adsorbent, and therefore, the dye molecules bind to the algal biomass in the third mechanism. The reduction of azo bond of dye by algae is considered as the main mechanism of decolorization in certain cases. Different genera of algae belonging to *Chlorella*, *Cosmarium*, *Oscillatoria*, *Phormidium*, *Spirogyra*, and *Synechocystis* have been

Table 4.4 Selected algal species for decolorization of synthetic dyes

Algae	Dye	Concentration (mg/l)	Decolorization (%)	Time	References
Enteromorpha flexuosa (dry biomass)	Crystal Violet Methylene Blue	20 20	88 94	90 min 90 min	Elgarahy et al. (2019)
Consortium of *Chlorella sorokiniana* XJK and *Aspergillus* sp. XJ-2	Disperse Red 3B	100	93	4 days	Tang et al. (2019)
Anabaena sp.	Sulfur Black Indigo	200 200	42 72	14 days 14 days	Dellamatrice et al. (2017)
Phormidium sp.	Remazol Brilliant Blue R Indigo	200 200	11 91	14 days 14 days	Dellamatrice et al. (2017)
Gracilaria tenuistipitata (dry biomass)	Lac dye	50	41	120 min	Chairat and Bremner (2016)
Spirogyra sp. (CKW1) *Cladophora* sp. (PKS33)	Reactive Blue Reactive Blue	100 100	95 93	7 days 7 days	Waqas et al. (2015)
Sargassum wightii (dry biomass)	Methylene Blue	100	99	10 min	Kumar et al. (2015)
Spirogyra sp. (dry biomass)	Acid Orange 7 Basic Blue 3 Basic Red 46	50 50 50	42 92 87	60 min 60 min 60 min	Khataee et al. (2013)
Cosmarium sp.	Malachite Green	15	74	210 min	Daneshvar et al. (2007)

used for decolorization and degradation of dyes. Table 4.4 narrates the application of selected algal cultures for synthetic dye removal. The color removal is achieved by both living and nonliving algal biomass. Nonliving biomass of *Spirogyra* sp. (Khalaf 2008), *Chlorella vulgaris* (Aksu and Tezer 2005), and *Ulva fasciata* and *Sargassum dentifolium* (Moghazy et al. 2019) are utilized as an effective biosorbent for the elimination of Synozol, Remazol Red, Remazol Golden Yellow and Methylene Blue. The living biomass of algae such as *Chlorella vulgaris* (Lim et al. 2010), *Caulerpa lentillifera* (Marungrueng and Pavasant 2006) and *Caulerpa scalpelliformis* (Aravindhan et al. 2007) are able to decolorize Lanaset Red 2GA, Supranol Red 3BW, Levafix Navy Blue EBNA, Astrazon Blue FRGL, and Basic Yellow by biosorption.

The management of dye-containing wastewater is performed by bioconversion or biodegradation approaches which eventually result into the formation of simpler compounds by the breakdown of dyes by algal biomass. For instance, the microalgae *Chara* sp. is used for biodegradation of Malachite Green. More than 90% dye removal is exhibited by live algal biomass. The dye decolorization is influenced by various operational parameters such as pH, initial dye concentration, cultivation temperature, the amount of algae, and reaction time. The complete biodegradation of Malachite Green by *Chara* sp. is achieved through the formation of intermediately compounds, namely methanone [4-(dimethylamino)phenyl]phenyl, benzoic acid trimethylsilyl ester, silane trimethyl(phenylmethoxy), and glyoxylic acid. The dye decolorization processes using algae are highly pH dependent. The dye removal efficiency of algae is linearly correlated with the increase in pH of dye solution. This is due to zero point of discharge for algal biomass, where the algal cell surfaces are most likely have positive charge in acidic solution and negative charge in alkaline solution. Many cationic dyes like Malachite Green are therefore effectively removed under alkaline condition (Khataee et al. 2010). The textile dyes Indigo, Remazol Brilliant Blue R and Sulfur Black, textile effluent and sludge are efficiently removed by cyanobacteria *Anabaena flos-aquae* UTCC64, *Phormidium autumnale* UTEX1580, and *Synechococcus* sp. PCC7942. The combined anaerobic–aerobic degradation system is quite effective for the complete degradation of complex and recalcitrant dyes as compared to separate anaerobic and aerobic conditions (Dellamatrice et al. 2017).

The activated carbon prepared from filamentous algal biomass provides exceptionally high specific surface area and porosity, reusability, as well as thermal stability for the removal of pollutants from effluent. Marine algae *Ulva lactuca* and *Systoceira stricta*–based activated carbon finds its application in the removal of Malachite Green and Safranine O from aqueous solution. The concurrent treatment of phosphoric acid and heat improves adsorptive capacity of activated carbon. The removal of dye is purely a physical interaction between dye (absorbate) and activated carbon (absorbent) (Salima et al. 2013). The packed-bed up-flow column equipped from dried biomass of blue-green algae *Spirulina platensis* is found to be effectual for the adsorption of Reactive Blue 19 from synthetic dye solution and raw textile industry wastewater. The dye removal is more with a higher column bed height; with this approach, 85% diminution of COD of raw wastewater is achieved (Devi et al. 2016).

The immobilization of algae in various matrixes offers several potential applications such as biotransformation and biosynthesis of newer compounds, production of energy in the form of electricity and hydrogen, and bioaccumulation of different waste compounds like nitrogen, phosphorus, heavy metals, and dyes from wastewater. The *Chlorella vulgaris* immobilized in calcium alginate beads has superior capacity to remove Supranol Red 3BW, Levafix Navy Blue EBNA, and Lanaset Red 2GA compared to suspension cultures (Chu et al. 2009). The decolorization of dye from textile wastewater has been obtained by marine algae *Isochrysis galbana*, *Chlorella marina*, *Tetraselmis* sp., *Nannochloropsis* sp., and *Dunaliella salina* and one fresh water algae *Chlorella* sp. immobilized with sodium alginate (Kumar et al.

2014). Vijayakumar and Manoharan (2012) have performed decolorization studies of textile effluent by indigenous cyanobacterium species under free floating and immobilized condition. This system is helpful not only for color removal but also for the reduction of the levels of the inorganic compounds such as nitrites, phosphates, ammonia, calcium, and magnesium.

4.7 Removal of Dyes by Actinomycetes

Actinomycetes represent a group of relatively copious and metabolically diverse bacteria in soils and other habitats rich in lignocelluloses. They produce a variety of extracellular enzymes, and consequently, they are considered as the best degrader of a number of highly recalcitrant compounds such as hydrocarbons, explosives, chlorinated solvents, plasticizers, and azo dyes by enzymatic oxidation, hydroxylation, and dealkylation reactions (Pillai et al. 2014). The removal of dyes by actinomycetes is mainly owing to adsorption of dyes to live or dead cell biomass or enzymatic degradation. The actinomycetes belonging to Streptomyces (El-Sersy et al. 2011), Nocardia (Chakravarthy et al. 2015), and Micromonospora (Jadhav et al. 2008) genera are explored for decolorization and degradation of a number of synthetic dyes. Table 4.5 portrays the use of selected actinomycetes for the decolorization of synthetic dyes.

Decolorization of 14 mono-azo dyes is obtained by *Streptomyces chromofuscus* A11 (Pasti-Grigsby et al. 1996). Based on the substitution pattern, they revealed that the dye with a hydroxy group in para position relative to the azo linkage and two methyl substitution groups in ortho position relative to the hydroxy group is the most susceptible to degradation by *Streptomyces chromofuscus* A11. The overall biodegradability of dyes can be improved by the replacement of the sulfonic group with a carboxylic group in the native dye structure. El-Sersy et al. (2011) have documented decolorization of Acid Fast Red and Congo Red using five strains of actinomyces (*Streptomyces globosus*, *Streptomyces alanosinicus*, *Streptomyces ruber*, *Streptomyces gancidicus*, and *Nocardia aegyptia*). The principle mechanism for dye removal is biosorption. The static condition with a lower value of DO is suitable for dye decolorization. The dye decolorization capacity of actinomycetes can be improved by increasing inoculum size and decreasing starch concentration in medium. Furthermore, the economic production of cellular biomass of *Streptomyces globosus* for maximum adsorption of dyes can be achieved by potato peel.

The biosorption approach using dead biomass of actinomycetes is applied for the removal of Reactive Yellow. However, the biodegradation mechanism is quite significant for complete fate of dyes. The consortium prepared by the combination of five actinomycetes has superior decolorization capability for Reactive Yellow dye than individual pure culture. The presence of glucose in the medium has stimulatory effect on cellular growth and aerobic degradation of dye. The concurrent stimulation of activities of enzymes like laccase, LiP, and tyrosinase in correlation with dye decolorization highlights their role in biodegradation of the dye (Bagewadi et al.

Table 4.5 Selected actinomycetes species for decolorization of synthetic dyes

Actinomycetes	Dye and concentration	Decolorization and time	Mechanism of color removal	References
Consortium of *Streptomyces* DJP15 and *Streptomyces* DJP27	Reactive Blue 222, 300 mg/l	89% in 36 h	Not clear	Pillai (2018)
Streptomyces DJP15	Azo Blue, 50 mg/l	78% in 48 h	Not clear	Pillai (2017)
Micromonospora sp. (KPMS1)	Amido Black, 100 mg/l	56% in 15 days	Enzymatic decolorization	Raja et al. (2016)
Streptomyces sp. (KPMS2)	Amido Black, 100 mg/l	42% in 15 days	Enzymatic decolorization	Raja et al. (2016)
Nocardia sp. (KN5)	Congo Red, 400 mg/ml	81% in 7 days	Not clear	Chakravarthy et al. (2015)
Streptomyces violaceoruber	Poly R-478, 0.01% w/v	63% in 24 h	Enzymatic decolorization	Abou-Dobara and Omar (2014)
Streptomyces spiroverticillatus	Poly R-478, 0.01% w/v	35% in 48 h	Enzymatic decolorization	Abou-Dobara and Omar (2014)
Streptomyces sp. C1 Laccase	Indigo Carmine, 25 μM Diamond Black PV, 25 μM	84% in 2 h 56% in 2 h	Enzymatic decolorization Enzymatic decolorization	Lu et al. (2013)
Streptomyces globosus	Acid Fast Red, 50 mg/ml Congo Red, 50 mg/ml	82% in 2 h 67% in 2 h	Biosorption Biosorption	El-Sersy et al. (2011)
Streptomyces alanosinicus	Acid Fast Red, 50 mg/ml Congo Red, 50 mg/ml	50% in 2 h 68% in 2 h	Biosorption Biosorption	El-Sersy et al. (2011)
Streptomyces ruber	Acid Fast Red, 50 mg/ml Congo Red, 50 mg/ml	80% in 2 h 73% in 2 h	Biosorption Biosorption	El-Sersy et al. (2011)
Streptomyces gancidicus	Acid Fast Red, 50 mg/ml Congo Red, 50 mg/ml	80% in 2 h 58% in 2 h	Biosorption Biosorption	El-Sersy et al. (2011)
Nocardiopsis aegyptia	Acid Fast Red, 50 mg/	60% in 2 h 63% in 2 h	Biosorption Biosorption	El-Sersy et al. (2011)

(continued)

Table 4.5 (continued)

Actinomycetes	Dye and concentration	Decolorization and time	Mechanism of color removal	References
	ml Congo Red, 50 mg/ml			

2011). The mesophilic actinomycetes *Streptomyces violaceoruber* and *Streptomyces spiroverticillatus* have very good capability for Poly R-478 dye decolorization and solubilization of lignocellulose. Both the strains are capable of utilizing the dye as sole carbon and nitrogen source for their growth. This appears to be real elimination of the pollutant from the environment. However, the color removal is accelerated by the addition of carbon sources. The production of acid-precipitable polymeric lignin (APPL) can be achieved by solubilization of rice and wheat straw by both actinomyceses. The higher activities of xylanase and peroxidase support the biodegradation of lignin (Abou-Dobara and Omar 2014). It is reported that lignin degrading microorganisms can decolorize polymeric dyes effectively (Chet et al. 1985; Platt et al. 1985). In many cases, the basic structures of dyes and lignin are fairly common. Therefore, the evaluation of decolorization of polymeric dyes provides exceptionally easy and rapid outcomes which can be correlated with ligninolytic system in microorganisms.

The actinomycetes from marine environment also exhibit very good potential for the decolorization of number of dyes. Chakravarthy et al. (2015) have reported decolorization of Reactive Red by 15 isolates of actinomycetes from marine sediment. In another study, 25 actinomycetes are isolated from mangrove soil; the isolate *Streptomyces cacaoi* subsp. *Cacaoi* has been found the most efficient dye decolorizer. Moreover, this isolate has good antifungal activity (Janaki 2016). The isolation of actinomycetes from marine sediments and further identification revealed *Micromonospora* and *Streptomyces* genera. These microorganisms are able to remove Amido Black dye by cellular adsorption mechanism. *Micromonospora* sp. has the potential to degrade dye under static-agitated sequential process with the supplementation of glucose as carbon source and yeast extract as nitrogen source (Raja et al. 2016).

The immobilization of actinomycetes is beneficial for decolorization of dyes than free culture. Immobilization can be performed using different materials. Jadhav et al. (2014) have used very simple materials like coconut coir, gunny bag, scotch-brite, and sugarcane bagasse for immobilization of actinomycetes strain BJ4. The decolorization of Rathiline Navy Blue dye is better with actinomycetes BJ4 immobilized in gunny bag. It is likely to decolorize dyes with enzymes obtained from actinomycetes. Laccase or laccase-like multicopper oxidases (LMCOs) have been isolated and purified from *Streptomyces* sp. C1. Based on comparative data, it is observed that the purified LMCO has significant capacity of decolorization of Indigo Carmine and Diamond Black PV in the presence of mediator. The absence of mediator in the reaction system has lower color removal value, signifying the importance of mediator for better decolorization of dyes (Lu et al. 2013).

4.8 Removal of Dyes by Plants (Phytoremediation)

The application of plants for bioremediation of contaminated soil and ground water is an emerging approach. The advantages of phytoremediation include larger biomass production, an autotrophic system requiring little nutrient input, effective, easier, and low-cost methodology for onsite bioremediation, and ready acceptance because of esthetics and environmental sustainability. The plants remediate contaminated environments by various mechanisms like phytoextraction, phytostabilization, phytotransformation, rhizofiltration, phytovolatilization, and rhizodegradation (Tahir et al. 2016). The plant species used, properties of medium, environmental conditions, interactions in the root zone, chemical properties and bioavailability of contaminants, and the effects of added chelating agents also influence overall plant-mediated remediation effectiveness and uptake of contaminants (Cunningham and Ow 1996; Tangahu et al. 2011). Certain enzymatic mechanisms of plants are responsible for the breakdown of complex structures of dyes. Therefore, plant-assisted remediation of textile industry effluents is seemed to be a potential green solution of heavily polluted soil (Khandare and Govindwar 2015). The phytoremediation of synthetic dyes by selected plant species is depicted in Table 4.6. Different macrophyte plant species like *Brassica juncea*, *Blumea malcolmii*, *Phragmites australis*, *Arundo donax*, and *Typhonium flagelliforme* are used for phytoremediation of dyes (Kagalkar et al. 2010). *Typhonium flagelliforme* has the capability to decolorize and degrade dyes within 96 h without any nutrients (Kagalkar et al. 2010).

Lemna minor L. (common duckweed) is a tiny free-floating macrophyte, which has considerable capacity to remove heavy metals, dyes, and some inorganic nutrients from wastewaters (Yaseen et al. 2017). The effect of *Lemna minor* L. on the decolorization of artificial textile wastewater containing the mixture of commercial dyes, Basic Red 46 and Reactive Blue 198, has been investigated by Yaseen and Scholz (2018). In addition to decolorization of dyes, the reduction of COD, suspended solids (SS), total dissolved solids (TDS), ammonium-nitrogen (NH_4-N), and nitrate-nitrogen (NO_3-N) to the acceptable range can be achieved by such plants grown in the laboratory-scale shallow ponds. The removal of dyes and complete mineralization of aromatic amine by plants is principally owing to phytotransformation and adsorption mechanisms. Almaamary et al. (2019) have obtained decolorization of Methyl Orange dye by *Scirpus grossus* plants. The plants are able to remove dye 64% and also reduced BOD, COD, and total organic carbon (TOC) of contaminated water. The *Typhonium flagelliforme*, *Portulaca grandiflora* Hook, and *Azolla pinnata* are used for decolorization and degradation of Brilliant Blue R, Navy Blue HE2R, and Methylene Blue (Kagalkar et al. 2010; Khandare et al. 2011; Al-Baldawi et al. 2018).

Table 4.6 Selected plant species for decolorization of synthetic dyes

Plant	Dye	Concentration (mg/l)	Decolorization and time	Mechanism of color removal	Reference
Tecoma stans var. *Angustata* (immobilized callus)	Brilliant Green	26	76% in 2 h	Adsorption and peroxidase activity	Rani and Abraham (2016)
Alternanthera philoxeroides	Remazol Red	70	100% in 72 h	Adsorption and enzymatic activity	Rane et al. (2015)
Nasturtium officinale	Acid Blue 92	20	60% in 4 days	Enzymatic activity	Torbati et al. (2015)
Chara vulgaris	Congo Red	50	95% in 24 h	Phytoextraction	Mahajan and Kaushal (2013)
Portulaca grandiflora	Navy Blue HE2R Navy Blue Rx Rubine GFL Navy blue 2R Blue GL solo Brown 3REL Red HE7B Orange HE2R	30 30 30 30 30 30 30 30	98% in 40 h 95% in 40 h 91% in 40 h 87% in 40 h 82% in 40 h 74% in 40 h 57% in 40 h 49% in 40 h	Adsorption and enzymatic activity	Khandare et al. (2011)
Brassica juncea roots	Methyl Orange	30	92% in 4 days	Enzymatic activity	Telke et al. (2011)
Glandularia pulchella	Reactive Orange HE2R Reactive Yellow MEG4 Brown 3REL Reactive Yellow GR Blue 2GL Remazol Red Green	20 20 20 20 20 20 20 20 20 20	56% in 48 h 32% in 48 h 26% in 48 h 38% in 48 h 35% in 48 h 84% in 48 h 94% in 48 h 65% in 48 h 36% in 48 h 27% in 48 h	Adsorption Adsorption Adsorption Adsorption Adsorption Adsorption Enzymatic activity Adsorption Adsorption Adsorption	Kabra et al. (2011)

(continued)

Table 4.6 (continued)

Plant	Dye	Concentration (mg/l)	Decolorization and time	Mechanism of color removal	Reference
	HE4B Blue 2RNL Malachite Green Patent Blue				
Blumea malcolmii	Malachite Green Red HE4B Methyl Orange Reactive Red 2 Direct Red 5B	20 20 20 20 20	97% in 72 h 88% in 72 h 80% in 72 h 42% in 72 h 77% in 72 h	Adsorption and enzymatic activity	Kagalkar et al. (2009)

It is evident that under optimum conditions, certain plant species exhibit the capability to absorb and decolorize different dyes. For instance, plant species like *Brassica alba*, *Solanum lycopersicum*, and *Vetiveria zizanioides* are used to remove ethidium bromide (EtBr) from contaminated soil (Uera et al. 2007). After absorption of dyes, plants execute localization and speciation of toxic dye molecules within the plant tissues like leaves, shoots, and roots. The biosorption capacity of *Eucalyptus* species has been explored for the removal of dyes from soil contaminated with paper and pulp industry effluents (Sureshvarr et al. 2010). Therefore, biosorption by a variety of plant species is one of the important phenomena for sequestration, accumulation, and subsequent metabolism of toxic dyes.

The enzymes produced by plant species have significant contribution in biodegradation of textile dyes. LiP, tyrosinase, DCIP reductase, riboflavin reductase, laccase, veratryl alcohol oxidase, and azoreductase are such enzymes. The augmentation of enzyme activities during dye decolorization by wild-type and tissue-cultured plants signifies their crucial role in dye metabolism (Khandare et al. 2011). Some enzymes are detected from root extracts of plant species which assist degradation of dyes. The detection of higher activities of laccase from hairy root extract of *Brassica juncea* has correspondence with concomitant decolorization of Methyl Orange (Telke et al. 2011). In some cases, either plant material or plant enzymes are entrapped and immobilized into various matrixes for dye removal applications (El-Aassar et al. 2018; Maddhinni et al. 2013). The root parts of *Arundo donax* L. are immobilized with chitosan, gelatin, and polyvinyl pyrrolidone beads and used for the removal of C.I. Basic Red 14 under shaking condition. These beads have significant dye adsorption capacity and reusability (El-Aassar et al. 2018). The synergistic performances of bacteria and plants are sometimes more suitable for bioremediation of dyes containing environment. The combination of plant *Petunia grandiflora* Juss and its rhizospheric bacterial isolate *Bacillus pumilus* strain PgJ has noteworthy phytotransformation capacity for Navy Blue RX dye under in vitro culture condition. The removal of dye is facilitated by LiP, tyrosinase, laccase, and riboflavin reductase enzyme found in both plant roots and bacteria. After treatment, the dye degradation metabolites are found to be less toxic to *Sorghum vulgare*, *Phaeseolus mungo*, and *Allium cepa* roots. This approach can be helpful for the bioremediation of real sites of dye wastewater disposal (Watharkar et al. 2013). In recent years, the nanoparticles have been synthesized from extracts of various parts of plant and are implemented for decolorization of different dyes. The silver nanoparticles derived from testa of *Anacardium occidentale* (Edison et al. 2016) and leaf extract of *Convolvulus arvensis* (Rasheed et al. 2018) have considerable potential to decolorize Reactive Black 5, Congo Red, and Methyl Orange dyes.

4.9 Conclusion

Synthetic organic dyes are indispensable to achieve variability and quality of colored substrates. The presence of dyes in textile as well as other industrial effluents has negative consequences on surroundings and environment. Biological removal of synthetic dyes has immense potential over physical and chemical methods due to the involvement of diverse creatures like bacteria, fungi, actinomycetes, yeast, algae, and plants. Decolorization of dyes is achieved by both live and dead cells/materials. The number of mechanisms ranging from simple biosorption to mineralization is possible by diverse activities of biological system. Therefore, detailed studies focusing on enzymatic systems, toxicity evaluation, scale-up, and economic competence of biological system are needed for sustainable treatment of dye containing environment.

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Chapter 5
Bioremediation of Waste Gases and Polluted Soils

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D. G. Panpatte, Y. K. Jhala (eds.), *Microbial Rejuvenation of Polluted Environment*,
Microorganisms for Sustainability 26, https://doi.org/10.1007/978-981-15-7455-9_5

Abstract The recent expansion of human industrial activity, including mining, smelting, and synthetic compounds, has increased the amount of toxic harmful gases released in the atmosphere, water, and soil which contaminated the environment directly and indirectly. There has been a significant rise in the levels of heavy metals (Pb, As, Hg, and Cd) and toxic gases due to their increased industrial usage, causing a severe concern to public health as well as enviornment. Accumulation of these heavy metals generates oxidative stress in the body, causing fatal effects to important biological processes leading to cell death. The ability to prevent and manage this problem is still a subject of much debate, with many technologies ineffective and others too expensive for practical large-scale use, especially for developed and developing nations where major pollution arising. Currently, green technologies require pressure to develop the management of contaminated sites which benefit the society directly and indirectly. Bioremediation, is another biological mechanism of waste recycling in another form which can be used and reused by other organisms. Therefore, to reduce the potential toxicity of any pollutant in the environment, by degradation, change, bioremediation is the form of bio-systems through microbes and plants, by stabilizing these undesirable substances into less harmful forms.

Keywords Bioremediation · Waste gases · Microbes · Plants · Pollution · Nanotechnology

5.1 Introduction

Bioremediation or natural remediation is a cost-effective eco-friendly biotechnological process. It includes the utilization of living beings such as plants and microscopic bacteria to remediate and stabilize polluted areas (Anyasi and Atagana 2011; Perelo 2010; Sharma 2012). In bioremediation, few advances have been acknowledged with the assistance of the different field of molecular biology, microbiology, environmental engineering, biochemistry, chemical and analytical chemistry, etc. The process of bioremediation is an alternative to incineration process and use of catalytic barrier and absorbents. It involves only biological agents such as plants and microorganisms to change and degrade contaminants into less hazardous or almost non-hazardous substances (Dua et al. 2002; Park et al. 2011). Different living

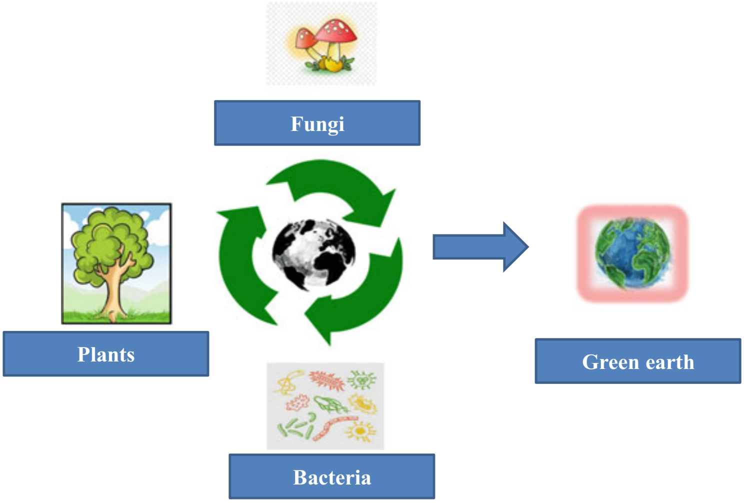

Fig. 5.1 Bioremediation through microbes and plants

organisms such as bacteria, fungi, yeast, algae, and plants have been used as natural operators to proficiently bioremediate hazardous pollutants and clean up the environment (Vidali 2001; Strong and Burgess 2008). With the increment in the population, the demand for food supply has likewise increased. This created pressure on natural resources. Thereby, farmers are forced for intensive agriculture by utilizing more and more pesticides to get more yields. But utilization of these pesticides degrades the texture nature and quality of the soil. Also, excess input of these wastes had prompted deficiency of clean soil and water and thus diminishing crop yield (Kamaludeen et al. 2003). So, bioremediation is being used as an effective method to clean up the environment from these hazardous substances such as hydrocarbons, organic compounds and solvents, nitrogenous compounds, herbicides, pesticides, nitrogenous waste gases, and heavy metals (Fig. 5.1) (Park et al. 2011). The contaminants and the hazardous substances present in the environment act as energy sources for the microbes and provide energy to carry out their metabolic activities (Tang et al. 2007). Microorganisms not only play a significant role in regulating the biogeochemical cycles (Griggs et al. 2013) but also help to sustain clean air by diminishing environmental pollutants from the environment (Morris et al. 2011) keeping us healthy. Also, they protect plants from the diseases and help them to develop and grow (Pineda et al. 2017). A widespread list of the microbes that bring about bioremediation processes is available (Satyanarayana et al. 2012; Prakash et al. 2013; Abou Seeda et al. 2017).

5.2 Need of Bioremediation

Nowadays, environmental pollution is a serious issue for mankind. Remediation approaches, such as physical and chemical methods, are insufficient to alleviate contamination issues in view of the constant age of novel recalcitrant toxins because of anthropogenic exercises. Bioremediation could find a better solution to this issue. It is an eco-friendly and socially acceptable alternative to conventional remediation approaches utilizing microbes (Dangi et al. 2018).

5.3 Bioremediation of "Composting" Soils

The dynamic "composting" of soils debased with (poly) aromatic hydrocarbons (PAHs) and alkanes in combination with critical amounts of composting feedstock materials is considered as a significant bioremediation treatment approach (Antizar-Ladislao et al. 2007; Sasek et al. 2003; Semple et al. 2001; Tran et al. 2018). This approach utilizes the addition of the known amount of compost (or other organic residues) to defiled soils by improving pH, porosity, oxygen diffusion (Semple et al. 2001), and contaminant desorption (Wu et al. 2013). This is possible as composts are generally rich in nutrients such as carbohydrates, nitrogen, and phosphorus that are potentially important in accomplishing an ideal activity of pollutant degraders indigenous to polluted soils (Komilis and Timotheatou 2011; Sarkar et al. 2005). Furthermore, compost/manure contains several different microorganism populations which may degrade organic contaminants present in the environment (Scelza et al. 2007). A few examples of the utilization of "mature" manure for the application of soil bioremediation can be found in the literature. For instance, Gomez and Sartaj (2013) used "mature" manure for the bioremediation of total petroleum hydrocarbon (TPH) from the polluted soil in cold conditions.

5.4 Enzymes Used in Bioremediation

Degradation of contaminants from the environment with the assistance of microorganisms is a slow process, which diminishes the achievability of the bioremediation process in actual practice (Ghosh et al. 2017). In the past few years, to overcome these limitations, microbial enzymes harvested from their cells have been used to carry out bioremediation when contrasted with utilizing the whole microorganisms (Thatoi et al. 2014). Enzymes are proteinaceous biological macro-molecules which act as a catalyst to carry out a number of biochemical reactions involved in the pollutant degradation pathways (Kalogerakis et al. 2017). In contrast to microbes, enzymes are more specific to their substrate and versatile in nature in light of their smaller size (Gianfreda and Bollag 2002). The process of bioremediation based on purified and partially purified enzyme does not rely upon the development of a specific microorganism in the polluted environment; however, it relies on the catalytic activity of the enzyme present in the microbes (Ruggaber and Talley 2006). In insufficient nutrient soil, bioremediation can be conceivable by utilizing a purified enzyme. Enzymatic biotransformation is a safer process as toxic side products are not produced during the process.

5.5 Bioremediation of Petroleum Hydrocarbons

Microbial bioremediation is a broadly utilized method for treating petroleum hydrocarbon contaminants from the environment including both terrestrial and aquatic ecosystems (Abbasian et al. 2015; Varjani and Srivastava 2015). In the last decades, several research studies based on biodegradation of hydrocarbon pollutants have been done (Sajna et al. 2015; Varjani et al. 2015; Varjani and Upasani 2016). Microorganisms are ubiquitous in nature and play a significant role in maintaining ecosystem balance to develop a sustainable environment (Varjani and Srivastava 2015). Microorganisms such as bacteria, fungi, and algae are accounted for their capacity to degrade hydrocarbon pollutants (Wilkes et al. 2016). Bacteria are considered as primary degraders and play a crucial role in degrading petroleum pollutants from the environment (Abbasian et al. 2015; Meckenstock et al. 2016). Few examples of bacteria that act as hydrocarbon degraders include *Acinetobacter, Achromobacter, Azoarcus, Micrococcus, Arthrobacter, Brevibacterium, Flavobacterium, Corynebacterium, Nocardia, Cellulomonas, Marinobacter, Stenotrophomaonas, Ochrobactrum, Pseudomonas, Vibrio,* etc. (Varjani and Upasani 2016). Besides, fungi that play a crucial role in degrading petroleum hydrocarbon pollutant include yeast, *Candida, Penicillium, Fusarium, Aspergillus, Neosartorya, Amorphoteca, Graphium, Talaromyces, Paecilomyces, Rhodotorula, Sporobolomyces, Pichia, Yarrowia, Pseudozyma,* etc. (Sajna et al. 2015; Wilkes et al. 2016). The essential criteria needed to understand the scope and strategies of pollutant removal via bioremediation include the understanding of properties of crude oil, mechanism, the fate of oil, the concerned environment, and factors that control its rate.

5.6 Bioremediation of Agricultural Waste

Globally, every year, about 38 billion metric tons of organic waste of human, livestock, and crops are produced. Eco-friendly disposal of this waste from the environment has become a global priority. Accordingly, in recent years, much attention has been paid to develop efficient and cost-effective strategies to convert these nutrient-rich organic wastes into valuable products for sustainable land practices. With the help of microorganisms and earthworms, this can be achieved. They help in the degradation of organic matter by molding to the substrate and altering the biological activity (Dominguez 2004; Suthar 2007). Several earthworms, such as *Eudrilus eugeniae, Eisenia fetida* (Savigny), *Perionyx sansibaricus* (Perrier), and *Perionyx excavatus* (Perrier), have been recognized as detritus feeders and potentially minimize the anthropogenic waste from the various sources (Garg et al. 2006).

5.7 Types of Bioremediation

Bioremediation can be categorized into two types: In situ bioremediation and ex situ bioremediation (Fig. 5.2) (Marykensa 2011). In situ bioremediation involves treatment of pollutants, e.g., contaminated water or soil at the site of occurrence. In contrast, ex situ bioremediation involves treatment of pollutants, e.g., contaminated soil or water once excavated from its initial site (Megharaj et al. 2014).

5.7.1 In Situ Bioremediation

In this type of bioremediation, contaminated soil is treated at the site of contamination where it occurred without its removal and transportation, for example, natural

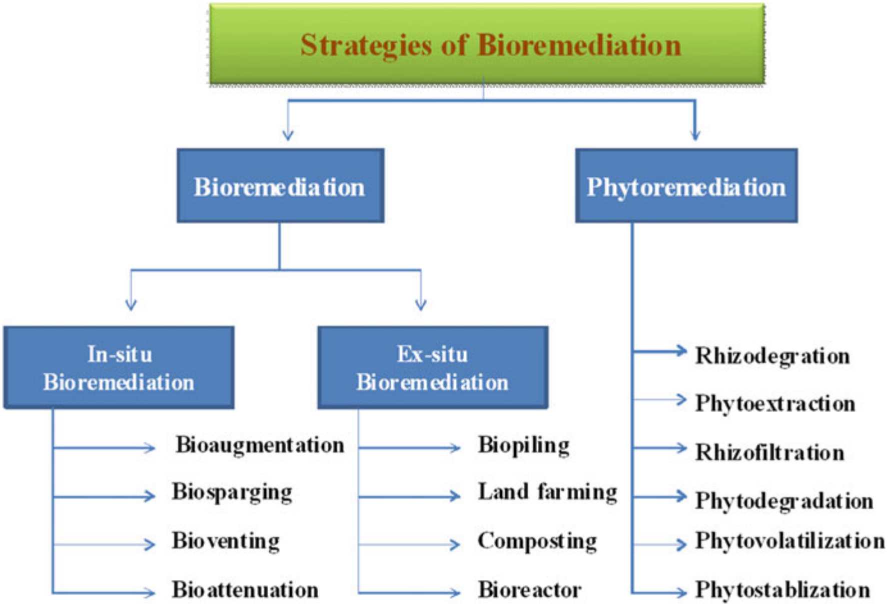

Fig. 5.2 Types of bioremediation techniques

attenuation, bio-venting, and bio-sparging. This method is considered as a natural biogeochemical process.

5.7.1.1 Bioaugmentation

It is the process of speeding up the rate of degradation of contaminants by the addition of indigenous or exogenous microorganisms to the contaminated sites containing the target contaminant. The addition of these microbial populations brings about catabolic activity and enhances the bioremediation process (Andreoni and Gianfreda 2007).

5.7.1.2 Bioattenuation

It is a set of naturally occurring phenomena used to diminish soil pollutants. It evacuates the degradation of pollutants with the help of several processes, such as by indigenous microorganisms, dispersion, chemical transformation, dilution, volatilization, and stabilization of contaminants (Guarino et al. 2017). Petroleum hydrocarbons can remain buried in soil for more than 50 years after spillage, despite treatment naturally using this strategy for remediation of TPH in freezing soil (Mair et al. 2013; Jiang et al. 2016).

5.7.1.3 Bioventing and Bio-Sparging

It is a type of bioremediation process that utilizes controlled airflow into the contaminated soil of an unsaturated zone to improve degradation activities of indigenous microorganisms. Controlled airflow rate guarantees that the contaminants get reduced because of microbial degradation instead of volatilization (Azubuike et al. 2016). Furthermore, bio-sparging is like bio-venting and aids in the movement of volatile pollutants from a saturated area to an unsaturated area (Azubuike et al. 2016).

5.7.2 Ex-Situ Bioremediation

It involves the treatment of pollutants away from the site of their occurrence. It includes excavation and transportation of contaminated soils to a protected and reliable place for their efficient treatment. On the basis of nature, severity, and geographical location of the contamination, ex situ bioremediation can be of several types. This method is a controlled remediation strategy where the treatment conditions can be overseen appropriately. A few investigations have reported the fruitful application of ex situ bioremediation methodologies for oil-polluted soil in low temperatures (Tomei and Daugulis 2013; Jeong et al. 2015).

5.7.2.1 Bio-Pile

In this process where excavated polluted soil is piled temperature and moisture control and nutrient amendments. The process involves temperature control mechanism which keeps up ideal situations even in low temperatures. This successfully helps to remediate polluted components from the cold environments also (Chemlal et al. 2012; Whelan et al. 2015).

5.7.2.2 Composting

It is the procedure of converting organic matter into humus-like non-toxic substances. During the process, active indigenous or augmented microorganisms catalyze the reaction and generate high temperature to optimize microbial activities and thus bring about degradation of the contaminants as the compost get matured (Kästner and Miltner 2016). For the successful implementation in low temperature composting can be equipped with bio-pile facilities (Sanscartier et al. 2009).

5.7.2.3 Land Farming

It is a process in which contaminated soil is spread in a bed and made accessible for biological treatment. It includes a broad range of environmental conditions, such as extreme cold and arid soil (Tomei and Daugulis 2013). Presently, for efficient degradation of pollutants, land farming methods have been improved by incorporating bioaugmentation and adding fertilizers, water, and surfactants (Jeong et al. 2015).

5.7.2.4 Bioreactor

It is a controlled system involving biological processes that can convert raw materials into useful products. In this system, a vessel (reactor) is utilized that brings about bioremediation. Bioreactors can be operated in different feed modes, such as batch, semi-continuous, and continuous. Besides, several physical (such as pH, temperature, aeration, and agitation) and biological (such as bacterial inoculums, nutrients, and substrate) parameters can be controlled in the bioreactor (Tomei and Daugulis 2013).

5.8 Phytoremediation

Though the studies were carried out in 1950s, the term "phytoremediation" was coined in 1991. Phytoremediation is a process that utilizes plants to remove contaminants from the environment (Kumar et al. 2011; Sharma and Pandey 2014). Green plants, such as herbs (e.g., *Brassica juncea*, *Thlaspi caerulescens*, and *Helianthus annuus*) and woody species (e.g., *Salix* spp. and *Populus* spp.), remove various contaminants (like heavy metals, organic compounds, and radioactive compounds in soil or water) from the environment by accumulating and transporting the contaminants via translocation (Tahir et al. 2015) (Fig. 5.3).

5.8.1 *Rhizodegradation*

Rhizodegradation occurs at a radical level of plant in a soil area called rhizosphere where biodegradation of the organic contaminants takes place. The process occurs with the help of bacteria, fungi, and yeasts. As root is a rich source of carbon and nitrogen, they expand the effectiveness of extraction and removal of contaminants (Leung et al. 2013; Liu et al. 2014).

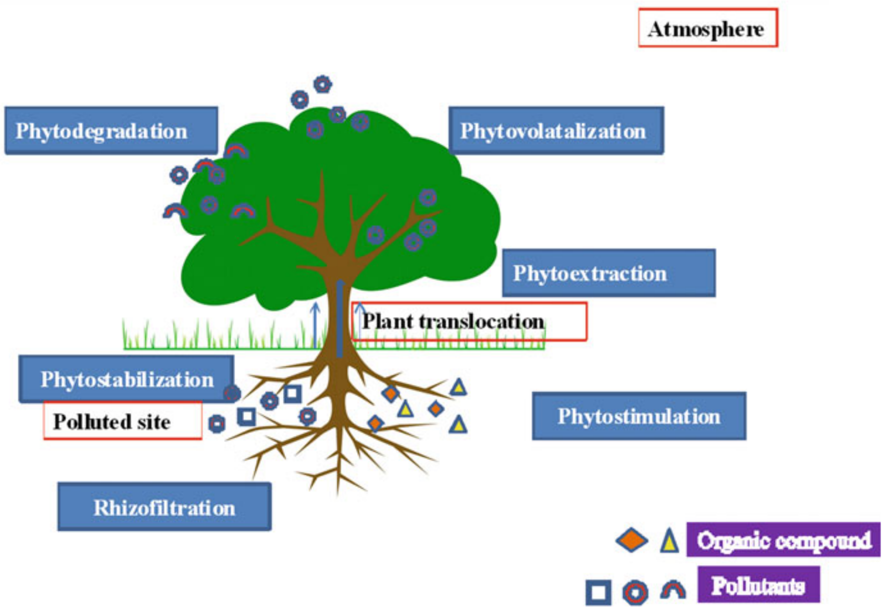

Fig. 5.3 Process of phytoremediation

5.8.2 Phytoextraction

It is an in situ strategy used for the treatment of contaminated soils (Alì et al. 2013; Van Oosten and Maggio 2014). Phytoextraction involves absorption of contaminants via roots and then their transportation and accumulation in shoots and leaves (Mahar et al. 2016; Sreelal and Jayanthi 2017). Plants engaged with this procedure should ideally have the ability to accumulate contaminants and produce high biomass.

5.8.3 Rhizofiltration

Rhizofiltration comprises biodegradation of organic and inorganic pollutants from the surface water, groundwater, or wastewater via adsorption of pollutants on the roots or around the root area (Zhang et al. 2009). This strategy is applied for the removal of heavy metals from the soil (Susarla et al. 2002) as they are maintained at the root level, and further, these elements will be harvested. The plants that are used in this process are tolerant of metal. They have a high absorption surface and tolerate hypoxia (e.g., *Salix* spp., *Populus* spp., *Brassica* spp.).

5.8.4 Phytodegradation

During phytodegradation, organic contaminants, after assimilation by the root framework, are degraded by the enzymatic activity, or they will be consolidated into the plant tissues (Alì et al. 2013; Sharma and Pandey 2014; Van Oosten and Maggio 2014). The enzymes that carry phytodegradation include peroxidase, dehalogenase, nitroreductase, nitrilase, and phosphatase (Winquist et al. 2013; Deng and Cao 2017).

5.8.5 Phytovolatilization

In this process, the contaminants are absorbed from the roots of the plant, transported through the xylem, and discharged into the atmosphere from the aerial parts of the plant in less toxic forms. The process can be applied to contaminants present in the soil, sediment, or water, particularly for organic contaminants like trichloromethane, tetrachloroethane, and tetrachloromethane (San Miguel et al. 2013) and for some high-volatile metals such as Hg and Se (Wang et al. 2012; Van Oosten and Maggio 2014).

5.8.6 Phytostabilization

The method is valuable for the treatment of Cd, Cu, Pb, As, Cr, and Zn (Zhao et al. 2016; Yang et al. 2016). The advantage of this technique consists of the changes of soil chemical composition induced by the presence of the plant itself, and such changes can facilitate the absorption or cause the precipitation of metals on the roots (Zhang et al. 2009). This process decreases contaminant versatility, avoiding movement into the groundwater and lessen the bioavailability in the food chain (Alì et al. 2013; Sharma and Pandey 2014).

5.8.7 Bioremediation of Industrial Pollution by Plants

Air pollution means "the presence of harmful or toxic substances in the atmosphere, which adversely effects on both living and non-living things." Main air pollutants are sulfur dioxide (SO_2), nitrogen dioxide (NO_2), particulate matters (PMs), volatile organic compounds (VOCs), and ground-level ozone (O_3) (Archibald et al. 2017). Bioremediation is an effective method because of its cheaper cost in comparison to different physicochemical techniques (Cheng et al. 2012; Philp et al. 2005). Exchange of gases is required by autotrophic plants for their survival; during this process, gaseous pollutants can be adsorbed/absorbed (Gawronski et al. 2017). Different policies, strategies, and models have been implemented or proposed for the removal of air pollution (Macpherson et al. 2017).

5.9 Remediation of Particulate Matters

PMs are the most hazardous pollutants in developing countries. The physical characteristics of leaves such as stomata, leaf shape, and trichomes or hairs significantly affect the collection of PM. More accumulation of $PM_{2.5}$ was reported in needle leaves than broader leaves (Terzaghi et al. 2013; Chen et al. 2017). Trichomes of the leaf have been demonstrating to high $PM_{2.5}$ accumulations. Accumulation of $PM_{2.5}$ was positively correlated with the density of trichomes of leaves and some plant with maximum hairs such as *Broussonetia papyrifera, Ulmus pumila*, and *Catalpa speciosa* were able to collect high $PM_{2.5}$ than those plants which have few hairs (Chen et al. 2017). Teper (2009) observed that needles of *Pinus sylvestris* accumulate 18,000 particles of mineral mm^{-2}. In *Hedera helix*, upper leaves received approximately 17,000 particles mm^{-2} (Ottele et al. 2010). Nowak et al. (2014) showed that trees present in the cities are responsible for the removal of fine particles from the atmosphere, which improved the quality of air and human health also. It is already demonstrated that outdoor plants can phytoremediate aerosol PM (Sæbø et al. 2012). In the period of 3 years, Popek et al. (2013) investigated that

13 woody species captured the sum amount of PMs ranging from 7.5 mg/cm^2 through *Catalpa bignonioides* to 32 mg/cm^2 through the leaves of *Syringa meyeri*.

5.10 Remediation of VOCs

The elimination of pollutants was plant-mediated; therefore, the expulsion of VOCs by the absorption of plants is through the process of normal gas exchange or absorption and adsorption with the help of plant surface (Omasa et al. 2002; Yoo et al. 2006; Ahmad et al. 2019). A hypothetical process involves aerial plant parts for the absorption of VOCs, where they can possibly enter through the Kelvin cycle, and eventually convert into amino acids through the metabolic process (Peterson et al. 2016). VOCs can undergo storage, excretion and degradation inside the plant system (Weyens et al. 2015).

5.11 Remediation of Other Harmful Gases

The concentration of atmospheric CO_2 has increased rapidly in recent decades. Contribution of CO_2 represents more than 50% of the total warming potential in all greenhouse gases (Cox et al. 2000). In the present scenario, the continuous change of climate is creating a series of problems for future generations. Various chemical and biological technologies have been introduced to remove CO_2 from the atmosphere. Many researchers have confirmed over the past few decades that plants extract CO_2 by photosynthesis (Torpy et al. 2018). Through many researches, it has been investigated that vegetative surfaces have the potential to reduce NO_2 (Chaparro-Suarez et al. 2011). Some plants can be survived in SO_2-polluted environment (Chung et al. 2010). From the air, O_3 can be removed through chemical reactions which react with reactive compounds, especially mono-terpenes that rely upon the vegetation (Di Carlo et al. 2004). Various diterpenoid organic compounds which are semi-volatile are released from the trichomes of leaves responsible for the removal of O_3 (Jud et al. 2016).

5.12 Microbial Remediation of Air Pollution and Soil

Generally, bioremediation is a process which uses the microorganisms to convert or degrade contamination into nontoxic products (Antizar-Ladislao 2010). Microorganisms such as fungi and bacteria are also responsible for bio-transforming or biodegrading pollutants into less toxic and non-toxic materials, called as microbial biodegradation (Ward et al. 1980; Ma et al. 2016). Microorganisms in the form of heterotrophs present almost everywhere, including plant shoot and roots. It has been reported that both shoots and roots are used to remediate the pollutants from the air (Weyens et al. 2015; Gawronski et al. 2017). However, a small credit has been granted to microbial activity. Bioremediation depends on the ability of microbes to breakdown the organic pollutants in the existence of optimal conditions of the environment and an adequate supply of nutrients and electron receiver (Adams et al. 2015). It should be emphasized that a soil treatment technique is not only aimed at reducing the concentrations of pollutants but also restoring the quality of soil (Epelde et al. 2010; Barrutia et al. 2011; Pardo et al. 2014). The optimum temperature typically means high levels of microbial action, which in turn possibly prioritizes increased metabolism of organic pollutants (Goiun et al. 2013).

Over the last several decades, many studies have been investigated that the microbial farming system responsible for the decrease of CO_2 from the atmosphere (Raeesossadati et al. 2014; Fernández et al. 2012). Microalgae have gained increasing interest with the recycling of CO_2 and bioremediation because of its potential to grow on non-agricultural lands and in saltwater. Weyens et al. (2010) used engineered endophytes to decrease the toxic metals and organic pollutants from polluted environments by phytoremediation. Various researchers have identified the possibility of epiphytic and endophytic microbiota, which reside on the leaves and shoots (and it is known as the phyllosphere) to remove VOCs (Khaksar et al. 2016; Sandhu et al. 2007). In addition to leaves of the plant, rhizospheric microbes also contribute to the depletion of VOCs from the internal environment (Llewellyn and Dixon 2011). Popek et al. (2015) demonstrated that trees and shrubs, forming a biofilter on the path of PM flow, have reduced the amount of PM about 50% that accumulates on the foliage of distant trees in the park. Sulfur oxidizing bacteria like *Paracoccus* and *Begiatoa* are capable of reducing sulfur compounds such as hydrogen sulfide (H_2S) to inorganic sulfur and thiosulfate to form sulfuric acid (H_2SO_4) (Pokoma and Zabranska 2015).

5.13 Role of Nanotechnology in Bioremediation of Industrial Air Pollution

Due to rapid urbanization, industrialization and increasing population pressure, are the major concerns that poses environmental pollution and human risks. Environmental pollution caused by a release of several air pollutants such as CO, chlorofluorocarbons, volatile organic compounds, hydrocarbons, and nitrogen oxide from the industries as well as other sources poses a human risk to several incurable disorders (Khan et al. 2014; Das et al. 2015; Krug 2009). Bioremediation is an eco-friendly, sustainable and economical approach that effectively restores polluted environments by utilizing microorganisms, by breaking down or transforming harmful to less toxic or non-lethal format. Meanwhile, living agents are utilized in the process of bioremediation to clean up the contaminated habitat/site, e.g., bacteria and fungi. Besides, these biomediators' advancements in science and technology gave birth to several new nanobiotechnological techniques. Nanotechnology refers to the pattern, characterization, formulation, and utilization of structures by changing shape and size at the nanometer scale (Hussain and Hussain 2015; Danish and Hussain 2019). But, due to the vast diversity of pollutants, no single bioremediation technique could serve as a "*silver bullet*" to recover the polluted environments.

5.13.1 Role of Nanotechnology in the Remediation of Toxic Gases Released from Industries

It produces novel materials with unique properties having small scale and high surface/volume ratio. These properties enable researchers to develop highly detailed and precise nanosensor appliances that significantly monitor environmental pollution. Besides, nanomaterials not only replace toxic material with a safety one but also react with impurity and degrade it into a non-lethal product (Falahi and Abbasi 2013; Chirag 2015; Ngo and Van de Voorde 2014). Also, coating technology involving nanostructures is also used to clean up such pollutants that show resistance as they possess self-cleaning features. Remediation using nanotechnology reduces air pollution in three different ways, namely adsorption of contaminants by using nano-absorptive materials, deterioration of contaminants by using nanocatalysis, and filtration/separation of contaminants by using nanofillers.

5.13.1.1 Nano-Adsorptive Materials

Nano-adsorbent could be used to clean up air pollution. Carbon nanostructures (e.g., fullerene, carbon nanotubes, graphene, and graphite) that have been used for industrial applications due to their high selectivity, affinity, and capacity (Bergmann and Machado 2015) are used as adsorbents to clean up air pollution. The addition of different functional groups to these nanostructures provides new receptive exterior sites or structure bonds for adsorption, making the process more effective by maximizing the adsorption volume of the system (Gupta and Saleh 2013; Wang et al. 2013). For example, the surface of CNTs with generous amine groups provides multiple chemical sites for CO_2 adsorption which makes CNTs ingest more CO_2 gases at low-temperature range (20–100 °C) and thus helps to reduce greenhouse gases from the environment (Su et al. 2009). Similarly, fullerene and graphene also speed up the process of adsorption to reduce greenhouse gases (Dong et al. 2015; Petit and Bandosz 2009).

5.13.1.2 Nanocatalyst Materials

The degradation of pollutants by utilizing semiconductor materials improves photocatalytic remediation by increasing surface area resulting in enhanced reaction efficiency (Özkar 2009). For example, the photocatalytic properties of titanium dioxide nanoparticles (TiO_2) are efficient to convert atmospheric contaminants such as nitrogen oxides and other pollutants into less toxic species (Shen et al. 2015). Further, TiO_2 nanoparticles are also used as an antibacterial agent. Besides, TiO_2 other nanocatalysts include nanogold-based catalysts (Singh and Tandon 2014), ZnO photocatalyst (Yadav et al. 2017), and bismuth oxybromide (BiOBr) nanoplate microsphere catalysts (Ai et al. 2009).

5.13.1.3 Nanofilters

Another approach for cleaning up air pollutants is the use of nanostructured sheets that have poured small abundance to separate contaminants from the source. Nowadays, nanofiber-coated filter media are used to filter air pollutants such as dust at industrial plants (Muralikrishnan et al. 2014). Bioaerosols, aerosols of biological origin such as viruses, bacteria, and fungi, are also air pollutants that cause many diseases such as allergies and infections. In this regard, silver nanoparticles and copper nanoparticles filters are extensively used in air filtration technology as antimicrobial agents (Lee et al. 2010).

5.14 Heavy Metals (HMs) in the Environment

Environmental pollution is one of the major challenges in modern human welfare (Ali and Khan 2017). Environmental contaminations and pollutants caused by heavy metals are a threat to the environment and are of serious concern (Alì et al. 2013; Hashem et al. 2017). Rapid industrialization and urbanization have caused contamination of the environment by heavy metals, and their rates of mobilization and transport in the environment have greatly accelerated since the 1940s (Khan et al. 2004; Merian 1984). Their natural sources in the environment are weathering of metal-containing rocks and volcanic eruptions, while industrial emissions, mining, smelting, and agricultural activities like the application of pesticides, phosphate, and other inorganic fertilizers are prominent anthropogenic sources.

According to Csuros and Csuros (2002), heavy metal is defined as “metal with a density greater than 5 g/cm^3 (i.e., specific gravity greater than 5).” The term “heavy metals” is often used as a group name for metals and semimetals (metalloids) that have been associated with contamination and potential toxicity or ecotoxicity (Duffus 2002). Very recently, we have proposed a broader definition for the term, and heavy metals have been defined as “naturally occurring metals having an atomic number greater than 20 and an elemental density greater than 5 g·cm^{-3}”.

5.14.1 Heavy Metals: Essential and Non-essential

Regarding their roles in biological systems, heavy metals are classified as essential and non-essential. Essential heavy metals are important for living organisms and may be required in the body in quite low concentrations, but non-essential heavy metals have no known biological role in living organisms. Examples of essential heavy metals are Mn, Fe, Cu, and Zn, while the heavy metals Cd, Pb, and Hg are toxic and are regarded as biologically non-essential (Ramírez 2013; Jović et al. 2012; Rahim et al. 2016; Türkmen et al. 2009). The heavy metals Mn, Fe, Co, Ni, Cu, Zn, and Mo are micronutrients or trace elements for plants. They are essential for growth and stress resistance as well as for biosynthesis and function of different biomolecules such as carbohydrates, chlorophyll, nucleic acids, growth chemicals, and secondary metabolites (Appenroth 2010). Either deficiency or excess of an essential heavy metal leads to abnormalities or diseases in organisms. However, the lists of essential heavy metals may be different for different groups of organisms such as plants, animals, and microorganisms. It means a heavy metal may be essential for a given group of organisms but nonessential for another one. The interactions of heavy metals with different groups of organisms are much complex (Chalkiadaki et al. 2014).

5.15 Sources of Industrial Wastes in the Environment

Sources of heavy metals in the environment can be natural, geogenic/lithogenic, and anthropogenic. The natural or geological sources of heavy metals in the environment are weathering of metal-bearing rocks and volcanic eruptions. The global trends of industrialization and urbanization on Earth have led to an increase in the anthropogenic sharing of heavy metals in the environment (Nagajyoti et al. 2010). The anthropogenic sources of heavy metals in the environment are mining and industrial and various agricultural activities. These metals (heavy metals) are released during mining and extraction of different elements from their respective ores. Heavy metals released to the atmosphere during mining, smelting, and other industrial processes return to the land through a dry and wet deposition. Discharge of wastewater such as industrial effluents and domestic sewage add heavy metals to the environment. Application of chemical fertilizers and combustion of fossil fuels also contribute to the anthropogenic input of heavy metals in the environment. Regarding contents of heavy metals in commercial chemical fertilizers, phosphate fertilizers are particularly important.

In general, phosphate fertilizers are produced from phosphate rock (PR) by acidulation. In the acidulation of single superphosphate (SSP), sulfuric acid is used, while in acidulation of triple superphosphate (TSP), phosphoric acid is used (Dissanayake and Chandrajith 2009). The final product contains all of the heavy metals present as constituents in the phosphate rock (Mortvedt 1996). Commercial inorganic fertilizers, particularly phosphate fertilizers, can potentially contribute to the global transport of heavy metals (de López Carnelo et al. 1997). Heavy metals added to agricultural soils through inorganic fertilizers may leach into groundwater and contaminate it (Dissanayake and Chandrajith 2009). Phosphate fertilizers are particularly rich in toxic heavy metals. The two main pathways for the transfer of toxic heavy metals from phosphate fertilizers to the human body are shown below (Dissanayake and Chandrajith 2009):

(a) Phosphate rock⟶fertilizer⟶soil⟶plant⟶food⟶human body.
(b) Phosphate rock⟶fertilizer⟶water⟶human body.

5.15.1 Human Exposure to Industrial Wastes and Heavy Metals

Humans are exposed to toxic heavy metals in the environment through different routes including ingestion, inhalation, and dermal absorption. People are more exposed to toxic metals in developing countries. Generally, people have no awareness and knowledge about exposure to heavy metals and their consequences on human health, especially in developing countries (Afrin et al. 2015). They may be exposed to heavy metals in the working place and in the environment. Human exposure to toxic chemicals in the working place is called occupational exposure, while exposure to such chemicals in the general environment is called non-occupational or environmental exposure. Workers are exposed to heavy metals in mining and industrial operations where they may inhale dust and particulate matter containing metal particles. People extracting gold through the amalgamation process are exposed to Hg vapors. It has been reported that welders with occupational prolonged exposure to welding fumes which had significantly higher levels of the heavy metals Cr, Ni, Cd, and Pb in blood than the control have shown increased oxidative stress (Mahmood et al. 2015). Cigarette smoking is also a principal source of human exposure to Cd (Järup 2003) and other toxic heavy metals present in the tobacco leaves.

Ingestion of heavy metals through food and drinking water is a major exposure source for the general human population. Industrialization, urbanization, and rapid economic development around the globe have led to intensification in industrial and agricultural activities. Such activities may cause contamination of water, air, and soils with toxic heavy metals. Growing human foods in heavy metal-contaminated media lead to bioaccumulation of these elements in the human food chains, from where these elements ultimately reach the human body.

5.15.2 Bioaccumulation and Biomagnification of Heavy Metals in the Human Food Chains

Humans are omnivorous, they may be exposed to toxic heavy metals through different food items such as fish, cereals, and vegetables. Contamination of these heavy metals in freshwater bodies such as rivers, lakes, and streams leads to bioaccumulation in freshwater fish, while such contamination in agricultural lands leads to bioaccumulation in agricultural crops. Contamination of human food chains with toxic heavy metals poses a threat to human health. Certain examples from the twentieth century have shown that such contamination is a serious issue for human health. Minamata disease (MD) and *itai-itai* disease both in Japan were caused by the consumption of Hg-contaminated fish and Cd contaminated rice, respectively. Figure 5.4 depicts the transfer of heavy metals from contaminated fish to humans.

Although biomagnifications of heavy metal is a controversial issue in metal eco-toxicology, numerous studies have reported biomagnifications of heavy metal in certain food chains. In the case of biomagnifications of these metals in food chains, organisms at higher tropic levels in the food chains are at greater risk. Higher concentrations of trace metals in organisms of higher tropic levels as a result of biomagnifications can pose a health risk to these organisms or to their human consumers (Barwick and Maher 2003). To protect human health from the harmful effects of toxic heavy metals, human food chains should be constantly monitored for bioaccumulation and biomagnifications of heavy metals. However, nondestructive

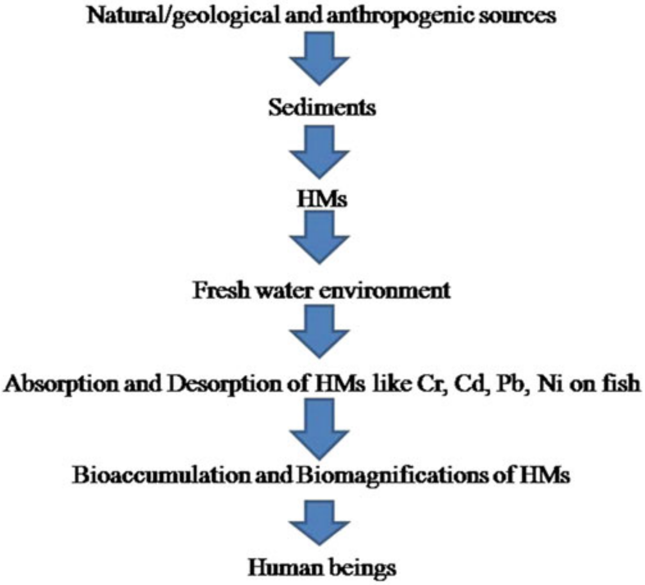

Fig. 5.4 Transfer of HMs from freshwater fish to humans in the human food chain

sampling techniques and use of environmental biomarkers should be opted to avoid loss of biota due to analysis. Furthermore, in order to avoid contamination of food chains with heavy metals, untreated municipal and industrial wastewater should not be drained into natural ecosystems such as rivers and farmlands (Balkhair and Ashraf 2016).

5.15.3 Toxicity of Heavy Metals

Although some heavy metals, called essential heavy metals, plays an important role in biological systems, they are generally toxic to living organisms depending on the dose and duration of exposure. It is a well-known fact in toxicology that "excess of everything is bad." Nonessential heavy metals (Cd, Pb, and Hg) and metalloids (As, etc.) may be toxic even at quite low concentrations. Essential heavy metals are required in trace quantities in the body but become toxic beyond certain limits or threshold concentrations. For some elements, the window of essentiality and toxicity is narrow. Heavy metals have been reported to be carcinogenic, mutagenic, and teratogenic. They cause the generation of reactive oxygenic species (ROS) and thus induce oxidative stress. Oxidative stress in organisms leads to the development of various diseases and abnormalities. Heavy metals also act as metabolic poisons. Heavy metal toxicity is primarily due to their reaction with sulfhydryl (SH) enzyme systems and their subsequent inhibition, e.g., those enzymes involved in cellular energy production (Csuros and Csuros). The reaction of heavy metal (M) with glutathione (GSH), (which is an important antioxidant in the body). Here, the metal replaces H atoms from SH groups on two adjacent glutathione molecules. The combination of these two glutathione molecules leads to the formation of strong bond with the metal that deactivates them for further reactions:

$$2 \text{ glutathione} + \text{metal ion } (M^{2+}) \longrightarrow M\,(\text{glutathione})_2 + 2H^+ \quad (3)$$

5.15.4 Effects of Toxic Heavy Metals on Human Health

Heavy metals Cd, Pb, Hg, and As deplete the major antioxidants of cells, particularly antioxidants and enzymes having the thiol group (-SH). Such metals may increase the generation of reactive oxygen species (ROS) like hydroxyl radical, superoxide radical, and hydrogen peroxide. Increased generation of ROS can devastate the inherent antioxidant defences of cells and lead to a condition called "oxidative stress" (Ercal et al. 2001). Heavy metals, including Cd, Pb, and Hg, are nephrotoxic, especially in the renal cortex (Wilk et al. 2017). The chemical form of heavy metals is important in toxicity. Mercury toxicity largely depends on Hg speciation (Ebrahimpour et al. 2010). Relatively higher concentrations of toxic heavy metals, i.e., Cr, Cd, and Pb, and relatively lower concentrations of the antioxidant element

Se have been found in cancer and diabetes patients compared to those in the normal subjects in Lahore city, Pakistan (Salman et al. 2011). We all should be aware of the potential hazards and keep in mind that studying them before applying anything in nature is one of the main challenges of future studies. New technologies are being invented throughout the year and developed/modified especially in the field of science, which can help us understand all processes better and use them very accurately in the field of bioremediation can do. Therefore, research in this area is very promising.

5.16 Conclusion

Day by day, increasing pollution threatens our health and damages the environment, affecting the sustainability of wildlife and our planet. Damage to our soil affects our ability to grow food, as summarized in our policy report on the subject of food security. Bioremediation can help reduce and eliminate the pollution we generate by providing clean water, air, and healthy soil for our generations to come.

Acknowledgment All the authors are very thankful to Dept. of Botany, AMU, Aligarh for their all the moral support and upliftment. None of the authors has conflict of interest.

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Chapter 6
E-Waste and Its Hazard Management by Specific Microbial Bioremediation Processes

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D. G. Panpatte, Y. K. Jhala (eds.), *Microbial Rejuvenation of Polluted Environment*,
Microorganisms for Sustainability 26, https://doi.org/10.1007/978-981-15-7455-9_6

Abstract E-waste generation and its effective remediation had been a tough task to be accomplished as these e-wastes generate hazardous components to place human and his environment at risk. Though various physical and chemical processes are present as to mitigate the problem associated with e-waste pollutants, but due to their hazards and high cost, these are less preferred as compared to microbial treatment (bioremediation). Microbial bioremediation involves biosorption, bioleaching, bioaccumulation, etc. as to recover heavy metals and remove other hazardous components. These processes along with environmental laws and legislations could be proved obliging in salvage the environment and its various components.

Keywords Bioremediation · E-waste · Bioleaching · Biosorption · Bioaccumulation · Heavy metals · Biodegradation

6.1 Introduction

In the era of this ever-changing world, the continuous advancing science, engineering, and technology play a significant role in modifying and elevating the life and lifestyle of humans. The remarkable developments in the recent times had made human life easy, fast, and more commutable. Various electrical and electronic gadgets assisted with computer programming had certainly added more luxury and ecstasy to the human experiences. But as every coin had two faces, these developments and advancements are kicked back with certain undesirable environmental issues (Babu et al. 2007; Leung et al. 2008; Pinto 2008). E-waste is such a problem which had increased manifold generating perilous effect to environmental components, thus affecting all flora and fauna including hominids. The toxic chemical and elements leaching through these e-wastes not only produce problems like cancer in human but after a permissible limit could be proved lethal (Mudila et al. 2018; Needhidasan et al. 2014; Rosariastuti et al. 2019). E-waste is generated by electrical and electronic leftovers which are obsolete or have completed their usable lifespan. In the current time, the technology advancement is in such a rapid pace that the existing technology becomes archaic within some years or even in months. The problem is too catastrophic because only a limited percentage of these e-wastes are being recycled else is being dumped in oceans, deep down the earth, or sometimes is thrown in open air (Monika and Kishore 2010). As reported by UNU, two million metric tons (MMt) of electronic waste is being piled every year over the globe, which is estimated to lead toward a heap of more than 50 MMt of e-waste by 2019 (about 41.8 MMt in 2014, 44.7 MMt in 2016) (Global E-waste Monitor 2017; Mmereki et al. 2016), out of this total e-waste about 20% is generated out through personally used digital devices. However, the data of generated e-waste varies from area to area and studies to studies as the definition of e-waste is different as suggested by different agencies. By observing a general trend associated with computer hardware that after every 2 years of span, the number of transistors used in ICs double its number, this Moore's Law had been taken as a goal by the electronic and electrical industry to produce more every year (Poppenheimer 2013), which generates the hazards in proportional rate.

6.2 Composition of E-Waste

E-waste (classified into ten categories by the European WEEE Directive) is generated from sort of sources which broadly can be categorized into following types: *consumer and business electronic gadgets* (phones, computer parts, video players/ recorders, calculators, photocopier, etc.), *laboratory equipments* (microscopes, calorimeters, sophisticated instruments, etc.), *kitchen wares* (microwave ovens, inductions, toasters, etc.), *medical equipment* (scanner, analyzers, ventilators, etc.), and *basic appliances used in homes* (air conditioners, hair drier, batteries, etc.). These e-waste sources generate metals, precious metals (Cu, Sn, Li, Co, Au, Ag, etc.), rare earth metals, heavy metals (Hg, Cd, Cr, As, Pb, etc.), VOCs, PAHs or PBDEs or/and PCBs, and polymers as major pollutants which are liberated in soil, water, air, and other components of ecosystem (Mudila et al. 2018; Mmereki et al. 2016) (Fig. 6.1).

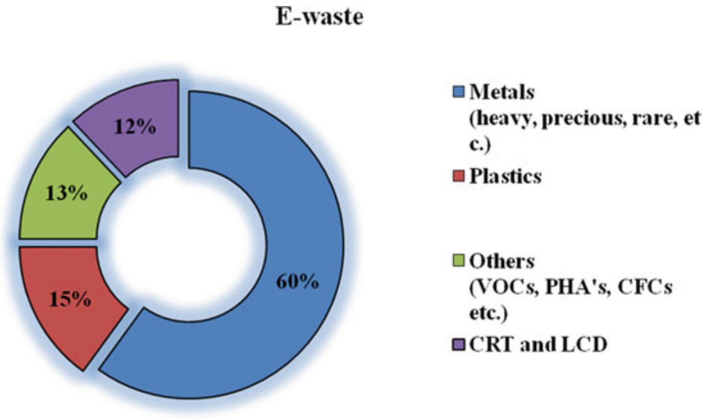

Fig. 6.1 Contributing type of e-waste generated from various sources (Mmereki et al. 2016)

6.3 Hazards of E-Waste

Industries related to electrical and electronics had emerged as one of the fastest evolving frameworks of the world from the start of the twenty-first century and is accepted to be evolving at much higher pace. Human lifestyle, more use of advance technology, and internet-supporting devices had brought boom in this sector which was in trifling up to the end of the last century. This increase in use of electronic gadgets had about significant and detrimental problem of e-waste (Sankhla et al. 2016). As per data as compared to the municipal waste material, e-wastes are being generated as three times more and had become a major global problem specially in countries like China, India, and many other underdeveloped countries, where IT devices are being imported (free trade) in addition to the internal electronic productions. Out of this e-waste, precious metals like Au, Cu, Al, Fe (~60%), plastics and polymers (~30%), and heavy metals (~3%) share their part (Li et al. 2011), and some rare earth metals (La, Nd, Y, etc.) are also included as the part of the composition (Poppenheimer 2013). When these metals are not recycled, then new sources (mining) are found to fabricate the future demanded consumer products.

Certainly, up to now, a number of studies had been put forward which suggest the menace of these e-waste components for human, other flora and fauna, and even microbes.

6.3.1 Effect on Environment

The hazardous chemicals listed in Table 6.1 are from direct contact of various strata of environment and thus mark their footprint over them. With the time the e-waste start to get disintegrated into simpler molecules and elements to release hazardous heavy metals, metals, and other organic wastes. These toxins/dioxins leach through different horizons of soil available to get absorbed by the plants or to percolate to water source, thus not only affecting the structure and composition of soil and water (fresh and marine) but also affecting the components of life directly benefiting through these abiotic components (Dharini et al. 2017; Das et al. 2009; Song and Li 2014; Wang et al. 2013). All over the globe, soil is highly exposed to metric tons of e-waste and being heaped up with excess of waste produced by numerous electronic and household wastes. One of the most affected components of the environment by e-waste is “soil.” Soil gets affected by two mechanisms: first, by coming directly in interaction with the hazardous material during the process of recycling or disposal, and second, through contaminated water (through various sources) used for irrigation purpose. It was suggested by Dharini et al. (2017) that the presence of toxic components in soil can increase the alkalinity, thus affecting the composition of water, and also it reduces the amount of free available nutrients like N, P, and K. In the process of dismantle, extracting exquisite metals, shredding, incineration, the heavy metal particle, and PBDEs are unrecovered and leached

Table 6.1 E-waste sources, component/pollutants and health issues (Needhidasan et al. 2014; Monika and Kishore 2010; Gaidajis et al. 2010; Verma and Agrawal 2014; Agnihotri 2011; Huang et al. 2014)

E-waste pollutants		E-waste sources	Health impact on humans
Heavy metals	Cd	Semiconductors, resistor chips, batteries, CRT screen, IR detectors, pigments	Bone disease, CNS damage, kidney and liver failure, teratogenic (affects embryo and fetus)
	Pb	Solder in circuit board, gasket computer monitor, lead batteries, glass panel, CRT screen, solar, transistors	Renal failure, CNS and PNS damage, affects reproductive system, affects circulatory system, affects brain development in minors
	Hg	Hg wetted relays and switches, printed circuit boards, alkaline batteries, fluorescent lamps, thermostat, sensors, medical equipment, mobile phones	Respiratory and skin problem, brain damage, affects liver, kidney and fetus, CNS and PNS damage
	Cr	Untreated galvanized (corrosion protector) steel plate, floppy disks, data tapes, decorative hardener, dyes and pigments, solar cells	Bronchitis and asthma, complications in the liver, kidney, and gastrointestinal tract, carcinogenic, DNA destruction
	As	LED (as gallium arsenide), circuit boards, LCD display and computer chips, solar cells, microwaves	Irritation in digestive system, carcinogenic (skin and liver)
Other hazardous metals	Li	Mobile phones, Li batteries, photographic equipment	Present in breast milk and harm infants, cause irregular heart rhythms, kidney problem, and thyroid problem
	Ni	Ni-Cd batteries, CRT electron gun, alloys, relays, semiconductors, pigments	Dermatitis, eczema, asthma, chronic bronchitis, cancer of the lung and nasal sinus, allergic
	Cu	Electric wires and cables, printed circuit board, pigments	Irritation, stomach cramps, nausea, liver damage (Wilson's disease), kidney damage
	Be	Motherboard, power supply boxes (containing Si controlled rectifiers), x-ray lens, finger clips	Respiratory disease, affects liver, kidneys, heart, nervous system, and the lymphatic system, skin sensitization
	Ag	Capacitors, switches, batteries, resistors	Argiria (skin pigmentation), skin irritation, drowsiness, kidney damage, eye damage, lung damage, liver damage, anemia, brain damage if taken in excessive amount
	Se	Pigments, fax machines, photocopiers, photoelectric cells	Higher concentration (fivefolds or more) leads to selenosis, deformation of nails and hairs, can impair lung tissues, and various commotion in regular functioning of body organs

(continued)

Table 6.1 (continued)

E-waste pollutants		E-waste sources	Health impact on humans
	Zn	Alloys (brass and steel), luminous materials, disposed batteries and rechargeable batteries	Burning skin, lowers blood pressure in diabetic patient, poses problem with blood Fe at higher concentration
	Co	Insulators	Thyroid and myocardial ailments, respiratory tract and skin inflammations, hyperplasia and polycythemia in bone marrow
Plastics			
Organic pollutants	VOCs	Paints, photo copiers, and printers	Detrimental for kidneys, liver and CNS, carcinogenic, memory and visual disorders
	PAHs	Contaminated soil and air near e-waste burning sites (incineration of polymers)	Irritation in eyes, throat, etc. as short-term effect, long-term effects involves cataracts, renal and liver mutilation
	PBDEs	Recycling e-waste components, PBDE treated electronic equipment viz. computer, televisions, etc.	Neurobehavioral deviations, damage reproductive and immune system, liver, and thyroid
	PCBs	Transformers (used as coolant), capacitors, and electrical gears, microscopes, fluorescent lighting	Cause liver, gall bladder, gastrointestinal breast, brain cancer, etc. chloracne (severe skin acne)

through the soil particles. Adesokan et al. (2016) assessed the effect of Pb, Cr, Cu, Cd, and Ni on soil composition, generated from e-waste recycling zones (of low, medium, and high activities). Various heavy metals were detected in different concentration range in the soil, viz. Pb (269–5650 mg/kg), Cr (3.30–42.4 mg/kg), Cu (203–3483 mg/kg), Cd (under detection limit to 2.50 mg/kg), and Ni (0.14–24.0 mg/kg). Presence of Pb (65%) and Cu (88%) more than the tolerable limits is the potential factors for the deviation in the natural conditions, and studies suggest that the increase in the %age of these two metals in soil get elevated with increased pH (6–7) of soil, due to the formation of soluble metal-organic frameworks. Needhidasan et al. (2014) had classified the electronic waste in three categories depending upon their hazards, white, brown, and gray, where the last one generated through computers, scanners, photo copiers, printers, etc. is more hazardous as compared to the initial two.

Studies on soil from dumpsites (Lagos and Ibadan, Nigeria) were carried out by Adeyi and Oyeleke (2017), and it was observed that the soil was contaminated with heavy metals and PAHs, the heavy metal concentration was between 114 and 28.40×10^2 mg/kg, in which Pb and Cd (not detectable, 6.50 mg/kg), Cu ($42.8–53.90 \times 10^2$ mg/kg), Zn ($27.5–34.20 \times 10^2$ mg/kg), Ni (11.0–128 mg/kg), and Cr (94.0–325 mg/kg) were resent in different concentrations. The concentration (μg/kg) of PAHs was found to range between $17.56–22.24 \times 10^2$ and $16.64–21.52 \times 10^2$ at the level (top-soil) of 0–15 cm and 15–30 cm while 278 μg/

kg concentration was determined in the sub-soil of the studied site, suggesting human-induced pyrogenic and petrogenic sources (contamination from incomplete hydrocarbon burning). Soil samples (50) were collected from e-waste recycling sites to determine the presence (and amount) of major heavy metals (As, Cd, Cr, Cu, Ni, Pb, and Zn); As (20.6 mg/kg), Cd (0.6 mg/kg), Cu (33.8 mg/kg), and Zn (141.4 mg/kg) were the potent pollutants in the recycling sites, and the CV was found to be over 50% for As, Cd, and Cu, suggesting the anthropogenic effect over the soil (He et al. 2017). Soil samples were collected from 22 farmlands nearby e-waste recovery spot in Qingyuan (South China), the collected samples were investigated for the presence, distribution, and % abundance of Cd (43.7–99.6%), Cr, Cu (39.6–93.9%), Pb (36.9–90.6%), Ni, and Zn. It was reported that ~73% of soil samples were found to be contaminated with one or more heavy metal ions, even in them Cd (greatest), Cu, Pb, and Zn were the potential contaminants, and also the contaminants were found to percolate through layers along with surface soil (Zhang et al. 2015).

Concentrations of 12 different heavy metals present in soil (surface, middle, and deep, 0–20, 30–50, and 60–80 cm, respectively) were measured from a desolate paddy field, an acid-leaching site, and a desolate site of Guiyu, China. The results show that the surface soil in acid-leaching site was heavily contaminated with Ni, Cu (684.1 mg/kg), Zn (572.8 mg/kg), Cd, Sn (3472 mg/kg), Sb (1706 mg/kg), and Pb, and in desolate paddy field, main concentration of heavy metals (Sb > Sn > Cu) was in surface and mid soil, while in desolate site, the heavy metal concentration was mainly in deep soil (Quan et al. 2015). E-waste salvaging site in Longtang, South China, was studied for the effect of e-waste-generated heavy metal on water and soil in nearby areas, the surface soil was contaminated with Cd and Cu (0.4 mg/kg and 1981 mg/kg respectively), and Pb due to incineration and acid leaching. Due to high pH and TOM (Total Organic Matter), the concentration of heavy metal is decreased down the depth, thus showing the higher contamination of heavy metals and acidic components in pond water as compared to well water, due to the transportation of these heavy metals along with runaway water, can be detrimental for human health if used for irrigation of agricultural fields (Wu et al. 2015). Soil samples (54) were studied for the presence of PBDE congener (14), and deep soil was observed to be less polluted as compared to surface soil with maximum presence of BDE209, BDE138, and BDE28, while penta- and deca-BDE were the main PBDE polluters, determined by PCA. Soil properties (studied by RDA) do have marginal effect [soil organic moisture (2.5%) and soil organic content (3.65)] of the concentration of PBDEs in the area (Wu et al. 2019a).

Heavy metal concentrations were determined in surface soil in Mandoli industrial area, Delhi, India. Pb and Zn were found to have a high concentration of 2645.3 and 776.8 mg/kg, respectively, while Cu (115.50 mg/kg), As (17.08 mg/kg), Se (12.67 mg/kg), and Cd (1.29 mg/kg) were detected to be in lower concentration. Water (pH 5.93) subjected to investigation was found to have higher concentration of trace metals as suggested by Indian and WHO standards (Pradhan and Kumar 2014). Shallow groundwater samples (12) and topsoil samples (187) were collected by Wu et al. (2014), to investigate the concentration of Cd in them. In soil samples, inverse trend of pH to heavy metal concentration was observed, while the effect of soil organic matter was not too effective in determining the magnitude of Cd in the soil. Also 9 water samples out of 12 were determined to have high concentration of heavy metals.

6.3.2 Effects on Plants

Toxins/dioxins generated from e-waste percolate through soil, water, and can bio-accumulate in the food particles. These food particles are consumed by various animals and by humans also which get bio-magnified with time gradually. Dharini et al. (2017) suggest increased amount of Ca in soil, and water can adversely affect the growth of plant by effecting the cell walls. It was also observed that the addition of lead and PCB as the part of landfills decreases the percentage of nitrogen, potassium, and phosphorus available in the soil due to change in pH, thus making soil sterile for plant growth.

Rice grain samples were taken for a period of 5 years (2006–2010) from the site of e-waste dismantling for probable detection of certain heavy metals (As, Cd, Cu, and Pb). GM study shows the presence of above trace metals in 111, 217, 4676, and 237 ng/g concentration, respectively. The concentration of As, Cd, and Cu shows the constant trend while for Pb the trend was observed to be negative. The results indicate the risk assessments for plant and thus humans due to the accumulation of these hazardous components in the physic of both, with the H_Q being highest for Cd (46% of H_I) and lowest for As (Fu et al. 2013). Wu et al. (2019b) studied the effect of contamination of paddy plants through less studied heavy metals (Ag, Sb, and Sn), PBDEs, and AHFRs near e-waste dissemination site due to the dispersion of these potent hazardous materials. Heavy metals were mainly transferred to the leaves (by transpiration, due to higher hydrophilicity) as compared to PBDEs and AHFRs (BCF of less than 0.15) posing health-related issues. However, selective metals were translocated due to the formation of chelates and complexation within the plant, while organic pollutants were bound to the lipid in xylem or in vacuole present in the root cells. High concentration of heavy metals was detected in the *Cynodon dactylon* plants (four samples) near the dismantling site in Mandoli Industrial site, Delhi, due to the presence of certain heavy metals in water and air (due to incineration) detected by ANOVA, among various heavy metals As, Cr, Hg, and Se were not found in any plant samples (Pradhan and Kumar 2014).

6.3.3 Effects on Human

Primitive method like incineration of cables, circuit boards, etc. for extracting precious metals produces hazardous cancerous gases; similarly dismantling equipment can cause serious injury to the workers. These toxins affects the central nervous system, immune system, and reproductive and digestive system, and these toxins also show effects like skin damage and ulcers especially in children who are more vulnerable to these as their body is still in the stage of development (Grant et al. 2013; Zeng et al. 2016). Bio-accumulated toxins in food entering human digestive system can also be proved precarious (Table 6.1). In many recovery sites over the world, the e-waste is generally recycled by informal segment manually (or using hazardous methods) for rapid recovery of precious metals. Handling e-waste is not easy due to the fact that various components present in the e-waste make it complex to decompose it via simple and in a single way. This complexation can lead toward accumulation of hazardous components of e-waste in different regimes of ecosystem, leading to prolonged exposure of an individual (infants and children especially) to them, thus showing physiological, neurological, and behavioral changes (Chan and Wong 2013). Safe and hazardless recycling units use advanced methods for extracting and recycling the hazardous chemicals and metals from the electronic gadgets, but these units are expensive to establish and are rare, thus causing occupational exposure to these hazards (Wong et al. 2007).

Five heavy metals Cd, Cu, Pb, Ni, and Zn (Zn highest and Ni lowest) were found to be present in the hairs of community (occupational and non-occupational) exposed to the waste generated from an e-waste recycling area. The elevated heavy metal concentration is an indication of increasing hazards to the community specially children and old people, signifying more stress toward the health of residents (Zheng et al. 2011a, b). Earlier similar studies were carried out by Wang et al. (2009a, b), for the presence of trace and heavy metals (As, Ba, Cd, Cr, Cu, Pb, Ni, and V) in the scalp hairs of the exposed workers and residents, suggesting scalp hair to be a significant biomarker. Studies based on GMs suggest the elevated abundance of Pd (39.8 μg/g) and Cu (49.5 μg/g) in the taken samples. BFRs (viz. PBDEs and DBDPE) as a component of e-waste were analyzed from human hairs (occupational workers) by Zheng et al. (2011a, b), which was observed to be threefold higher as compared to non-occupational residents. BDE209 instead of DBDPE was the major BFR present in hairs and was responsible for observed hazards. It was suggested that the nano-BDEs were formed due to the degradation of BDE209 which had half-life (37–91 days) more than BDE209 and can get accumulated in human body.

Children (3–7 years of age) living near dismantling site were taken under investigation for the presence of ten heavy metals (As, Cd, Cr, Cu, Hg, Mn, Ni, Pb, Se, and Zn) and seven antibodies (DPT, hepatitis B, Japanese encephalitis, measles, and polio), established on Spearman rank correlation analysis, and all antibodies were found to be negatively correlated with the blood concentrations of Cu, Pb, and Zn. Concentration of antibodies amplified with phase, high blood concentration of heavy metals (Cd, Mn, and Ni), and BMI. This investigation suggests that with higher metal exposure, the immunity in children is decreased due to the reduced antibody levels against the inoculations (Lin et al. 2017). Health risk assessment on particle size pollutant was done in the area of heavy metal recovery site, it was observed that the metal particles, viz. As, Cd, Pb, Se, Sb, and Zn (anthropogenically generated), remains in fine particles form while heavy metals like Co, Fe, and Ti were as accumulated as granular particles. It was also determined that the ingestion through inhalation of these heavy metal particles is way less as compared to other way of ingestions, the H_Q was found to be above 1 for adults and children, also the carcinogenic risk from the metals was high (Huang et al. 2016). Luo et al. (2014) studied the effect of airborne HFRs specially PBDE ($H_Q = 5.6 \times 10^{-4}$) pollutants on the human health; the head airways were found to be deposited with granular particles (size >1.8 μm) and the alveolar region was dominated with fine particles (size <1.8 μm). The inhaled percentage of PBDEs was nearly equal to the ingestion done by other ways (food and other non-e-waste sources) with great chances of carcinogenic effects.

6.4 Method of Treating E-Waste

E-waste management (recovery/removal) from particular site is essential so as to minimize the dreadful hazards of the pollutants generated through it, and it also provides the recovery of various valuable metals and other elements so as to save the natural resources, save environment by reducing pollution, preserve landfill space, save energy, slice the manufacture waste, and create employment. Though e-waste treatment is being done by a variety of methods, still such methods are required which can decrease the aftermath of these components of hazards. Thus to remove, recycle, and recover these components of e-waste, various existing techniques are present which had their own advantages and disadvantages (Gupta et al. 2014) (Fig. 6.2).

6.4.1 Physical Methods

Various physical methods are employed to recover the essential and valuable metals from the printed circuit boards and other components of e-wastes (Cui and Forssberg 2003). Factors like easy, convenient, and simple processing, environment benign, and low processing cost make physical methods advantageous to operate. Few of the physical methods are discussed below.

6.4.1.1 Mechanical Recycling

This method involves disassembling of the printed circuit boards into powdered form which is then exposed to Eddy current separators for the separation of metal particles, and further, the powdered samples are passed through density separation procedure (Zhang and Forssberg 1993; Zhang and Forssberg 1997; Copani et al. 2019). Conditioned to density and particle dimension, separation of individual metal can be observed in the liquid column (Rohwerder et al. 2003).

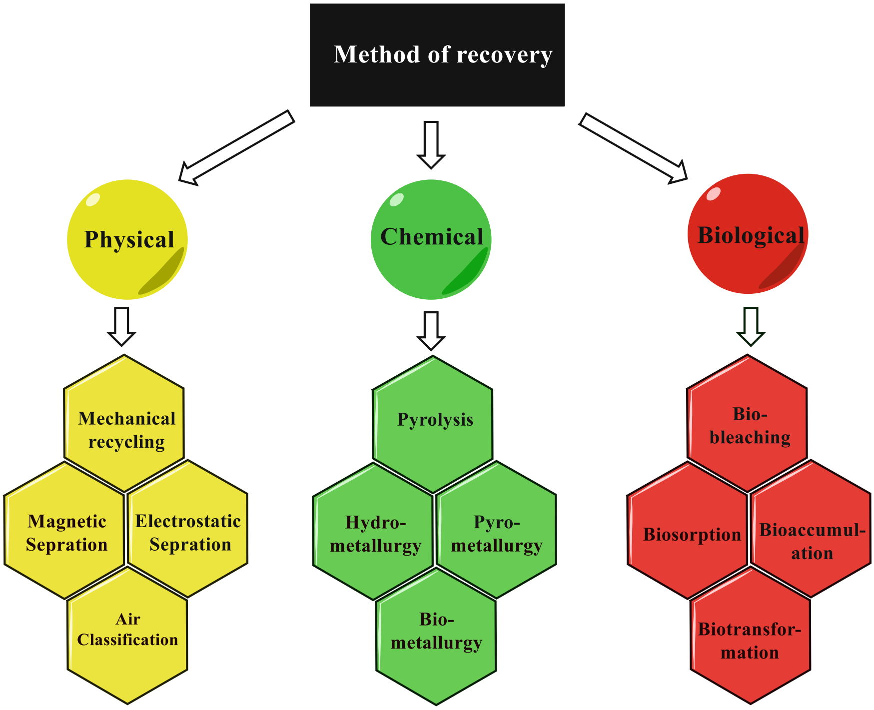

Fig. 6.2 Various methods of recovery of valuable materials from e-waste

6.4.1.2 Air Classification

It includes the separation on the basis of weight of the various components of e-waste. Printed circuit boards were subjected to mechanical milling after determining the chemical, physical, and electrical properties of the components. Air classification was done for serration of light-weighted components of the e-waste while Al and Cu were separated effectively (Laurmaa et al. 2011).

6.4.1.3 Magnetic Separation

Various magnetic and nonmagnetic e-waste composition can be separated by this method; however, agglomeration of particles is one of the major drawbacks for this process, as a result the nonferrous material can be pulled in by the magnet along with magnetic active components (Hanafi et al. 2012; Sohaili et al. 2012).

6.4.1.4 Electrostatic Separation

This method is based on the electrical conductivity of the materials subjected to separation (Kaya 2016a, b). Guo et al. (2008) used Eddy current to separate and recover Al (2.8%) from the scraped printed circuit boards, which is further sent to Al smelter for further procedure. Corona-electrostatic separation is also used as to separate fine particles of size less than 0.6 mm (Hadi et al. 2015).

However, few factors viz. difficulty in separation of metallic and nonmetallic components from the printed circuit boards and generation of dust (during shredding and grinding) brought certain unwanted limitation of these physical processes of recovery of metals from e-wastes (Tsydenova and Bengtsson 2011).

6.4.2 Chemical Methods

Processes like pyrolysis, hydrometallurgy gasification, de-polymerization (by supercritical solvents), and hydrogenolytic degradation processes are employed to remove and recover useful components from the e-waste (Kaya 2016a, b). Organic and metallic fractions are separated with chemical separation method, where metals can be separated via different metallurgical methods.

6.4.2.1 Pyrolysis

It is the process to heat the material in the absence of oxygen to recover purified metal from the e-waste. During the process, organic materials are decomposed to materials of lower molecular mass (gases, liquid, tar, char, etc. to be used as fuel), while metals along with glass are retained as solid components (Guo et al. 2008; Zeng et al. 2012). Centrifugal separation assisted by vacuum pyrolysis was used by Zhou and Qiu (2010). For effective recovery of organic waste and solder, when printed circuit boards were heated at 240 °C, with 1400 rpm for 6 min spasmodically the solder was found to be separated out. The pyrolyzed component consists of 69.5–75.7 wt% residue, 27.8–20.0 wt% oil, and 2.7–4.3 wt% gas, which were used as fuel.

6.4.2.2 Hydrometallurgy

Hydrometallurgical process e-wastes are treated with successive use of acids to leach out the precious metals from them. The treatment is further followed by separation and purification (through abstraction, adsorption, and ion exchange method) to recover the exquisite metal (Ashiq et al. 2019). It had been observed that this method generates flexible and less hazards, is energy efficient as compared to pyrolysis, also is of less cost, and produces leached metal (usually metallic ferrous components) in solid form as to extract it easily and efficiently (Ghosh et al. 2015; Sethurajan et al. 2019); however, the liquid waste generated should be disposed judiciously to minimize the hazards. Hydrometallurgy process employs a variety of leachants viz. H_2SO_4, $HCl:HNO_3$ (aqua regia), HNO_3, and certain cyanide solutions. Metals leach out in the case of nonmetallic substrate scan be recovered by electrochemical processing (Kinoshita 2003; Li et al. 2004). Samples were prepared after crushing, pulverizing, and decontaminating a certain amount of e-wastes, which was further washed with water and treated with HNO_3 to dissolve valuable metals like Cu and Ag, while Au remains in the solid components which was treated with aqua regia to leach out (99.9%). Factors viz. acid used (proportion, 1:1 $HCl:HNO_3$), time span (60 min), and applied temperature (60 °C) did not find their effect over the dissolution of Au (Mikaeli et al. 2015). Kasper and Veit (2018) used ammonium and sodium thiosulfate as alternative of CN as leaching agents for the recovery of gold electrometallurgical route. Primarily, the relative amount of gold present in the printed circuit board of mobile phones was determined, followed by the use of alternative leaching agents (in different concentrations) for different range of time. A control sample of cyanide-based solution was also established as to compare the obtained results. The control (i.e., cyanide-based solution) extracted 88% of the gold, while sodium and ammonium thiosulfate–leached gold was extracted in 70% and 75% (142–700 g/ton), respectively. While the electro winning trials presented a higher recovery of the gold (94%) in thiosulfate solutions.

6.4.3 *Bioremediation*

Microbes (bacteria, algae, archaea, yeast, fungi, etc.) due to their exceptional property to grow in diverse and adverse conditions can be employed for the degradation of a variety of pollutants, termed as bioremediation (biological remedy of environmental pollutants) (Mudila et al. 2018; Gupta et al. 2016). The microbial activity is done as to generate biomass or energy from the degradation of these pollutants and reinstating the natural ecosystem. Bioremediation involves degradation, modification/alteration, sequestration, removal, or decontamination of pollutants via various mechanisms. Bioremediators are actually composed of certain enzymes (of class isomerase, hydrolase, transferase, oxidoreductase, ligase, lyase, etc.) which allows the biological pollutants to be acquired as nutrients for their growth and biomass (Abatenh et al. 2017; Singh et al. 2014). Following are certain mechanisms adopted by the microbes for sequestration and degradation of hazardous pollutants.

6.4.3.1 Biosorption

It is a mechanism of binding, absorption, and accumulation of material on the surface of biomass (microbial and plant) from the source, microbial biomasses (dead/alive) viz. bacteria, fungi, algae, yeast, etc. that do have this property of binding with the biosorbate. Biosorbent surface is equipped with certain function groups (amine, amide, carbonyl, carboxyl, phenolic, imine, and phosphate, phosphodiester, etc.) to attract the heavy metals on the surface of the biomass (Fig. 6.3). Biosorption is a simple and advantageous mechanism which generates effective decontamination, with high efficiency and easy regeneration of bio-absorbent used, and endures unfavorable circumstances, and also the operational cost for the process is extremely low (Kanamarlapudi et al. 2017). Dead microbes are preferred over alive as they did not require nutrient and BOD/COD monitoring.

Following equation can be employed to figure out the amount of biosorbate absorbed by the biosorbent,

$$q_{\mathrm{e}} = C_{\mathrm{i}} - C_{\mathrm{e}} \times V \times m \tag{6.1}$$

where q_{e} is the amount of absorbent (mg/g), C_{i} is the initial concentration of absorbent (mg/L), C_{e} is the equilibrium constant of absorbent (mg/L), V is the

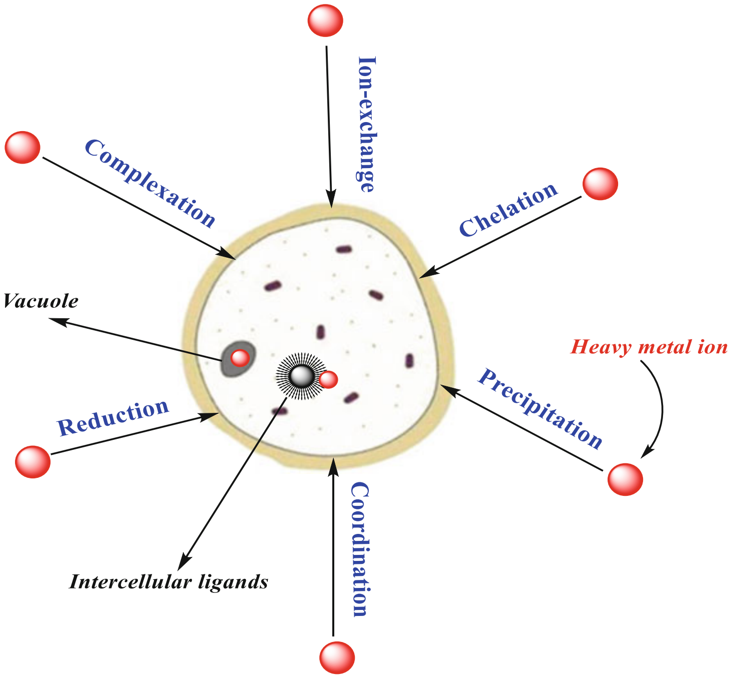

Fig. 6.3 Various mechanisms of biosorption in microbes

volume of the solution (L), and m is the mass of the absorbate (g). Biosorption efficiency (biosorption, $R\%$) for the metal can be calculated (Kanamarlapudi et al. 2017).

$$R\% = C_{\mathrm{i}} - C_{\mathrm{e}} \times C_{\mathrm{i}} \times 100 \tag{6.2}$$

The efficiency of biosorption depends upon various factors viz. chemical and physical properties of metal ion, properties of microbial biomass (biosorbent), types and available number of bioactive (binding) sites, and other physical factors (temperature, pH, concentration). While complexation, chelation, coordination, ion exchange, precipitation (bio-mineralization), and reduction are few of the known mechanism for biosorption.

Bacillus megaterium (2 g, dead biomass) at pH 5 was employed as to recover Cu (65%) from printed circuit boards for a contact period of 1 h (agitation of 150 rpm). Optimum absorbent concentration of *Bacillus megaterium* was found to be 14 mg at an optimum time of 0.5 h. The data for biosorbent was fitted with Langmuir model while monolayer adsorption was indicated to be followed with pseudo second-order rate (Nivetha and Karthick 2018). *Lactobacillus acidophilus* along with ammonium thiosulfate (provides longer life to the bacterial strain and increases active sites) was used for selective and efficient abstraction of Au (85%) from printed circuit boards. The leaching was reached maximum after day 10 (by the reaction like acidolysis, redoxlysis, and comlexolysis) which reached the maximum extraction after 90 days' time span (Sheel and Pant 2018). Cr^{4+}, Cu^{2+}, Cd^{2+}, and Ni^{2+} were taken under investigation for their detection and recovery of waste water by *Pseudomonas* strains (*P. fluorescens* resistant to Cr^{4+}, *P. putida* resistant to Cu^{2+}, Cd^{2+}, and Ni^{2+}). Most of the heavy metal ions were impounded within 10 min of contact, and the absorption was found maximum for Ni^{2+} followed by Cd^{2+} (35–88%), Cu^{2+} (50–93%), and Cr^{4+} (16–38%) (Hussein et al. 2004). *Chlorella vulgaris* (algae) was used to extract Nd^{3+} (Neodymium, a rare earth metal) from HD drive magnets, and 188.68 mg/g of Nd^{3+} at pH 5 and 35 °C was absorbed. With increase in biosorbent dose, biosorption was found to increase. Pseudo second-order reaction was followed and Langmuir absorption isotherm was fitted (Kucuker et al. 2017).

Action of *Aspergillus* sp. (fungi) and *Saccharomyces* sp. (yeast) was studied for the removal of trace Pt^{4+} and Pd^{2+} from water waste (sewage and road run-off). *Aspergillus* sp. shows an ultimate adsorption capacity of 5.5 mg/g (pH ~ 2) and 4.3 mg/g (pH ~ 2.5) obtained for Pt^{4+} and Pd^{2+}, respectively, at equilibrium (attained in 45 min) which was much higher than *Saccharomyces* sp. (Żyłkiewicz et al. 2019). Cd^{2+} and Mg^{2+} ions were investigated by Hou et al. (2015) for their absorption by bacteria *Klebsiella* sp. which was found to be resistant to heavy metal activity. A maximum of 170.4 mg/g and 114.1 mg/g of Cd^{2+} and Mg^{2+}, respectively, were absorbed at pH 5.0 and 30 °C. The binding constant for the two ions were obtained to be 0.98 (Cd^{2+}) and 0.86 (Mg^{2+}). Biosorption of Pb (concentration 10–25 ppm in soil) was explored by using *Bacillus licheniformis,* and it was observed that 74.94% (10 ppm) to 89.39% (25 ppm) of Pb was recovered from the medium. Effect of temperature over absorption shows that with increasing temperature, the absorption gets augmented with a threshold temperature of 37 °C (58.8% absorption) (Gayatri et al. 2017). A consortium of *Saccharomyces cerevisiae* and *Chlorella* sp. was employed for recovery of Cu^{2+} at different concentration (3–20 mg/L) and temperature (25–35 °C). A maximum absorption of 83.4% was observed at 30 °C, pH 4, and 2 h (detention time) with 200 mg of biosorbent (Siwi et al. 2018). Filamentous Cd-tolerant fungi [*Aspergillus* (isolate 3 and 4) and *Penicillium* (isolate 6)] were isolated by Manguilimotan and Bitacura (2018), and isolate 3 was found to generate highest absorption of 13.87% while lowest 10.71% was for isolate 4 (Manguilimotan and Bitacura 2018). Sulfate-reducing bacteria (*Desulfovibrio desulfuricans*) over zeolite were designed by Kim et al. (2015), for effective recovery of Cr^{6+} (99.8%), Ni^{2+} (90.1%), and Cu^{2+} (98.2%) from seawater at 37 °C.

6.4.3.2 Bio-leaching

Toxicity of hazardous components present in e-waste get augmented with increase in concentration and their combination. Bio-leaching is a natural method applied by the microbes to covert the nonsoluble heavy metals to their soluble and extractable form. These biological components are adept of transmuting the heavy metals present in the e-waste (Pant et al. 2017), and metals in their basic or compound state can be worked upon. Bio-leaching is broadly classified into direct and indirect, in the previous one, the organic acids produced by the microbes are used to convert (oxidize) the insoluble metal into their soluble ion form, while in the later, the bacteria consortium surrounds the metal to be oxidised (Patel and Kasture 2014; Dave et al. 2018). For the process of bio-leaching, various mechanisms are involved, namely complexolysis, acidolysis, redoxolysis, and bioaccumulation. Needhidasan et al. (2014) describe the few major microbe groups which are majorly involved in heavy metal bio-leaching, viz. autotrophic bacteria (e.g., mesophilic: *Leptospirillum* sp., *Thiobacillus* sp.; thermophilic: *Acidianus* sp., *Sulfolobus* sp.), heterotrophic bacteria (e.g., *Pseudomonas* sp., *Bacillus* sp., *Staphylococcus* sp., *Rhodococcus* sp.), and heterotrophic fungi (e.g., *Aspergillus* sp., *Penicillium* sp.). Many acidophilic bacteria play a key role in bio-leaching of the heavy metals generated from e-wastes due to their higher lenience toward heavy metal components. Certain strains of *Acidithiobacillus ferrooxidans*, *Acidithiobacillus thiooxidans*, *Leptospirillum ferrooxidans*, *Sulfolobus* sp., etc. are employed comprehensively in bio-leaching of e-wastes. These specific strains of bacteria are thought to generate energy from oxidation of sulfur (generate H_2SO_4) and Fe^{2+} (generate Fe^{3+}) which endorses the dissolution of metallic components to get oxidized (Valix 2017). Acidophile is the major collection of microorganism employed for bio-leaching process. Wang et al. (2009a, b) used co-culture of *Acidithiobacillus ferrooxidans* and *Acidithiobacillus thiooxidans* to recover Cu from printed wire boards. *Chromobacterium violaceum* and *Pseudomonas fluorescens* were proved to be helpful in extracting gold [$Au\ (CN)^{2-}$] from printed circuits by bioleaching (Patel and Kasture 2014). A mixed culture of unknown acidophilic culture along with *Sulfobacillus thermosulfidooxidans* was used for the recovery of various metal from e-waste by Pant et al. (2012) (viz. Ni, Cu, Al and Zn in 81, 89, 79, and 83%, respectively).

Cultural supernatant bacteria (Fe/S-oxidizing bacteria) were reported to recover 100% of Cu in 2 h from printed circuit board (5 g/L, containing 65% Cu) and more that 93% from 100 g/L in 9 days by following indirect non-contact mechanism (Wu et al. 2018). *Bacillus* sp. isolated from *Hymeniacidon heliophila* sponge cells (marine) was observed to show bio-leaching action (Cu recovery) by Rozas et al. (2017). Bacterial growth (rod shaped, filamentous) was found at the surface of e-waste, secreted chemical was bound to metal surface at 30 °C, while at 40 °C metallic nanoparticles were found to grow inside of the bacterial cell. *Aspergillus niger* MXPE6 along with *Aspergillus niger* MX7(fungal association) was used by Delira et al. (2019) for the isolation of Au from the printed circuit board of mobile phone device, the pH level generated by fungal consortium was as low as 2.8 which was lower as compared to *Aspergillus niger* MXPE6 only (pH = 4.0), thus increasing the isolation of Au by nearly 40%, also the fungal association help in bio-leaching without agitation and thus saves energy (Delira et al. 2019). PCB was subjected to activity of *Burkholderia xenovorans* LB400 by Payne et al. (2013), and nearly 80% of degradation within 12 days of activity was reported. DBDE was degraded to 45% of its initial concentration when was acted by *Pseudomonas aeruginosa* (Shi et al. 2013). *Chromobacterium violaceum*, *Pseudomonas aeruginosa*, and *Pseudomonas fluorescens* consortium was applied for two-step bio-leaching process followed by cyanidation process. All the strains alone and in association were able to mobilize metals depending upon their competences. Ag, Fe, Zn, Au, and Cu were immobilized in 8%, 13%, 49%, 73%, and 83%, respectively (Pradhan and Kumar 2012). Metabiologically modified *Chromobacterium violaceum* was found to produce cyanide lixiviant which was helpful in extracting (twice) Au from the e-waste as compared to wild counterpart. A recovery of 25–30% was obtained after 8 days of exposure to different engineered strains (pTAC and pBAD) (Tay et al. 2013).

6.4.3.3 Bioaccumulation

It is a natural phenomenon of accumulation of foreign contaminant in the body of living beings, which leads to bio-magnification (through food chain) of these hazardous contaminants in the body of the species. Microbes are considered to be one of the best remedies for bioremediation of heavy metals ions in environment owing to their exceptional property to bind to them. Microbes with their importer complexes (lipid bilayer) uptake contaminants into intracellular sites and impounded by metal-binding sites (peptides, polyphosphates, etc.) (Diep et al. 2018).

Bioaccumulation behavior of highly heavy metal–tolerant *Bacillus licheniformis* [recover Cu (71.3%) and Pb (70.1%)] *Bacillus polymyxa, Micrococcus roseus, Pseudomonas aeruginosa* [recovers Zn (74.1%)], *Aspergillus niger* [recovers Zn (and 78.3%)], and *Aspergillus flavus* [recovers Pb (65.76%)], was studied by Aderonke et al. (2017), after isolation of these from contaminated sites while bioaccumulation of heavy metals was in the range of 200–3200 mg/kg for different strains. Concentration and accumulation of PBDEs and PCBs released from e-waste near dismantling area were studied by the presence of these in soil, rice plants samples, and animal testers. High concentration of PBDEs and PCBs in soil results in increased concentration and bio-magnification factor in plant samples, and the average value of PCBs in different sample was between 120 and 12,120 ng/g w/w (Han et al. 2017). 16SrDNA sequencing technique as was employed to determine the potential of *Citrobacter freundii* for bioaccumulation and remediation of Cu (5–800 ppm) (Sharma and Fulekar 2009). *Arthrobacter*-dominated consortium was found to be well grown in Zn but was observed to recover only 15% of the heavy metal, while selected NH1 strain was found to remove 90% of Zn (Kvasnova et al. 2017). Out of 34 bacterial isolates [*Pseudomonas* (23), *Bacillus* (5), and *Staphylococcus* (6)], three *Pseudomonas* isolates (SN7, SN28, and SN30) were selected for unveiling their co-resistance against various heavy metals (Hg^{2+}, Cu^{2+}, Ni^{2+}, Cd^{2+}, Cr^{3+}, Pb^{2+}, Cr^{6+}, and Zn^{2+}). These three isolates SN7, SN28, and SN30 accumulate 29, 25, and 26 mg/g of Zn^{2+} and 20, 25, and 22 mg/g Cu^{2+}, respectively (Ahemad and Malik 2012). Ash Dyke isolated *Bacillus cereus* (isolates SM2 and SM3) and *Bacillus subtilis* (isolate SM12) after 16SrDNA sequencing was used for Pb^{2+}, Hg^{2+}, Ni^{2+}, Co^{2+}, Cu^{2+}, Mn^{2+} accumulation at pH 6 and 35 °C (Banerjee et al. 2015). *Bacillus megaterium* (isolate BM30) was isolated from soil for the recovery of heavy metals (Fe, Cu, Mn, and Zn). Studies cleared that Cu was most accumulated while Zn and Mn were least (Stefanescu 2015).

6.5 Other Mechanism

Apart from the above three most followed processes of bioremediation of e-waste, various other methods are present to bioremediate the pollutants from the ecosystem.

6.5.1 Bio-stimulation

This specific process involves the supplement of desired nutrient (trace metals, fertilizers, etc.) and environmental conditions (pH, oxygen supply, temperature, etc.) to the pollutant-affected site so as to stimulate the biomass.

6.5.2 Biotransformation

It involves the chemical transformation of a particular chemical structure to another, thus altering their chemical properties and making them less hazardous. Biotransformation involves two mechanism: first is direct transformation in which enzymes present in microbes reduces the multivalent heavy metal ions, and second is indirect transformation where metal- or sulfate-reducing bacteria (Fe/S bacteria) reduce the multivalent heavy metal ions (Patel and Kasture 2014).

6.5.3 Bio-attenuation and Bio-augmentation

Bio-attenuation involves natural/physical phenomena and chemical reactions which help in growth and activity of the microbes in the selected polluted sites, while in bio-augmentation microbes are selected (which grow effectively in presence of pollutants) from the site of remediation, cultured, cultivated, or genetically modified and are restored to the remediation sites.

6.5.4 Bioventing

In bioventing process, in order to enhance bioremediation, oxygen is allowed to flow to unsaturated region so as to increase the activities of ethnic microbes. In addition, nutrients and moisture are provided to improve bioremediation to achieve harmless microbial transformation of metals, etc. (Philp and Atlas 2005).

6.6 Genetically Modified Microbes

The microbial community can be modified/engineered genetically to improve their microbial (bioremediation) characteristics by recombinant DNA technology. The recombinant DNA technology uses the alteration in the genetic material by choosing natural or artificial genes. These genetically modified microbial community had been observed to decontaminate the site from the unwanted pollutants (in laboratory conditions) (Perpetuo et al. 2011; Joutey et al. 2013). These GEMs have potential to show their activity over wide range of hazardous chemical pollutants present in soil, water, air, and other components of environments (Kumar et al. 2013). This modification in the genes can help in remediation of those chemical contaminates which were previous reluctant to the microbes. GEMs involve four strategies:

1. Alteration in the specificity and empathy of enzymes.
2. Establishment and regulation of newer biochemical pathway.
3. Development, screening, and regulation of bioprocess involved.
4. Bioaffinity, chemical sensing (by biosensors), toxicity discount, and end-point investigation.

GEMs could be proved as potential contender for current and future assignment processes of bioremediation (Pant et al. 2012). Metabiologically modified

Chromobacterium violaceum was found to produce cyanide lixiviant which was helpful in extracting (twice) Au from the e-waste as compared to wild counterpart. A recovery of 25–30% was obtained after 8 days of exposure to different engineered strains (pTAC and pBAD) (Tay et al. 2013).

Chromobacterium violaceum genes had been identified as potential mediator in ecological detoxification (Carepo et al. 2004). Cyanogenic bacterial strains (comprising *C. violaceum*, *P. aeruginosa*, and *P. fluorescens*) were used for bioleaching of metals generated from e-waste. The investigation consists of a two-step bioleaching procedure which was further followed by cyanide-forming circumstances. It was observed that single as well as consortium of the cyanogenic bacteria were competent of assemble and mobilize the metals from e-waste depending upon their potential. Strain of *C. violaceum* was found to be proficient of leaching more than that of Cu (79%), Au (69%), Zn (46%), Fe (9%), and Ag (7%) from e-waste (1% w/v). The consortium of *C. violaceum* and *P. aeruginosa* leached different metals, Cu (83%), Au (73%), Zn (49%), Fe (13%), and Ag (08%), was higher as compared to the individual strains (Pradhan and Kumar 2012). An Au–cyanide complex was observed to be formed by *C. violaceum* to recover Au (18–22.5%) from electronic waste with the formation of CN as a secondary metabolite. Activity of alkali treatment was examined over the bacterial community. Alkaline solution provides much better condition for the bacterial to grow (in pH 9–10) and bioleach the metal present in e-waste. Au recovery of 11%, 18%, 22.5%, and 19% was observed at pH 7, 9, 9.5, and 10, respectively (Natarajan and Ting 2014).

6.7 Advantages and Disadvantages of Bioremediation

Bioremediation provides diverse, cost-effective, efficient, and easy way to restore the natural sites from the e-waste pollutants. Microbes are the crucial player in various established process of bioremediation processes; hence, their assortment, profusion, genetics, and community present in the subjected site determine the fate of the hazardous chemical and also the fate of the remediation process applied so as to achieve maximum results (Philp and Atlas 2005).

Advantages

1. Equipment required for bioremediation is minimum (easily available) as well as cost-effective (per unit volume) as compared to chemical and physical processes.
2. Microbial bioremediation provides a complete degradation of organic contaminants to some harmless smaller molecules in a natural way. This is possible as the process does not translocate the contaminants to other components of ecosystem in any form.
3. Is applicable in a wide range of environmental strata as well as can be implemented as in situ and ex situ processes depending upon the existing situations (Sharma and Reddy 2004).

Disadvantages

1. Bioremediation process should be controlled, if not the biodegradation could not take place completely, and the resulting components (molecules) could get translocated to other strata of ecosystem and could prove more detrimental as compared to earlier contaminants.
2. Bioremediation process is sensitive (i.e., activity of microbe) toward the physical (time, temperature, availability of oxygen, etc.) and chemical (pH, humidity, nutrition, etc.) environmental conditions.
3. A check on the rate of biodegradation (decontamination) is required to understand the activity of microbial response toward the concentration of pollutants.
4. Bioremediation is observed to be a slow and longer process (depends on the physical and chemical conditions available or provided) of remediation, and also the contaminants treated effectively depend upon the concentration as well as the type of compounds which actually get degraded.
5. Controlling VOCs (volatile organic compounds) is not easy, and also residues can be leaved back in high amount where persistence in environment could be proved toxic.

6.8 Barriers in Commercial Use of Bioremediation

Though bioremediation provides numerous advantages to human in quest to minimize the adverse effect of e-waste-generated pollutants, still many major barriers do hinder the employment of technology to be used in bioremediation process. The major obstructions can be recognized as in the areas of research, technology, and legislation (Sood et al. 2016; Azubuike et al. 2016).

6.8.1 Research Barriers

Scientific community needs to study, learn, observe, and interpret a lot of scientific data and reports in order to provide profound result of effect of bioremediation and its advantages over the existing physical and chemical procedures. The source (household commodities, electronic and electrical components, machinery parts, high-end instruments, etc.), site (dumpsites, radioactive discards, etc.), and type of waste (organic, metals, etc.) generated by electrical and electronic component are to be observed and studied in detail to understand and apply the right bioremediation technique (also by understanding microbial functioning, biochemical nature, genetic behavior, etc.) on the subjected problem.

6.8.2 Technology Barriers

Still being an effective and less hazardous method of remediation of hazards generated by e-waste components, sluggish pace of remediation makes it a weak contender as compared to physical and chemical processes. The use of bioremediation technique should be designed in accordance to the type of waste and the sources generating it. Each source, site, and type of waste need specific consideration so as to minimize the effects.

6.8.3 Legislative Barriers

Various rules and regulations are to be followed to use specific recovery/remediation process. Generally, biotechnology use minimizes the hazardous components of the e-waste, but few times higher residues are left over as compared to the conventional method of recovery. Also different policies, rules, etc. are framed by the regulating bodies in different countries which do not have parallel agreement with the limits set by the international governing bodies like WHO. Deficiency of rigorous policies in developing countries like India increases the issue with regard to e-waste management, thus the informal sector exploits the existing legislations to continue to employ the undeveloped techniques (burning, heating to melt the circuit boards, dumping, or acid treatment) of lethal e-waste disposal, recycling, and recovery.

6.9 Conclusion

E-wastes are the problem of current and future generation which can cause severe impact on humans and its ecosystem. The presence of various heavy metal ions, plastics, volatile organic compounds, etc. had taken this threat to the next level of consideration for the researchers to find a viable and targeted solution toward it. One such natural attempt is bioremediation (including biosorption, bioaccumulation, bioleaching, etc.) which can be proved significant with certain bio-engineering process to minimize the menace of E-waste-generated pollutants. More than half of the global population (under many countries) are sheltered by e-waste statute, still more exertions are encouraged/required to implement the rules to cultivate e-waste policies.

Acknowledgments The authors acknowledge the support provided by S.D. Agricultural University, Gujrat and U.P.E.S. Dehradun, Uttarakhand.

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Chapter 7
Current Methods of Enhancing Bacterial Bioremediation of Pesticide Residues in Agricultural Farmlands

Saphan Anode and Justus Onguso

Contents

Abstract The accumulation of recalcitrant xenobiotic compounds is due to continuous efflux from population and agricultural and industrial inputs that have created a serious impact on the pristine nature of our aquatic and terrestrial environment. Apart from this, these compounds are mostly carcinogenic, posing health hazards which persist over a long period of time. Metabolic pathways and specific operon systems have been found in diverse but limited groups of microbes that are responsible for the transformation of xenobiotic compounds. Distinct catabolic genes are either present on mobile genetic elements, such as transposons and plasmids, or the chromosome itself that facilitates horizontal gene transfer and enhances the rapid microbial transformation of toxic xenobiotic chemical compounds. Both natural and anthropogenic activities result in the accumulation of wide ranges of toxic xenobiotic compounds in the environment, causing a global concern. Bacteria, fungi, and actinomycetes are the main transformers and pesticide degraders. They generally biotransform pesticides and other xenobiotics by introducing minor chemical

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D. G. Panpatte, Y. K. Jhala (eds.), *Microbial Rejuvenation of Polluted Environment*, Microorganisms for Sustainability 26, https://doi.org/10.1007/978-981-15-7455-9_7

structural changes to the molecule, rendering them nontoxic. Several bacterial genera are adapted to grow in pesticide contaminated soils. These microorganisms have enzymes involved in the hydrolysis of P-O, P-F, P-S, C-Cl, P-C, and other chemical bonds, which are found in a wide variety of chemical pesticides. Most of the genes responsible for catabolic degradation are located on the chromosomes, but in a few cases, these genes are found in plasmids or transposons. The recent advances in metagenomics and whole genome sequencing have opened up new avenues for searching the novel pollutant degradative genes and their regulatory elements from both culturable and nonculturable microorganisms from the environment. Microorganisms respond differently to various kinds of stresses and gain fitness in the polluted environment. This process can be accelerated by applying genetic engineering techniques. The recombinant DNA and other molecular biological techniques have enabled amplification; disruption, and/or modification of the targeted genes that encode the enzymes in the metabolic pathways; minimization of pathway bottlenecks; enhancement of redox and energy generation; and recruiting heterologous genes to give new characteristics.

Keywords Accelerated biodegradation · Bacterial bioremediation · Recalcitrant compounds · Xenobiotic pesticides · Lake Naivasha

7.1 Introduction

Bioremediation is described as the use of microorganisms to destroy or immobilize waste materials. This process of detoxification targets the harmful chemicals by mineralization, transformation, or alteration (Shannon and Unterman 1993). For centuries, civilizations have used natural bioremediation in wastewater treatment, but intentional use for the reduction of hazardous wastes is a more recent development.

Modern bioremediation and the use of microbes to consume pollutants are credited, in part, to George Robinson (US Microbics 2003). He used microbes to consume an oil spill along the coast of Santa Barbara, California in the late 1960s. Since the 1980s, bioremediation of oil spills and other environmental catastrophes has received more consideration (Shannon and Unterman 1993).

Different methods have been developed for the remediation of contaminated sites and for the treatment of pesticide residues and/or obsolete pesticides to reduce the effects of pesticides on the environment and health. Some of these technologies are those that apply physical treatments, such as adsorption and percolator filters; chemical treatments such as the advanced oxidation which involve the use of powerful transient species, mainly the hydroxyl radical. Other technique used for the degradation of pesticides involves the heterogeneous photocatalysis with TiO_2 is a method for producing the radical mentioned (Mansee et al. 2005). A method currently used is high-temperature incineration in special furnaces: pesticides are packaged in the places where they were abandoned, then transported to a country that has special facilities to dispose of hazardous wastes. FAO estimates that the cost of these operations varies between 3000 and 4000 USD/ton (WHO Guidelines, 2004). Other strategies that have been studied for the degradation of these compounds include the photodegradation (Mansee et al. 2005). However, all these methods have several disadvantages such as the use of chemical catalysts like titanium dioxide (TiO_2) and the use of more complicated and expensive technological methods. For some pesticides like most organophosphate, alkaline hydrolysis is used, and the process requires rigorous control of the conditions under which the experiments are performed, such as maintenance of alkaline pH, as well as the presence of complexes formed with metal ions, which involves the formation of secondary pollutants.

These conventional physicochemical approaches are generally expensive, and remediation process is often incomplete due to the conversion of the parent compound to metabolites which are more persistent and equally or more toxic to non-target organisms than the parent compound (Kang et al. 2006).

7.2 Xenobiotic Pesticides and Environmental Pollution

The pesticides belong to a category of chemicals used worldwide such as herbicides, insecticides, fungicides, rodenticides, molluscicides, nematicides, and plant growth regulators in order to control weeds, pests, and diseases in crops as well as for health care of humans and animals.

The positive aspect of application of pesticides renders enhanced crop/food productivity and drastic reduction of vector-borne diseases (Agrawal et al. 2010; Damalas 2009). A pesticide is any substance or mixture of substances intended for preventing, destroying, repelling, or mitigating any pest (insects, mites, nematodes, weeds, rats, etc.), including insecticide, herbicide, fungicide, and various other substances used to control pests (Damalas 2009). The definition of pesticide varies with times and countries. However, the essence of pesticide remains basically constant: it is a (mixed) substance that is poisonous and efficient to target organisms and is safe to non-target organisms and environments (EPA Report 2012; Zhang et al. 2011) (Fig. 7.1).

Although pesticides are beneficial in controlling the proliferation of pests, their unregulated and indiscriminate applications for the application of pesticides can cause adverse effects to human health, to different life forms, and to the ecosystems, which depend on the degree of sensitivity of organisms and toxicity of pesticides. The continued application of pesticides has increased its concentration in soils and waters, besides; they enter into the food chains. Dispersion mechanisms also have increased the level of environmental risk for the occupationally exposed population and the inhabitants of surrounding villages. Despite ban on application of some of the environmentally persistent and least biodegradable pesticides like

Fig. 7.1 Manual pesticides spraying for flowers in Greenhouse (Source: www.Fresh Produce Exporters Association of Kenya.com., 2010)

organochlorides, they are still being in many countries (Anode et al. 2018; Dasgupta et al. 2010). Pesticides cause serious health hazards to living systems because of their rapid fat solubility and bioaccumulation in non-target organisms (Dasgupta et al. 2010). The main forms of pollution are direct applications to agricultural crops, accidental spills during transport and manufacturing, as well as waste from tanks where cattle are treated to ectoparasites control (Dasgupta et al. 2010; Martínez 2004; Besse-Hoggan et al. 2009).

The introduction of pesticides into the environment results in several ecological and health effects since these chemicals are consequently introduced into the food chain. These effects may be summarized as follows (Dasgupta et al. 2010):

(a) Producing a change in the decline of populations of phytoplankton and zooplankton (indicators of water pollution).
(b) Direct health effects like carcinogenic, neurotoxic, and fertility and viability (in invertebrates, fish, amphibians, insects, and mammals and of their descendants).
(c) The presence of pesticides in the environment has caused the resistance of organisms considered as pests and disease vectors (e.g. malaria, dengue, and other vectors), and instead other beneficial insect populations are diminished (like pollinators).
(d) Alteration of biogeochemical cycles by decreasing the macro and microbiota.
(e) Leaching of pesticides pollute water bodies, resulting in severe aquatic environmental pollution.
(f) Chemical reactions resulting in processes that enhance adsorption of pesticides when soil particles interact with positively or negatively charged, thus increasing their persistence in the environment.
(g) Acute intoxications (especially in occupationally exposed populations) or indirect exposure of the general population (through air, water, and food contaminated with pesticide residues).

In natural environments, pesticides or their degradation products may be further transformed or degraded by other microorganisms or eventually leading to complete degradation by the microbial consortium. However, persistent xenobiotics like pesticides and metabolic dead-end products will accumulate in the environment, become part of the soil humus, or enter the food chain leading to biomagnification.

The fate of pesticides in the environment is strongly related to the soil sorption processes that control not only their transfer but also their bioavailability (Martínez 2004). Contamination of soil from pesticides as a result of their bulk handling at the farmyard or following application in the field or accidental release may lead occasionally to the contamination of surface and ground water (Besse-Hoggan et al. 2009).

The behavior of pesticides in soils, the efficiency, persistence, and potential as environmental contaminants depend on their retention and degradation on soil constituents (Worrall et al. 2001). In soils, several parameters influence the rate of biodegradation processes: environmental factors such as moisture and temperature, physicochemical properties of the soil, presence of other nitrogen sources or carbon, etc. can completely modify the microbial population and therefore the microbial activity (Martínez 2004).

7.3 Strategies to Reduce the Impact of Xenobiotic Pesticides to the Environment and Health

Several technologies have been used to reduce the accumulation of xenobiotic chemicals in the ecosystem. Some of these technologies apply physical treatments, such as adsorption and percolator filters; chemical treatments such as the advanced oxidation which involve the use of powerful transient species, mainly the hydroxyl radical. Other technique used for the degradation of pesticides and other xenobiotic chemicals includes the heterogeneous photocatalysis with TiO_2 which results in the production of some radicals (Ortiz-Hernández and Sánchez-Salinas 2010). A method currently used is high-temperature incineration in special furnaces in which pesticides and obsolete pesticides are packaged in the places where they abandoned, then transported to a country that has special facilities to dispose of hazardous wastes in high-temperature furnaces. FAO estimates that the cost of these operations varies between 3000 and 4000 USD/ton (EPA Report 2012). Other strategies that have been studied for the degradation of these compounds include the photodegradation (Torres-Duarte et al. 2009). However, all these methods have several disadvantages such as the use of chemical catalysts, like TiO_2 which also have some adverse environmental effects, and the use of high-temperature furnaces which are more expensive. For some pesticides like organophosphates, alkaline hydrolysis is used. The process involves a rigorous control of the conditions under which the experiments are performed, such as maintenance of alkaline pH, as well as the presence of complexes formed with metal ions, which involves the formation of secondary pollutants (Torres-Duarte et al. 2009).

These conventional physicochemical approaches are generally expensive, and remediation process is often incomplete due to the conversion of the parent compound to metabolites which are more persistent and equally or more toxic to non-target organisms (Torres-Duarte et al. 2009; Worrall et al. 2001).

Bioremediation process which involves degradation of xenobiotic chemicals by microorganisms like bacteria and fungi is one of the most environmental friendly and modern method currently employed to degrade these chemicals and reduce their harmful effects in the environment. This technique relies on the ability of microorganisms to convert organic contaminants into simple and harmless compounds to the environment. Bioremediation overcomes the limitations of traditional physicochemical methods since it has no harmful effect in the environment, is less costly and more efficient in detoxification of the xenobiotic chemicals (Singleton 2004). Consequently, in the last years, bioremediation technology has progressed to an unknown virtual technology considered for the degradation of a wide range of pollutant compounds. Bioremediation can offer an efficient and cheap option for decontamination of polluted ecosystems and destruction of pesticides (Singleton 2004; Qiu et al. 2007; Wang and Leung 2009; Wang et al. 2007, 2010). As an efficient, economical, and environmentally friendly technique, biodegradation has emerged as a potential alternative to the conventional techniques. However, the biodegradation process of many pesticides has not been fully investigated (Qiu et al. 2007).

7.4 Microorganisms Involved in the Biodegradation of Pesticides

Bacteria and fungi are the most common microorganisms used in the bioremediation of xenobiotic pesticide. However, some green and blue algae isolated from soil and water have been found to biodegrade some organophosphorus insecticide chlorpyriphos, monocrotophos, and quinalphos. *Actinomycete* spp. have shown the degradation of herbicide pendimethalin (Zhang et al. 2010; Mukherjee et al. 2004). *Pseudomonas* sp. or *Aspergillus niger* biodegrade factory wastes, hydroxylating 2,4-D residues (Gopal et al. 2005) by hydroxylating 2,4-D residues (Gopal et al. 2005).

Degradation of benzonitrile herbicide, bromoxynil (3,5-dibromohydroxybenzonitrile), ioxynil (3,5diiodo-4-hydroxybenzonitrile), dichlobenil (2,6-dichlorobenzonitrile), and their mixture by the soil microorganism *Agrobacterium radiobacter* was studied in batch culture. The mixture of bacterial culture enhances the degradation of carbofuran residues to 96% in 10 days (Paterson and Clarke 1997). Bacteria that grow on rotting waste can break down organochloride pesticides like DDT (Paras et al. 2015). The ability of plasmid transfer can be exploited to create microorganisms with novel characteristics. For example, *Alcaligenes* sp. degrades 4-chlorophenol to 5-chlo-2-hydroxymuconicsemialdehyde (by *meta*-cleavage of the ring) which is toxic (Paterson and Clarke 1997). *Pseudomonas strain* B13 has a plasmid-borne gene which encodes the enzyme 1,2-di-oxygenase, the enzyme that cleaves 4-chlorophenol by ortho pathway (Paras et al. 2015; Song et al. 2004).

White rot fungi, which can degrade lignin present in wood, has also shown the ability to degrade wide varieties of different chemicals, even those which did not have any structural relationship with lignin (Paras et al. 2015). Among the various species, *Phanerochaete chrysosporium* was reported to be the most important as it could degrade several environmentally persistent organic pollutants like DDT, lindane, benzopyrene, azo-dyes, and dioxin. Degradation of lindane by white rot fungi has also been reported (Paras et al. 2015; Song et al. 2004).

Two different species of white rot fungi, namely *Cyathus bulleri* and *Phanerochaete sordida*, have been studied for their ability to degrade the xenobiotic pesticides. Degradation of various organophosphorus compounds by different fungi has also been documented (Paras et al. 2015).

Highest degradation has been observed in case of *Aspergillus sydouri* followed by *A. flavus* and *Fusarium oxysporum*. *Aspergillus niger* has demonstrated the ability degrade endosulfan up to 40% by the first day, followed by fast dissipation to 98.6% by day 15. *A. niger* could also degrade chlorpyrifos. Up to 95.7% degradation of chlorpyrifos has been obtained by using the fungus *Trichoderma viride* within 14 days (Paras et al. 2015; Song et al. 2004). Degradation of cyfluthrin by a strain of *T. viride* and identification of the products formed are also documented. Metolachlor herbicide could be degraded by a mixed fungal culture isolated from a metolachlor acclimated field soil. Processes like hydrolytic dechlorination, N-dealkylation, and amide bond cleavage appeared to be the dominant ways of transformation of metolachlor (Paras et al. 2015; Song et al. 2004; Moredo et al. 2003; Pointing 2001).

According to Anode et al. (2018) who studied the rate of biodegradation of xenobiotic pesticide residues in flower farms around Lake Naivasha basin in Kenya, there was significant bioremediation of organochlorides and organophosphate pesticide residues by the bacterial species *Pseudomonas aeruginosa*, *Escherichia coli*, *Rhodococcus erythropolis*, and *Bacillus subtilis* under study. The highest degradation rate was observed in *B. subtilis* against dimethoate organophosphate pesticide residues at 66.81% during the 21 days incubation period while the lowest biodegradation rate was observed in *R. erythropolis* against aldrin organochloride pesticide at 40.34% (Anode et al. 2018). Furthermore, physical degradation rate was very slow compared to biodegradation rate. For example, the biodegradation of aldrin organochloride in *R. erythropolis* consortium which was the lowest bioremediation rate and longest number of days required to degrade 50% of the incubated pesticide residue (DT_{50}) of 25.66 days was still comparatively shorter than the physical degradation rate of aldrin withDT_{50} of 1308 days.

7.5 Bacterial Tolerance and Growth in Pesticide Consortia

According to Liu et al. (2007) who studied the tolerance of bacterial isolates against organochlorides and organophosphates pesticide residues extracted from flower farm soil around Lake Naivasha, Kenya, all the tested bacterial species showed remarkable tolerance and growth in individual and mixture of pesticide consortia. Bacterial growth in pesticide consortia was quantified by monitoring colony growth of the species in liquid culture over time. Anode et al. (2018) and Liu et al. (2007) performed experimental setup in two ways. The first approach was to add pesticide standard equivalent to the analyzed concentration of the residues in the soil samples (spiking) and incubate the bacterial isolates in MM media to each pesticide soil sample residues plus the standard and the growth of the isolates measured after every 2 days, 10 days, 15 days, and 21 days and the growth compared with isolates in MM media only. The second approach was to incubate the bacterial isolates in MM media to soil samples containing mixtures of pesticide residues and the growth of each bacterial isolates measured after 2 days, 10 days, 15 days, and 21 days and compared with isolates in MM media only.

Cells were collected by centrifugation (6000 × *g* for 5 min), washed twice, and resuspended to an $OD_{696nm} = 0.8$ (Lambda Bio Spectrophotometer, Perkin Elmer, USA) in sterile water. The cell suspension (approximately 1×10^8 cells mL^{-1}) was used to inoculate (2% w/v) 100 mL flasks of MSM and LB with soil samples and incubated at 28 °C on a rotary shaker (150 rpm). Uninoculated MSM/LB (without soil samples) served as the negative control and each treatment was replicated three times. The viable cell counts were determined turbidimetrically to give OD values at 696 nm in Lambda Bio Spectrophotometer (Perkin Elmer, USA). Standardization was done using 0.5 Mc'Farland solution ($1.0\ OD_{696nm} = 1.5 \times 10^8$ CFU/ml) (Anode et al. 2018; Liu et al. 2007).

The bacteria predominant in farm soil are largely derived from soil organic and inorganic contents, as well as oxygen contents (Anode et al. 2018; Liu et al. 2007; Kang et al. 2006). Basically, the bacteria are responsible for the degradation of organic and inorganic compounds. They derive their nutritional requirement from the compounds presented to them in the farm soil (Liu et al. 2007). They are able to synthesize their enzymes, metabolic intermediates, structural proteins, lipids, and nucleic acids from carbon compound in the soil together with other elements. They derive energy from metabolism of either organic compounds (chemoorganotrophic metabolism) or inorganic compounds (chemolithotrophic metabolism), such as reduced sulfur or nitrogen compounds (Kang et al. 2006; Saikia et al. 2005). Very extensive colonization of the pesticide consortiums were observed as this organic substrate represents a source of nutrients for the bacterial inoculant, but also for the indigenous soil micro flora (Anode et al. 2018; Liu et al. 2007; Kang et al. 2006). Under the conditions used in the present study, all the four test bacterial isolates, i.e., *P. aeruginosa*, *E. coli*, *R. erythropolis*, and *B. subtilis* were viable in natural soil, overcoming the competition with the native soil micro flora. All the tested bacterial species showed remarkable growth rates in both pesticide consortia inoculated with MSM nutrient (Anode et al. 2018).

Table 7.1 shows the growth rate of bacterial species isolated from flower farm soil in specific pesticide consortia and in a mixture of all the pesticide consortia. Bacterial species incubated with nutrient media only (without pesticide consortia) acted as negative control (Anode et al. 2018).

The results obtained by HPLC analysis of selected organochlorides and organophosphate pesticide residue degradation by the bacterial species show near disappearances of the pesticide residues. Different bacterial species had different metabolic affinity for each pesticide samples. Differences in metabolic requirements like affinity for oxygen, nutrients and accumulation of metabolic products could have contributed to differences in DT_{50} values during the biodegradation process. The rate of biodegradation decreased as the days of incubation increased in all the bacterial inoculant. This is due to the accumulation of pesticide metabolites in the consortia some of which may be toxic to the bacterial species or may inhibit the enzymatic pathway involved in the biochemical breakdown of xenobiotic organic compounds (Anode et al. 2018; Liu et al. 2007; Kang et al. 2006).

However, the rate of biodegradation of pesticide residues was comparatively faster and higher than the physical degradation process where there was no bacterial species added in the pesticide residue consortia. There was also higher significant differences in the concentration of organophosphate pesticide than organochloride pesticides during the degradation between biological and nonbiological processes (Anode et al. 2018). The bacterial consortium isolated from the sample was made up of a group of species whose action was reflected in significant pesticide depletion. Unfortunately in vitro laboratory methods are only capable of isolating 1–10% of all bacteria growing in soil, so several of the bacteria interfering in the degradation processes in natural environments cannot be obtained in a laboratory (Liu et al. 2007; Kang et al. 2006).

7.6 Mechanisms of Biodegradation of Xenobiotic Pesticides

Xenobiotic compounds may be recalcitrant from natural physico-chemical and biological degradation processes due to one or more of the following reasons (Paras et al. 2015):

(a) Nucleophilic substitution of H atom by halogen atom in hydrocarbon compounds resulting in C-Cl bond that requires considerable energy to cleavage.
(b) Substitution of H by other group like nitro, sulfonate, methoxy, amino, and carbonyl groups.
(c) Presence of cyclic and aromatic rings moieties in organic compounds which are more recalcitrant than linear chain or aliphatic compounds.
(d) Branched linear chains resist biodegradation.

Table 7.1 Growth rate for *P. aeruginosa*, *E. coli*, *R. erythropolis*, and *B. subtilis* species subjected to aldrin, dieldrin, endosulfan, dimethoate, malathion, and parathion pesticides individually and as mixture of pesticides and the control augmented with MM media at 15 °C

	Days	Control	OC1	OC2	OC3	OP1	OP2	OP3	Mixture
P. aeruginosa	0	0.19 ± 0.00^{a}	0.19 ± 0.00^{a}	0.19 ± 0.00^{a}	0.19 ± 0.00^{a}	0.19 ± 0.00^{a}	0.19 ± 0.00^{a}	0.19 ± 0.00^{a}	0.19 ± 0.00^{a}
	2	0.34 ± 0.02^{d}	0.32 ± 0.03^{c}	0.28 ± 0.03^{cd}	0.43 ± 0.01^{b}	0.54 ± 0.01^{a}	0.45 ± 0.01^{b}	0.56 ± 0.01^{a}	0.41 ± 0.04^{b}
	10	0.45 ± 0.03^{e}	0.78 ± 0.01^{bc}	0.62 ± 0.02^{d}	0.68 ± 0.02^{cd}	0.77 ± 0.01^{bc}	0.95 ± 0.01^{a}	0.84 ± 0.01^{ab}	0.77 ± 0.11^{bc}
	15	0.26 ± 0.01^{d}	0.86 ± 0.01^{c}	0.88 ± 0.02^{c}	1.21 ± 0.04^{b}	0.89 ± 0.01^{c}	1.65 ± 0.01^{a}	1.25 ± 0.01^{b}	0.95 ± 0.05^{c}
	21	0.52 ± 0.05^{d}	0.96 ± 0.01^{c}	1.45 ± 0.00^{ab}	1.45 ± 0.02^{ab}	1.43 ± 0.01^{ab}	1.65 ± 0.10^{a}	1.42 ± 0.00^{ab}	1.27 ± 0.04^{b}
E. coli	0	0.13 ± 0.00^{a}	0.13 ± 0.00^{a}	0.13 ± 0.00^{a}	0.13 ± 0.00^{a}	0.13 ± 0.00^{a}	0.13 ± 0.00^{a}	0.13 ± 0.00^{a}	0.13 ± 0.00^{a}
	2	0.48 ± 0.03^{a}	0.25 ± 0.01^{c}	0.36 ± 0.01^{bc}	0.42 ± 0.02^{ab}	0.44 ± 0.01^{ab}	0.34 ± 0.01^{bc}	0.25 ± 0.01^{c}	0.45 ± 0.01^{ab}
	10	0.70 ± 0.04^{b}	0.47 ± 0.01^{cd}	0.67 ± 0.01^{abc}	0.75 ± 0.01^{ab}	0.86 ± 0.04^{a}	0.65 ± 0.00^{bcd}	0.45 ± 0.02^{d}	0.76 ± 0.06^{ab}
	15	0.94 ± 0.07^{cd}	0.88 ± 0.02^{bcd}	0.86 ± 0.03^{cd}	1.25 ± 0.00^{ab}	1.48 ± 0.00^{a}	0.96 ± 0.03^{bcd}	0.65 ± 0.02^{d}	1.05 ± 0.10^{bc}
	21	1.44 ± 0.09^{a}	1.25 ± 0.02^{a}	1.34 ± 0.01^{a}	1.45 ± 0.01^{a}	1.66 ± 0.02^{a}	1.65 ± 0.01^{a}	1.24 ± 0.02^{a}	1.31 ± 0.04^{a}
R. erythropolis	0	0.21 ± 0.00^{a}	0.21 ± 0.00^{a}	0.21 ± 0.00^{a}	0.21 ± 0.00^{a}	0.21 ± 0.00^{a}	0.21 ± 0.00^{a}	0.21 ± 0.00^{a}	0.21 ± 0.00^{a}
	2	0.40 ± 0.02^{a}	0.48 ± 0.10^{a}	0.40 ± 0.03^{a}	0.47 ± 0.07^{a}	0.48 ± 0.03^{a}	0.39 ± 0.05^{a}	0.48 ± 0.04^{a}	0.52 ± 0.03^{a}
	10	0.70 ± 0.02^{b}	0.69 ± 0.12^{b}	0.75 ± 0.06^{ab}	0.65 ± 0.00^{b}	0.77 ± 0.06^{ab}	0.80 ± 0.06^{ab}	0.87 ± 0.01^{a}	0.76 ± 0.06^{ab}
	15	0.95 ± 0.03^{b}	0.95 ± 0.04^{ab}	0.94 ± 0.06^{ab}	0.88 ± 0.03^{b}	0.99 ± 0.06^{ab}	1.06 ± 0.08^{ab}	1.12 ± 0.11^{a}	0.88 ± 0.06^{b}
	21	1.33 ± 0.04^{a}	1.39 ± 0.09^{a}	1.41 ± 0.04^{a}	1.31 ± 0.06^{a}	1.44 ± 0.06^{a}	1.45 ± 0.06^{a}	1.39 ± 0.10^{a}	1.44 ± 0.11^{a}
B. subtilis	0	0.22 ± 0.00^{a}	0.22 ± 0.00^{a}	0.22 ± 0.00^{a}	0.22 ± 0.00^{a}	0.22 ± 0.00^{a}	0.22 ± 0.00^{a}	0.22 ± 0.00^{a}	0.22 ± 0.00^{a}
	2	0.37 ± 0.02^{b}	0.37 ± 0.04^{ab}	0.36 ± 0.03^{ab}	0.43 ± 0.12^{ab}	0.48 ± 0.04^{ab}	0.48 ± 0.07^{ab}	0.50 ± 0.06^{a}	0.48 ± 0.04^{ab}
	10	0.68 ± 0.03^{b}	0.73 ± 0.04^{ab}	0.77 ± 0.00^{ab}	0.62 ± 0.20^{b}	0.91 ± 0.04^{a}	0.71 ± 0.04^{ab}	0.80 ± 0.03^{ab}	0.80 ± 0.03^{ab}
	15	0.94 ± 0.04^{b}	0.88 ± 0.00^{b}	0.96 ± 0.04^{b}	0.77 ± 0.27^{b}	1.42 ± 0.02^{a}	1.00 ± 0.02^{b}	0.91 ± 0.04^{b}	0.94 ± 0.06^{b}
	21	1.50 ± 0.04^{a}	1.41 ± 0.04^{ab}	1.45 ± 0.06^{ab}	1.01 ± 0.39^{c}	1.17 ± 0.06^{a}	1.51 ± 0.03^{ab}	$1.480.09^{ab}$	1.77 ± 0.07^{bc}

OC2 = dieldrin; OC3 = endosulfan; OP1 = dimethoate; OP2 = malathion; OP3 = parathion

Means on the rows with different superscripts letters are significantly different for each bacteria. OC1 = aldrin; (average of three replicates ± mean standard deviation) expressed in OD (696 nm)

Control: Isolates not incubated with any pesticide

Most biodegradation processes involve redox reactions in which cytochrome P-450 enzyme is the facilitator. Cytochrome P-450 (Cyt P-450) catalyzes hydroxylation in which organic substrate, RH is hydroxylated to R-OH, incorporating one oxygen atom. Several enzymes catalyze metabolic reactions including hydrolysis, oxidation, addition of an oxygen to a double bound, oxidation of an amino group (NH_2) to a nitro group, addition of a hydroxyl group to a benzene ring, dehalogenation, reduction of a nitro group (NO_2) to an amino group, replacement of a sulfur with an oxygen, metabolism of side chains, and ring cleavage. The process of biodegradation depends on the metabolic potential of microorganisms to detoxify or transform the pollutant molecule, which is dependent on both accessibility and bioavailability (Ramakrishnan et al. 2011).

The microbial transformation may be driven by energy needs, or a need to detoxify the pollutants, or may be fortuitous in nature (co-metabolism). Because of the ubiquitous nature of microorganisms, their numbers and large biomass relative to other living organisms in the earth, wider diversity and capabilities in their catalytic mechanisms (Paul et al. 2005), and their ability to function even in the absence of oxygen and other extreme conditions, the search for pollutant degrading microorganisms, understanding their genetics and biochemistry, and developing methods for their application in the field have become an important human endeavor (Paul et al. 2005; Megharaj et al. 2011).

The microbial populations of soil or aquatic environments are composed of diverse, synergistic, or antagonistic communities rather than a single strain.

In natural environments, biodegradation involves transferring the substrates and products within a well-coordinated microbial community, a process referred to as metabolic cooperation (Abraham et al. 2002).

7.6.1 Enzymatic Activities in Pesticide Biodegradation

Enzymes are central to the catabolism of many pesticides (Riya and Jagatpati 2002). Applying enzymes to transform or degrade pesticides is an innovative treatment technique for the removal of these chemicals from polluted environments. Enzyme-catalyzed degradation of a pesticide may be more effective than abiotic physico-chemical methods. These enzymatic degradation mechanisms occur through intrinsic detoxification mechanisms and evolved metabolic resistance, and in the wider environment, via biodegradation by soil and water microorganisms (Scott et al. 2008).

Most of these enzymatic mechanisms are interrelated (Scott et al. 2008; Trigo and Valencia 2009) and the following modes of enzymatic biodegradation of xenobiotic pesticides are suggested:

1. Central metabolism of the global biodegradation networks involves transferases, isomerases, hydrolases, and ligases.
2. Linear pathways converging on particular intermediates form a funnel topology.

3. The novel reactions exist in the exterior part of the network.
4. The possible pathway between compounds and the central metabolism can be arrived at by considering all the required enzymes in a given organism and intermediate compounds.

Hydrolases, esterases, and mixed function oxidases (MFO) are involved in the initial metabolic stages of pesticide degradation while glutathione *S*-transferases (GST) systems are involved mainly in the final stages of pesticide degradation (Trigo and Valencia 2009).

Metabolism of pesticides may involve a three-phase process. In Phase I metabolism, the initial physico-chemical properties of a parent organic compound are transformed through oxidation, reduction, or hydrolysis to produce a more water-soluble and usually a less toxic product than the parent. The second phase involves conjugation of a pesticide or pesticide metabolite to a sugar or amino acid, which increases the water solubility and reduces toxicity compared with the parent pesticide. The third phase involves conversion of Phase II conjugate metabolites into secondary conjugates, which are also non-toxic. Bacteria and some fungi are involved in these processes by producing intracellular or extracellular enzymes like hydrolytic enzymes, peroxidases, and oxygenases that catalyze these reactions (Ortiz-Hernández et al. 2011; Van Eerd et al. 2003).

The following enzymatic reactions are the most common in biodegradation of xenobiotic pesticides in situ.

7.6.1.1 Hydrolases

Hydrolases catalyze the hydrolysis of several major biochemical classes of pesticide (esters, peptide bonds, carbon-halide bonds, ureas, thioesters, etc.) and generally operate in the absence of redox cofactors, making them ideal candidates for all of the current bioremediation strategies (Scott et al. 2008). For example, the hydrolytic degradation of carbofuran, a pesticide, and the group of carbamates results in several metabolites like 3-hydroxycarbofuran, 4-hydroxycarbofuran, 5-hydroxycarbofuran, carbofuran-7-phenol, and ketocarbofuran. Different organisms isolated from contaminated sites have been identified and characterized as transformers of carbofuran, resulting in different metabolites (Yan et al. 2007).

The following hydrolases are involved in biodegradation of xenobiotic pesticides.

7.6.1.2 Phosphotriesterases (PTEs)

These enzymes have been isolated from different microorganisms that hydrolyze and detoxify organophosphate pesticides (OPs). This reduces OP toxicity by decreasing the ability of OPs to inactivate AchE (Besse-Hoggan et al. 2009; Shen et al. 2010). The first isolated phosphotriesterase belongs to the *Pseudomonas diminuta* MG species. The PTEs are encoded by a gene called *opd* (organophosphate-degrading).

Flavobacterium ATCC 27551 presents the *opd* gene encoding to a PTE (Shen et al. 2010; Theriot and Grunden 2010). The gene was cloned and sequenced by Theriot and Grunden (2010). These enzymes specifically hydrolyze phosphoester bonds, such as P–O, P–F, P–NC, and P–S. OP hydrolase (OPH; encoded by the *opd* gene), methyl-parathion hydrolase (MPH; encoded by the *mpd* gene), and hydrolysis of coroxon (HOCA; encoded by the *hocA*gene), which were isolated from *Flavobacterium* sp. Sethunathan and Yoshida 1973), *Plesimonas* sp. strain M6 (Cui et al. 2001), and *Pseudomonas moteilli* (Horne et al. 2002) have the ability to hydrolyze some OPs like methlyparathion OP.

The PTE hydrolyze OPs by removing a proton from water, activating the molecule. The activated water directly attacks the central phosphorus of the pesticide molecule producing an inversion in its configuration. The oxygen is polarized by the active site; Zn acts as cofactor for the enzyme (Kapoor and Rajagopal 2011).

7.6.1.3 Esterases

Esterases are enzymes that catalyze hydrolysis reactions over carboxylic esters (carboxiesterases), bamides (amidases), phosphate esters (phosphatases), etc. (Kapoor and Rajagopal 2011). Hydrolysis of a wide range of ester substrates occurs during the catalytic process.

Many insecticides such as organophosphates, carbamates, and pyrethroids have associated carboxylic ester which are hydrolyzed by esterases specifically referred to as carboxyl esterases.

Esterases A, which contain a Cysteine (Cys) residue, interact with the functional group-SH in P=S, which is easily hydrolyzed by H_2O. Esterases B contain a Serine (Ser) residue that interact with the SER-OH forming a P=O bond that is not hydrolyzed by H_2O. OPs that bind to the esterase B stoichiometrically inhibit its enzymatic activity.

Esterases are a diverse group that protects the target site AChE by catalyzing the hydrolysis of insecticides, or acting as an alternative blank (Reiner et al. 1989). Esterases in general have a wide range of substrate specificities; they are capable of binding to phosphate triesters, esters, thioesters, amides, and peptides (Dary et al. 1990).

7.6.1.4 Oxidoreductases

Oxidoreductases are a broad group of enzymes that catalyze the transfer of electrons from one molecule (the reductant or electron donor) to another (the oxidant, or electron acceptor). Many of these enzymes require additional cofactors, to act as either electron donors, electron acceptors, or both. Oxidoreductases have been further subclassified into 22 subclasses (EC1.1–1.21 and 1.97) [28]. Several of these have applications in bioremediation, albeit their need for cofactors complicates their use in some applications. There are enzymes that catalyze redox reactions by reducing oxygen (as electron acceptor) to H_2O or H_2O_2 (Kapoor and Rajagopal 2011).

For example, endosulfan (*1,2,5,6,7,7-hexachloro-5-norbornene-2,3-dimethanolcyclic sulfite*) is an organochloride (OC) insecticide, highly toxic, and endocrine disruptor. The molecular structure has two stereochemical isomers α and β endosulfan. The end-use product of endosulfan is a mixture of two isomers, typically in a 2:1 ratio.

However, oxidation of endosulfan or endosulfan sulfate by the monooxygenase encoded by *ese* in *Arthrobacte* sp. yields endosulfan monoalcohol (Weir et al. 2006). Both *ese* and *esd* proteins are part of the unique Two Component Flavin Dependent Monooxygenase Family, which require reduced flavin adenine dinucleotide ($FADH_2$). They are conditionally expressed when no or very little sulfate or sulfite is available, and endosulfan is available to provide sulfur in these starved conditions (Paras et al. 2015; Dary et al. 1990; Weir et al. 2006).

Alternatively, hydrolysis of endosulfan in some bacteria (*Pseudomonas aeruginosa*, *Burkholderia cepaeia*) yields the less toxic metabolite endosulfan diol (Kumar et al. 2007). Endosulfan can spontaneously hydrolyze to the diol in alkaline conditions, so it is difficult to separate bacteria through abiotic hydrolysis. The diol can be converted to endosulfan ether or endosulfan hydroxyether and then endosulfan lactone (Kumar et al. 2007; Hussain et al. 2007). Hydrolysis of endosulfan lactone yields endosulfan hydroxycarboxylate.

These various branches of endosulfan degradation all result in desulfurization while leaving the chlorines intact, exhibiting the recalcitrance to bioremediation found in many organohalogen aromatic compounds (Paras et al. 2015; Hussain et al. 2007).

7.6.1.5 Mixed Function Oxidases (MFO)

In the reaction catalyzed by the MFO (EC 1.14.14.1), an atom of one molecule of oxygen is incorporated into the substrate, while the other is reduced to H_2O. Hence, MFO requires nicotinamide adenine dinucleotide phosphate (NADPH) and O_2 for its catalytic activity.

It is an enzyme system comprising two enzymes, cyt P-450 and NADPH-cyt P-450 reductase (also known as dependent cytochrome P-450 monooxygenases or P-450 system). Cyt P-450 enzymes are active in the metabolism of wide variety of xenobiotics (Khaled et al. 2012).

7.6.1.6 Glutathione S-Transferases (GST)

The GSTs (EC 2.5.1.18) are a group of enzymes that catalyze the conjugation of hydrophobic components with the tripeptide glutathione. In this reaction, the thiol group of glutathione undergo nucleophilic substitution with the target compound to form a conjugate which can be metabolized or excreted. These enzymes are involved in many cellular physiological activities, such as detoxification of endogenous and xenobiotic compounds, intracellular transport, biosynthesis of hormones, and protection against oxidative stress (Shi et al. 2012).

7.7 Genetics and Genomics of Pesticide Bioremediation

Most of genes responsible for catabolic degradation are located on the chromosomes, but in a few cases, these genes are found in plasmids or transposons (Ortiz-Hernández et al. 2013). The recent advances in metagenomics and whole genome sequencing have opened up new avenues for searching the novel pollutant degradative genes and their regulatory elements from both culturable and nonculturable microorganisms from the environment. Mobile genetic elements such as plasmids and transposons have been shown to encode enzymes responsible for the degradation of several pesticides. The isolation of pesticide degrading microorganisms and the characterization of genes encoding pesticide degradation enzymes, combined with new techniques for isolating and examining nucleic acids from soil microorganisms, will yield unique insights into the molecular events that lead to the development of enhanced pesticide degradation phenomenon (Ochieng et al. 2018; Anode et al. 2018).

The recombinant DNA and other molecular biological techniques have enabled some of the recent successes in bioremediation techniques (Shimizu 2002). Some of these breakthrough are:

1. Amplification, disruption, and/or modification of the targeted genes that encode the enzymes in the metabolic pathways.
2. Minimization of pathway bottlenecks.
3. Enhancement of redox and energy generation.
4. Recruiting heterologous genes to give new characteristics.

Various genetic approaches have been developed and used to optimize the enzymes, metabolic pathways, and organisms relevant for biodegradation (Pieper and Reineke 2011).

7.7.1 Metagenomics and Functional Genomics in Bioremediation

Metagenome technology has led to the accumulation of DNA sequences, and these sequences are exploited for novel biotechnological applications (Zhao and Poh 2008; Rajendhran and Gunasekaran 2008). Due to the overwhelming majority of non-culturable microbes in any environment, metagenome searches will always result in identification of hitherto unknown genes and proteins (Zhao and Poh 2008; Rajendhran and Gunasekaran 2008).

Functional genomics has emerged recently as a new discipline employing major innovative technologies for genome-wide analysis supported by bioinformatics. These new techniques include proteomics for protein identification, characterization, expression, interactions, and transcriptomic profiling by microarrays and metabolic engineering (Zhao and Poh 2008). The application of proteomics in environmental bioremediation research provides a global view of the protein compositions of the microbial cells and offers a promising approach to address the molecular mechanisms of bioremediation.

The fundamental strategy in a functional genomics approach is to expand the scope of biological investigations from studying a single gene or protein to studying all the genes or proteins simultaneously in a systematic fashion. The classic approach to assess gene function is to identify which gene is required for a certain biological function at a given condition through gene disruption or complementation. With the combination of technologies, such as transcriptomics and proteomics complementing traditional genetic approaches, the detailed understanding of gene functions becomes feasible (Zhao and Poh 2008; Rajendhran and Gunasekaran 2008; Rayu et al. 2002).

Metabolic engineering combines systematic analysis of metabolic and other pathways with molecular biological techniques to improve cellular properties by designing and implementing rational genetic modifications (Zhao and Poh 2008).

With these new genomics tools, scientists are in a better position to answer questions such as how oxygen stress, nutrient availability, or high contaminant concentrations along differing geochemical gradients or at transitional interfaces impact the organohalides respiring community structure and function. Ultimately, by tracking the overall microbial community structure and function in addition to key functional players, informed decisions can then be made regarding how to best manipulate the field conditions to achieve effective bioremediation of xenobiotic organic compounds like pesticides in the environment (Paras et al. 2015; Zhao and Poh 2008).

7.8 Current Strategies Used to Accelerate Bioremediation of Xenobiotic Pesticides

Cell immobilization has been employed for biological removal of pesticides because it confers the possibility of maintaining catalytic activity over long periods of time (Richins et al. 2000; Martin et al. 2000). Whole-cell immobilization has been shown to have remarkable advantages over conventional biological systems using free cells, such as the possibility of employing a high cell density, the avoidance of cell washout, even at high dilution rates, easy separation of cells from the reaction system, repeated use of cells, and better protection of cells from harsh environments

(Martin et al. 2000; Chen and Georgiou 2002; Ha et al. 2008). There is evidence indicating that immobilized cells are much more tolerant to perturbations in the reaction environment and less susceptible to toxic substances, which makes immobilized cell systems particularly attractive for the treatment of toxic substances like pesticides (Chen and Georgiou 2002; Ha et al. 2008). In addition, the enhanced degradation capacity of immobilized cells is due primarily to the protection of the cells from inhibitory substances present in the environment. The degradation rates for repeated operations were observed to increase for successive batches, indicating that cells became better adapted to the reaction conditions overtime (Chen and Georgiou 2002).

There are two types of processes for cell immobilization: those based on physical retention (entrapment and inclusion membrane) and those based on chemical bonds, such as biofilm formation (Martin et al. 2000; Chen and Georgiou 2002). Various materials or substrates such as inorganic (clays, silicates, glass, and ceramics) and organic (cellulose, starch, dextran, agarose, alginate, chitin, collagen, keratin, etc.) are used as support matrix (Martin et al. 2000; Chen and Georgiou 2002; Ha et al. 2008). Entrapment in polymeric natural gels has become the preferred technique for the immobilization of cells; however, immobilized cell on supports have been used more frequently in xenobiotics biodegradation as pesticides (Ha et al. 2008).

Hence, the cell immobilization method may be formulated as *active* that induces the capture of microorganisms in a matrix and as *passive* that uses the tendency of microorganisms to attack surfaces either natural or synthetic, which form biofilms (Paras et al. 2015; Pedersen and Christensen 2000; Ha et al. 2009).

Communication between microorganisms usually referred to as quorum sensing enables them to regulate and express specific genes through signaling molecules that mediate intercellular communication (Martin et al. 2000; Ha et al. 2008). This characteristic is dependent on cell density; for example, biofilm with a high cell density, it induces expression of resistance genes that provide protection and survival (Ha et al. 2008).

The loofa sponge (*Luffa cylindrica*) has been used as carrier material for immobilizing various microorganisms for the purpose of either adsorption or degradation of various xenobiotics organic compounds (Paras et al. 2015; Pedersen and Christensen 2000; Ha et al. 2009). This sponge have been used as natural support to immobilize various organisms such as *Chlorella sorokiniana, Porphyridium cruentrum, Penicillium cyrlopium*, and *Funalia trogii* for nickel and cadmium II treatment, besides dyes and chlorinated substances (Paras et al. 2015; Pedersen and Christensen 2000; Ha et al. 2009).

7.9 Conclusion

Microbes and their enzymes are responsible for bioremediation of several xenobiotic compounds in the environment and are therefore very useful in the development of advanced and efficient bioremediation technology tools and technique. It is therefore very important to understand the molecular mechanisms involved in enzymatic catalysis, which will be possible to design new alternative sand/or efficient tools for the treatment of pesticide residues or for the bioremediation of contaminated sites. This information could be used in the future to treat pesticide residues in situ in both aquatic and terrestrial ecosystems and hence reduce and subsequently eliminate hazards caused by such compounds. Moreover, in implementing and developing these strategies like cell immobilization techniques to increase the efficiency of degradation, new tools to abate the existence of obsolete pesticide will also be innovated.

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Chapter 8
Mechanism of Actions Involved in Sustainable Ecorestoration of Petroleum Hydrocarbons Polluted Soil by the Beneficial Microorganism

Charles Oluwaseun Adetunji, Osikemekha Anthony Anani, and Deepak Panpatte

Contents

Abstract Globally, the utilization of crude oil as a major source of energy cannot be over emphasized. Petroleum is one of the products from crude oil. Its exploitation as well as overuse has led to a significant environmental pollution in water and soil ecosystem. This situation was aggravated by the high level of industrialization, which increase the over dependence on petrochemicals, and some other petroleum products. Therefore, there is a need to search for a sustainable remediation techniques and proper land use management that will preserve the natural constituents of the environment. In order to remediate this, the application of bioremediation

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D. G. Panpatte, Y. K. Jhala (eds.), *Microbial Rejuvenation of Polluted Environment*, Microorganisms for Sustainability 26, https://doi.org/10.1007/978-981-15-7455-9_8

techniques using beneficial microorganisms and some sustainable technologies such as bioagumentation, immobilization, natural attenuation, biostimulation could serve as sustainable tools for the ecorestoration of petroleum and petrochemical hydrocarbons polluted environment. In view of the aforementioned, this chapter intends to provide a general overview on the modes of action utilized by beneficial microorganisms. The application of biostimulant together with beneficial microorganism for the stimulation of indigenous microorganism was also discussed in detail. Detailed information on some strategies that are inexpensive were also highlighted as well as the role of inoculating microbial consortium for the bioremediation of heavily polluted environment.

Keywords Petrochemical · Petroleum hydrocarbons · Pollutants · Microorganisms · Bioagumentation · Biostimulation

8.1 Introduction

Crude oil has been recognized as one of the major natural resources used by both the developing and developed nations of the world, and has contributed immensely to almost all facets of human's activities and development (Sun 2009). It has been recounted that human activities and over dependency on petroleum, a major product of crude oil, has increased globally (Xue et al. 2015). The over exploitation of this resource had led to environmental pollution (Chen et al. 2015; Wang et al. 2018a, b). Crude oil contamination in environment, especially in wetlands, polar regions, deserts, deep sea areas, has caused life-threatening issues for aquatic and land biota causing environmental deteriorations (Dombrowski et al. 2016; Dvořák et al. 2017).

The level of natural crude oil spills in the environment has been estimated to be approximately 600,000 metric tons, with about 200,000 metric tons unaccounted for yearly (Kvenvolden and Cooper 2003). The continual release of hydrocarbons has been linked as the main causes of water and soil pollution (Holliger et al. 1997). This might lead to buildup of contaminants in plant, animal and human which might result into mutation or high level of mortality (Alvarez and Vogel 1991). Most of the technology utilized for soil remediation such as burying, washing, dispersion, and evaporation has been highlighted with several challenges such as incomplete decomposition of these pollutants and high cost of these methodologies.

However, microbial remediation has been proposed to be one of the most effective and sustainable ways of remediating crude oil wastes because it is biocompatible, eco-friendly, and cheap to use (Leahy and Colwell 1990; April et al. 2000; Ulrici 2000; Medina-Bellver et al. 2005; Adetunji et al. 2017a, b, c, d, 2018a, b, c, d, e, 2019, 2020; Lea-Smith et al. 2015; Guerra et al. 2018). Atlas and Bartha (1992) documented that this process could act under certain metabolic conditions such as sufficient nutrient, oxygen and pH most especially between 6 and 9 to reduce the pollutant into less or nontoxic forms.

This chapter described in details the application of beneficial microorganisms for the sustainable bioremediation of petroleum hydrocarbon polluted soil. Highlights on various microbial modes of actions were documented. Specific examples of the application of microbes in the bioremediation of heavily polluted environment as well as the ecorestoration procedures, were discussed.

8.2 Application of Beneficial Microorganism for the Bioremediation of Heavily Polluted Environment with Petroleum Hydrocarbon

Chimezie Dirisu (2015) isolated, characterized and evaluated the hydrocarbon-utilizing fungi that could be utilized for the bioremediation of polluted freshwater ecoystem. The level of fungal growth was determined using visual assessment of mycelia tissue while pH was determined by a pH meter. The result obtained showed that the level of the hydrocarbon-utilizing fungi and total fungi count varied from $2.27 \pm 0.30 \times 10^3$ to $4.2 \pm 1.08 \times 10^3$ CFU/g. It was discovered that *Mucor* species were found more in the liquid medium when compared to *Penicillium* that exhibited a sparse growth in the culture medium. The pH of the culturing medium varies from 5.5 to 5.8 and 5.4 to 6.0 which decrease the level of acidity and toxicity which might be linked to the presence of petroleum hydrocarbon. There was also no significant difference between the pH changes and the fungal count after the process of hydrocarbon utilization ($p > 0.05$). The study showed that the utilization of fungal genera could utilize petroleum hydrocarbon as a source of energy and carbon, which led to decrease in acidity which showed that could be used in the bioremediation of oil available in the susceptible terrestrial environments and therefore, reducing of noxiousness due to an oil spill on arable land.

The consequence of pollution due to hydrocarbon contamination has been highlighted to be responsible for the high level of environmental pollution which might be linked to the petrochemical industry. The highest rate of petroleum product discharged into the environment has been a major point of concern. Most of these hydrocarbons have been highlighted to constitute a major source of health hazards, which is responsible for neurotoxic organic pollutants and carcinogens. Moreover, the application of chemical and mechanical techniques, have been highlighted to be imperfect, inefficient, and expensive for the ecorestoration of heavily polluted soil with hydrocarbons. The application of bioremediation has been discovered as a promising technology that could help in the remediation of these polluted sites with total mineralization. Bioremediation functions principally on biodegradation which ensure total mineralization of organic pollutant into inorganic compounds, carbon dioxide, cell protein, water or transformation of complex organic contaminates into simpler organic compounds through biological agents such as beneficial microorganisms. It has been discovered that numerous local microorganisms present in soil and water possess the capability to degrade hydrocarbon pollutants. On this note, Das and Chandran (2011) wrote a comprehensive review of the potential of beneficial microorganisms for the bioremediation of petroleum hydrocarbon in different ecosystems. The authors stated that the rapid rise in human population and an increase in modernization in the society have constituted several environmental pollutants which have led to high level of pollution. The application of petroleum hydrocarbon-degrading bacteria has been recognized to be abundant in nature and also possess the potential to utilize energy and carbon derived from crude oil sources. The utilization of bacteria having such capability has been highlighted for high utilization for the bioremediation of petroleum oil contaminated environments. This biotechnology has been identified as an alternative to numerous conventional techniques, but could be hampered by several environmental factors which limit its practical utilization on a larger scale.

Xu et al. (2018), wrote a comprehensive review on the application of bacteria as biodegraders. The authors stated several challenges that could hamper their utilization and implementation. They also proffered suggestions and development that could enhance the large-scale utilization of microorganisms in the bioremediation of heavily polluted soils.

Mehrasbi et al. (2013) evaluated the biodegradation of petroleum hydrocarbons containing 20 g/kg dry weight of soil using 3 media with various petroleum fractions. This was performed in the laboratory experiments for a period of 5 months. The influence of dehydrogenase enzyme and petroleum hydrocarbon-degrading microorganisms was done ex situ too. The assessment carried out using gas chromatography indicated that biological decontaminations for gas, oil, kerosene and synthetic mixture (gas, oil, kerosene and furnace oil) were 60%, 36%, and 55%, respectively. The Dehydrogenase activity was determined using TTC approaches. The result obtained showed that there was a positive correlation between the number of microorganisms and all the parameters evaluated. The Spearman rank correlation coefficients (r) derived from the polluted soil with gas, oil, kerosene and synthetic mixture were 0.79, 0.80, and 0.69, respectively.

One of the most significant environmental challenges is the decontamination of petroleum hydrocarbons contaminated soil, especially in an oil-rich country. Bioremediation has been identified as the most efficient technique for the remediation of contaminants in the soil.

The application of spending mushroom compost has been identified as an alternative solution that could be utilized for decomposition of soil with crude oil especially by Agaricomycetes. Mohammadi-Sichani et al. (2017), performed a biological experiment on soil sample contaminated with spent oil by using fungi sourced from compost as a remediator. The result from the molecular characterization performed using amplified fragment (18 s rDNA) sequence on the mushroom indicated that the strain belonged to *Pleurotus ostreatus* species. It was also established that the *Pleurotus ostreatus* species were able to degrade the petroleum hydrocarbons polluted soil effectively after a period of 3 months. Petroleum polluted soil modified with spent mushroom compost 10% and fertilizer disinterested 64.7%

of total petroleum hydrocarbons compared to control while the ecotoxicity tests based on the germination index (%) vary from 60.4 to 93.8%. Their study indicated that soil that was amended with mushroom was able to exhibit a high level of bioremediation of petroleum hydrocarbons, especially soil amended with 10% spent mushroom compost while there was a decrease in the level of soil toxicity in less than 3 months.

Zhang et al. (2019) evaluated the application of biochar as an effective means of amending heavily contaminated soil. The authors established the effect of petroleum-degrading bacteria that was immobilized on the biochar, free bacteria, biochar alone on the removal of total petroleum hydrocarbons available in the samples after treatment using gas chromatography-mass spectrometry and gravimetric evaluation. The results from the biological experiment, revealed that the immobilized bacteria exhibited a more enhanced bioremediation potential when compared to other treatment groups with reduced content of n-alkanes with C12–18 and total petroleum hydrocarbons. The differences in the features of enzymatic activities were observed in the application of biochar. This enhanced the level of the carbon storage as well as improved the level of soil respiration. Moreover, it was observed that the process of immobilization enhanced the bacterial activities and the physicochemical features of the soil while the level of bioavailability of hydrocarbons and the bacterial population were enhanced by the addition of the petroleum-degrading bacteria and the biochar. The study showed that the application of immobilized microorganisms on biochar enhanced the process of biodegradation of petroleum hydrocarbons.

Nwinyi et al. (2014) evaluated the level of bacterial diversity available in the diesel-polluted soil utilizing diesel oxidation in gradient cultures dynamics (pH and OD) of the pure cultures. The level of diesel dependent growths from this strain was evaluated for a period of 15 days by studying the gradient fluxes in the optical density and pH of the media. The result obtained indicates an enhancement in optical density as well as variation in pH values. The average optical density data obtained was 0.515–1.187 with pH of 6.95–7.2. The characterization of the potential isolates was performed using biochemical and morphological characterization, established that isolate S2P2, S3P2, S1P1, S2P1, S3P3 which belongs to the members of the genera *Pseudomonas* and *Bacillus*, as well as *Mycobacterium* species. Their study showed that these strains could be utilized for the bioremediation of heavily contaminated soil with diesels most especially for tropical ecosystems.

It has been discovered that wastes derived from oil industries have been identified as a major sources of soil pollution of the environment. Mainly the effect of crude residues and drill cuttings has been recognized to be a major source of hazards which might be linked to the occurrence of polycyclic aromatic hydrocarbons. Several bioremediation technologies such as biostimulation, composting, and bioaugmentation have been identified as a sustainable bioremediation technology which might be liked, to the facts that they are environmentally friendly, and cheaper alternatives when compared to other techniques. In view of the aforementioned, the effect of numerous strains of *Pleurotus sp.* was assessed. And evaluated their effect on the ecorestoration of oil polluted wastes and drill cuttings disposed in open-air soil, lots, or storage tanks for many years. The result obtained showed that the synergistic effect of direct fungal degradation and natural attenuation mechanism might be a sustainable bioremediation technique for the remediation of remediation of profoundly petroleum-contaminated soils and drilling wastes both at the and in field conditions and at laboratory condition. Furthermore, the authors present more data on the potential of *Pleurotus* genera to degrade asphaltenes, as one of the most intractable fractions of petroleum. This study recommends a method that at the same time can treat soils polluted with bottoms of crude storage tanks and waste from drill cuttings.

Ojewumi et al. (2018) tested the effectiveness of *Pseudomonas aeruginosa* and *Aspergillus niger* for the bioremediation of treated crude petroleum and soil polluted with raw petroleum. This evaluated by monitoring the organic carbon content available in the soil for a period of 45 days and the influence of pH for a period of 25 days. The experiment was performed with four systems containing 500 g of soil which has been contaminated with 40 g of treated crude petroleum while four systems were polluted with raw crude petroleum. The eight systems were targeted accordingly. The result revealed that pH did not affect the level of bioremediation. It was observed that the application of *P. aeruginosa* and *A. niger* when applied separately, enhanced the level of bioremediation of the raw crude polluted soil when compared to the treated crude polluted soil, which was evaluated on the 45th day of the experiment when Total Organic Carbon was evaluated.

The removal of various types of wastes and contaminants from the environment has been highlighted as a sustainable means of support the rapid development of our environment. In view of the aforementioned, Ataikiru et al. (2018) performed a study that based on the bioremediation of polluted environment for the using bioagumentation techniques for the bioremediation hydrocarbons contaminated soil with the aids of yeast isolates. The yeast isolates utilized were MYA-4700 of *Candida taoyuanica and strain* ZIM 2468 of *Candida adriatica.* The local isolates identified from the soil include *Saccharomyces, Alternaria, Rhodotorula, Aspergillus*, *Candida*, *Trichoderma*, *Penicillium*, *Mucor*, *Fusarium*, and *Rhizopus*. The experiment was performed with 1 kg of fresh soil sample that was contaminated with crude oil (10%). The physicochemical evaluation of the soil was determined before and after the pollution. The experiment was performed with *Candida taoyuanica* MYA-4700 and *Candida adriatica* ZIM 2468 together with the consortium of microorganism containing isolates inoculated into various microcosms to enhance the number of microorganisms. On the whole, the treatment of both *Candida* species showed they could be applied in the bioremediation of hydrocarbon polluted soil.

An increase in the rate of industrialization coupled with high population growth and high request and over reliance on petrochemical products could result into exceptional economic growth and development. Moreover, the high rate of dependency on fossil fuels has resulted to serious level in pollution of the environment over several decades. It has been stated that the persistence of hydrocarbon could lead to serious detrimental environmental and health hazards as well has a serious ecotoxicological effect. Therefore, the application of environmental biotechnology-based approaches could lead to the detoxification of toxicants available in a particular environment, especially by these petrogenic compounds. Among several strategies that have been applied for the treatment of environmental pollution, Bioremediation has been highlighted as a sustainable environmental solution. This might be linked to its sustainability, eco-friendly with high rate of organic contaminant metabolizing and preventing the ecological influence of oil spills. Though, it has been observed that the process of biodegradation takes a longer period when compared to the conventional remediation technologies. Several factors such as environmental and biological have been highlighted to be responsible for the degradation of hydrocarbon which includes bioavailability of contaminants to microbial attack, the pH of the soil, survival of hydrocarbon-degrading microbes, temperature, oxygen availability, and nutrient content. Koshlaf and Ball (2017) wrote a comprehensive review on the wide perspective of numerous researchers working on bioremediation. The various bioremediation techniques utilized by various scientists were highlighted. The modes of action by which most of these biodegradations occur were also discussed in detail, especially from the degradation of petrogenic hydrocarbons by microorganisms.

Thapa et al. (2012) wrote a comprehensive review on the advantage and demerits of utilizing bioremediation process for the remediation of petroleum polluted soil. The authors stated the significance of bioremediation together with some other processes for the remediation of heavily contaminated soil. They also highlighted that numerous microorganisms have been utilized for the bioremediation of hydrocarbon present in polluted soil. The bioremediation is simpler; require minimum labor with more acceptance by the general public. Their study also established that bioremediation can be considered as one of the greatest technologies that could be utilized for the bioremediation of heavily polluted soil.

Bioremediation has been highlighted as a sustainable biotechnological technology for the prevention of complex and poisonous contaminants from water and soil environment by metabolizing the contaminant available into harmless compounds. In view of the aforementioned, Suryatmana et al. (2018) utilized the application of *Azotobacter vinelandii* and mushroom log waste for the bioremediation of heavily polluted soil with petroleum degradation while the evaluation of the functional microbial available in the soil system was also carried out. The result obtained showed that the hydrocarbons degradation rate of mushroom log waste treatment reached 0.026354 days^{-1}, with a biodegradation effectiveness of 81.716%. While the application of *A. vinelandii* treatment augmented the hydrocarbon degradation rate from 0.007811 day^{-1} to 0.011038 day^{-1}. Moreover, it was discovered that the *Azotobacter* spp. growth rate boosted from 0.057886 day^{-1} to 0.250719 day^{-1} while mushroom log waste also enhanced bacterial petrophylic growth rate from 0.263029 day^{-1} to 0.357115 day^{-1}. Their study showed that mushroom log waste could be utilized for the bioremediation of petroleum waste which also enhances the occurrence of *Azotobacter* spp. population.

8.3 Specific Examples of Microorganisms Used for Bioremediation of Polluted Soil with Petroleum Hydrocarbons, Their Modes of Action and Ecorestoration Strategies

The alteration of any ecosystem caused by the introduction of petrochemical pollutants via natural and anthropogenic sources, has been recorded as one of the greatest threats to humans and the ecosystem because of the carcinogenicity they pose. Mahjoubi et al. (2017) in a review, looked at the bioremediation of petroleum hydrocarbon in a marine ecosystem. In the past, various synthetic methods using chemicals to degrade pollutants have been invoked. The authors recommend that for an effective bioremediation process to take place, an activation (bioaugmentation) and stimulation of the remediation process (biostimulation) using effective engineered microorganism and a stimulator such as biosurfacant are highly encouraged.

Zhang et al. (2019) tested and evaluated the bioremediation potential of polluted soil with petroleum hydrocarbon (n-alkanes and TPHs) using a mixture of biochar and microorganisms during a 60-day investigation period. The outcome of the investigation showed that the microbes-biochar treatments as compared to the control, was able to remediate the polluted soil with the petrochemical complexes. The mode of action of the bacterial enzymes improved the soil quality, physical, chemical, and the CO_2 storage. Furthermore, the diversity of the microbial consortia was also enhanced. The findings from their study showed that the combination of the microbes and the biochar mixture, served as an immobilizer and accelerator (bioaugmentation and biostimulation) respectively for bioremediation process.

Koshlaf and Ball (2017) in a review, looked at the bioremediation potentials of petroleum hydrocarbon in a contaminated soil. They linked the impacts of pollutants on the ecosystem to rapid industrial growth as well as population explosion. The authors recounted the probable health risk and ecotoxicity impacts of petroleum hydrocarbons on the ecological structure. They suggested that there is a dire need to detoxify the contaminants in the soil ecosystem via bioremediation. This remediation technique represents an economical and sustainable tool for transforming pollutants into useable form, thus reducing the ecological impacts of oil spills.

Environmental pollution that stems from petroleum hydrocarbons have recently been taken into cognizance because of the great impacts it portends. Xu et al. (2018) did a review of the degradation of petroleum hydrocarbons using microbes in an aerobic setting. The authors reported the benefits that can be derived from the use of this biotechnology. In conclusion, they recommend a better understanding of the biological and ecological factors that might affect the efficiency of microbes in the degradation of pollutants such as petroleum hydrocarbons in a contaminated soil.

Brown et al. (2017) did a review of the biodegradation of oil spills in soil by microbes. The authors recounted the various bioremediation techniques (bioaugmentation and biostimulation) utilized in the degradation of petroleum hydrocarbons as well as the technique to ascertain the level of natural influence on the bioprocess (bioattenuation). The utilization of these biotechnology in situ and ex situ, have a specificity in their customization. However, *the ex situ application* has been proven to be cheap compared with its counterpart in situ. In the other hand utilization is restricted. While the latter has proven to be effective in increase coverage to pollutants and more control in its operation. The authors stated that degrading microbes are usually found in the substratum of the petroleum hydrocarbons as well as more effective in their mode of actions. However, several ecological factors (redox conditions, moisture, nutrient availability, pH, and temperature) might have great influence in their activities. In conclusion, the authors recommend the utilization of biosurfactant in enhancing the hydrophobic-hydrocarbon complexes that elicit the coverage of the microbes and its efficacy. Bioremediation of petroleum hydrocarbon using microbial-biosurfactant, has been proven to be the best candidate for future remediation of petroleum complexes, because of their eco-friendly nature and green technology.

Yuniati (2018) did a review of the biodegradation of petroleum hydrocarbon in a contaminated soil using soil microbes. The authors recounted the ecological and health risks associated with soils contaminated with petroleum complexes. Microbial decontamination of soils polluted with petroleum hydrocarbons is in the forefronts in modern biotechnology. The authors, however stated that several ecological and biological factors militate against this process, but however, recommends that an understating of the entire factors is inevitable to the enhancement of the biological process.

The sediment or soil of any aquatic body serves as a sink of pollutants. The marine environment plays a significant role in aquatic biodiversity and the recipient of so many pollutants especially petroleum complexes. However, these pollutants pose a serious threat to the life forms therein, and health risk along the food chain. Ite and Ibok (2019) in a review looked at the phytoremediation and microbial remediation of petroleum complexes of polluted soils and sediments. The authors stated that impacts from petrochemical complexes portend serious negative socio-economic effects on the communities where the impacts pervade. The role of flora and microorganisms in the decontamination of petrochemical complexes in sediments and soils has aided in the biotransformation of pollutants into useable forms and resulted to the ecorestoration of the infused ecosystem which have been seen as an alternative to the chemical method. Bioremediation using plants/flora and microbes have been proven to be cheap, eco-friendly, and sustainable. Successive bioremediation of petrochemical complex outcomes has been linked with the interaction of the roots (rhizopheric) with the bacterial consortia. The authors opined that the fate of the pollutants can determine the recalcitrant level in the ecosystem. In conclusion, the authors recommend a better insight on the factors that influence the in situ bioremediation process in order to mitigate the potential risk they might pose during the biological remediation of the petroleum compounds.

Tian et al. (2018) evaluated and isolated hydrocarbon-decontaminating microbes for the management of wastewater oil in the sediments. Six hydrocarbon-decontaminating microbes were selected and identified belonging to the genus *Bacillus* and *Pseudomonas* for 14 days. The results showed that the strain YJ01 was able to decontaminate 76.30% crude oil alkanes and 80.64% crude oil, which are significantly good impacts in the degradation process. The results of the bio-decontamination markers (phytane and pristine) also indicated significant proportion of 78.23 and 46.75%, respectively. The result of the kinetic scrutiny showed a single first-order pattern of degradation potential (t1/2 of 15 g/L) at day 5 day. These results reflected that the strain YJ01 has the potential to reduce a wide range of crude oil as well as some environmental recalcitrant compounds.

Shen et al. (2018) did a review of the recent developments of biodegradation technology on petroleum complexes. The authors stated that petrochemical complexes is one of the worst pollutants in the environment and require special environmental attention. The current technique used in the remediation without leaving residues of pollutants in the ecosystem is microbes. Controlling and renewing petrochemical complex is a better way toward ecorestoration. In conclusion, the authors recommend bioremediation as a first-class biotechnology in the decontamination of wastes, especially petrochemical complexes in water and other related media. More so, a better understanding of the factors that influence the biological process should be put into cognizance and understudy the contamination site before and during the remediation process.

Jain et al. (2011) in a review looked at the bioremediation potentials of microorganisms in the decontamination of water and soil with petrochemical complexes. The authors recounted the toxic nature of petrochemical complexes on the health of the ecosystem, plants, and humans. They are typical immunotoxicants and carcinogenic agents. The utilization of microorganisms in the remediation of recalcitrant substances like petroleum hydrocarbon, is a wakeup call for ecorestoration and environmental cleanup. Microbial remediation has been proven to be more efficient in the decontamination of pollutants as against the conventional chemical techniques because of their sustainable use, cost effectiveness, and treatment efficiency. In conclusion, the authors recommend the utilization of microorganisms in the decontamination of environmental concerned pollutants for large-scale purposes.

Abioye et al. (2019) tested and evaluated the removal of Cd and Pb in a diesel-polluted soil. Soils polluted with 0.05% Cd and 0.1% Pb of mass 200 g were contaminated with diesel (5% w/w; 10 g) for 84. The internal environmental factors (organic matter, organic carbon, phosphorus and nitrogen) were regulated. The soil microorganisms were specifically from the genus *Pseudomonas* and *Bacillus*. The results of the study showed that the polluted diesel soil contaminated by the heavy metals, had a degrading efficiency of 89.5% (Cd) and 80.54% (Pb) correspondingly, when compared with the control (23.36%) after the investigation period. This indicated that both metals are co-pollutants in the contaminated soil and was used to reduce the pollutants in the diesel alongside with the microbes. The authors recommend effective and good degradation as a panacea for future ecorestoration.

8.4 Oil Degradation Taking Microbial Help and Bioremediation

Rathi and Yadav (2019) in review looked at the role of microbes in decontaminating and breaking down oil pollutants. The authors opined that because of the great energy, petroleum emit, they are known as the most efficient hydrocarbons. That accidental oil spills resulting to prolong ecological and health risks if it is not attended via remediation on time. Physical and chemical cleanup technique use in the immediate of pollutants, specifically oils from spills, have been proven experimentally tasking, inefficient, expensive, and not long-lasting in its utilization. The authors in conclusion, recommend the utilization of biological technique using microorganisms in the decontamination and breakdown of crude oil as a result from spills because of the advantages (environmentally friendly, cheap, and sustainable) it has over the physical and chemical methods.

Liu et al. (2017) tested and evaluated the bioremediation potential of aerobic microbes in the decontamination of crude oil from four provinces in China. The regions assessed were Xiamen, Dagang Oilfield, Northeast China, and Bohai Sea. A small-scale study (microcosm) was carried out for 112 days of messing up petroleum hydrocarbons around these regions. The results from the molecular analysis, showed that the variety of the bacterial consortia genes were altered when used in the breakdown of the crude oil. It was also observed that the TPHs breakdown by the bacterial consortia in the sand from Northeast China and Bohai Sea, showed an enhanced bacterial mineralization of the pollutant when compared to Xiamen and Dagang Oilfield. A denaturing gradient gel electrophoresis and molecular sequencing profiles verified a restored microbial consortium in all the studied soils. It was also noted that Firmicutes was the most dominant phylum sourced from clay soil in Xiamen region. While the phylum Proteobacteria was observed in Bohia, Northeast China, and Dagang, in sandy and silty soils. The enzyme; alkane monooxygenase and AlkB were enhanced from 10 to 1000 and were correlated positively to the level of the breakdown of n-alkanes C13–C30 and TPHs, respectively. The enzyme, dioxygenase gene (Nah) of naphthalene was correlated positively to the level of breakdown of PAHs and naphthalene, respectively. The results of the RDA (redundancy analysis) revealed abiotic influences were the major resistance to the bioremediation process. The authors in conclusion recommend a closer look on the biotic (biological factors) and abiotic (ecological) factors that will militate against degradation of soil pollutants.

Kaufmann et al. (2004) evaluated the impact of the degradation potentials of microbial consortia on petroleum hydrocarbons in Vaerose, Denmark. The results of the study showed that the RDA, had a positive impact on the bacteria consortium. The sum of the microbial cell correlated with the nitrogen and organic carbon contents of the soils. The results of the CO_2 and dry mass content (biomass) variation in the soil parameters were 46–39. A reduction of 8% in values, indicating a perfect degradation efficiency by the soil microbes. The CLPP (community level and physiological profiles) of the microbial consortia revealed that 35.9% of variation in data of the pollutants and soil parameters had close association and contact with the petroleum hydrocarbons. In conclusion, the authors stated that in the nutrient deficient site, there were heterogeneity and dominance of microbial consortia which influenced the degradation potentials of the petrochemical complexes.

Nwogu et al. (2015) tested and evaluated the improved biodegradation pattern of soil synthetically polluted with petrochemical complexes using microbes along with the guano of goat in a fourteen-day interval. The results at the end of the experiment showed that there was a decrease (62.08%) of the amount of total petroleum hydrocarbons in the modified sample as against the unmodified sample (8.15%) with a significant difference ($p < 0.05$) at different interim. In the same vein, here was a steady reduction in the amount of potassium, phosphorus, nitrogen and organic carbon contents of the soil in both the modified and unmodified samples. The results of the hydrocarbon cultured bacteria for both samples, increased significantly from $8.5 \times 105–2.70 \times 10^6$ cfu/g in the modified sample and from $8.0 \times 10^5–1.78 \times 10^6$ cfu/g in the unmodified sample. The most abundant species of microbes in the modified and sample were of the genus *Staphylococcus*, *Pseudomonas*, *Micrococcus*, *Klebsiella*, *Flavobacterium*, *Bacillus*, *Achromobacter,* and *Acinetobacter*. The findings from their study, showed that microbes along the guano of goat are good bioaugmentation and biostimulant for the remediation of petrochemical complexes such as TPH (total petroleum hydrocarbons) resulting in significant reduction of the complexes.

In today's environmental watch, hydrocarbon pollution is on the increase. Fortuitous release of hydrocarbon complexes into the ecosystem has raised serious concern because of their neurotoxic and carcinogenic constituents. However, environmental restoration using current biotechnological approach is the solution for an eco-safety and sustainable clean environment Das and Chandran (2011) in a review looked on the bioremediation potentials of petroleum pollutants using microorganisms. The authors opined that biodegradation is a promising tool for the decontamination of pollutants on sites which result to total mineralization of simple organic compounds, cell protein, inorganic compounds, water, and CO_2. The authors in conclusion, recommend the utilization of native microorganisms in soil and water for the degradation of hydrocarbon pollutants in diverse media.

During the exploration and production process of oil and gas, wastes are being generated which might have harmful effects to the ecosystem and unforeseen health impacts. Wang et al. (2017) in a review looked at the damages petrochemical complexes cause, as well as the remediation prospects. The authors stated that ecorestoration of the environment from pollutants involves a larger complex procedure. That the conventional methods used in the remediation of crude oil have been proven to be inefficient of recent, because of the disadvantages it poses. An alternative biotechnology method- bioremediation using microbes and plants, has been chosen to be more effective, cheap, eco-friendly and sustainable in its usage. Microorganisms and flora, play a synergistic role when combined to degrade soil pollutants. The authors stated that phytoremediation possess many attributes for degradation such as the microbial-rhizophere renovation of soil pollutants into effective bye-products. In conclusion, the authors recommend that for suitable degradation of petrochemical complexes in the soil, a combination of the physical, chemical, microbes, and plants should be used together for a better remediation purpose(s).

Paniagua-Micheland and Rosales (2015) did a review of the long-lasting bioremediation technology in the remediation of petrochemical compounds in a marine ecosystem. The authors recounted that bioremediation has been proven to be successful in the abatement of site pollutants in petroleum compounds. The marine microbes have so many advantages in the decontamination of petroleum hydrocarbons and restoring the environment back to normalcy and for the sustenance of biodiversity. The authors also stated that the utilization of biosurfactants produced by marine microalgae and bacteria also has the potential to degrade petroleum hydrocarbons and more preferably to other strains sourced from non-marine sources. In conclusion, the authors recommend biosurfactants marine microalgae and bacteria as perfect tools for the cleanup of noxious wastes like petrochemical complexes in the marine environment.

Adnan et al. (2018) in a review stated the standard of utilization of microbial remediation in the degradation of petrochemical complexes. The authors opined that petroleum hydrocarbons are known as one of the largest organic compounds that have high degradation resistance and toxic effects. The major sources are via petroleum refinery and oil spilling. Human contacts might result to mutagenicity, teratogenicity, and carcinogenicity. Petroleum hydrocarbons can be degraded by a reengineered consortium of bacteria with modified enzymatic action, energy, and carbon sources. However, this process can be influenced by both abiotic and biotic factors such as microbial consortia, bioavailability of substrates, physical conditions, and food or nutrients. They also stated that the understanding of the bacterial degrading consortia and their mode of actions, will aid in forecasting the ecological fate of pollutants as well as prospective future remediation techniques that will be more economical, easy to operate and replicate, and environmentally sustainable. In conclusion, the authors recommend that further study should be carried on the efficacy of new isolated strains and employ them on other media like water remediation. More so, the factors and contrivances that govern bioremediation should be studied in order to ascertain new technique for effective process.

Globally, petroleum hydrocarbon products have been known to cause serious environmental degradation in the ecosystem and probable health risk to humans. Borah (2018) in a review looked at the potential of bacterial in the remediation of petroleum hydrocarbons. The authors recounted the environmental disastrous impact caused by crude oil-based petroleum products (butane, propane, ethane, methane, paraffin, and volatile organic compounds) and heavy metals (vanadium, copper, nickel, and iron) which might result to serious human health risks like kidney, liver, and lung diseases. That bioremediation of recalcitrant pollutants is an essential treatment procedure which aid in installing normalcy to an unsettled ecosystem. The authors stressed the need in augmenting bioremediation with nutrients and reengineered microbes for a successful biological process. In conclusion, they recommend that to create a stress-free environment, soil microorganisms that are less tolerant to petroleum hydrocarbons should be genetically reengineered in order to compete with the biological and ecological stress they encounter in the bioremediation process.

Mahmoud et al. (2019) reviewed the mode of actions of microorganisms in the degradation of petroleum hydrocarbons. The authors recounted the ecological and health risks associated with the exposure of petrochemical complexes. That population explosion and industrial developments, have led to more need or petroleum products. With these, continuous release of hydrocarbon pollutants still persists, especially in the exploration and production phases. This might result to prolong residues along the food chain, cancers, mutagenicity, teterogenicity, and lethal health conditions. However, the authors recounted that these contaminants can be cleaned off from the ecosystem via bioremediation using a more vigorous microbe. Microbes have been proven to be more effective, unlike the conventional methods (physical and chemical) in cleaning up xenobiotic elements in the ecosystem because it has a sound environmental remedy, easy to be utilized, adaptability, and energy and cost efficient. In conclusion, the authors recommend the utilization of yeast and fungi in the degradation of petrochemical complexes in any ecosystem. Moreover, choosing the right microorganism to be used in bioremediation process is the very key for an efficacious biological outcome.

8.5 Conclusion and Future Recommendations

This chapter has discussed the application of bioremediation technologies for the remediation of petroleum hydrocarbons in the environments. The application of ex situ and in situ bioremediation technologies was also highlighted. The state-of-science on the utilization of beneficial microorganisms was elaborated in details. The modes of actively involved in the process of bioremediation of petroleum hydrocarbons were also highlighted. The biological, physical, and chemical features of the bioremediated soil need to be established so as to affirm their effectiveness for the growth of plants as well as their suitability for providing adequate condition for microbial activities in order for them to demonstrate their bioremediation effectiveness. Attention needs to be paid on some soil physical features such as water status, texture, structure, aeration condition because they also play a significant role during bioremediation processes. There is a need to establish proper knowledge of physical features together with necessary soil–plant–microbe management for proper maintenance of a cleaner environment most especially the petroleum polluted hydrocarbon soils.

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Chapter 9
Biosorption: An Eco-Friendly Technology for Pollutant Removal

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Abstract Water is the most important resource and crucial for all the living being on earth. Industrial and agricultural expansion generates a lot of wastes that contaminate water resources of the earth. These contaminated waste water threatens the human health and ecosystem. Numerous conventional and eco-friendly methods have been implemented to address water pollution. Amongst various methods, biosorption process emerged as unique method for the removal of persistent, toxic pollutant from the industrial waste water. In biosorption process live or dead microbial species like bacteria, fungi, algae and agricultural wastes are used as biosorbent for the removal of potentially toxic pollutants like heavy metals, dye and polycyclic aromatic hydrocarbons. Biosorption is a complex process which involves physical and chemical binding, chelation, precipitation and complexation mechanism. Researches demonstrate that study of biosorption kinetic model is important in designing industrial-scale biosorption process. Various operating parameters such as pH, temperature, biosorbent dose, and agitation speed are important in optimizing biosorption process. Further, this chapter also reviews the desorption process which makes the biosorption process more economical due to the recovery of sorbate molecule from the loaded biomass.

Keywords Biosorption · Biosorbent · Heavy metals · Dye · Polycyclic aromatic hydrocarbons

9.1 Introduction

Water pollution is a general global problem that results from the expansion of industrial and agricultural activities (Wang et al. 2019). There are many sources of water pollution, which are categorized as organic and inorganic pollutants. Organic water pollutants include solvents, volatile organic compounds, pesticides, herbicides, insecticides, polycyclic aromatic hydrocarbons (PAHs) and food and pharmaceutical industrial wastes. Inorganic water pollutants include fertilizers and mainly heavy metals present in industrial discharges (Vijayaraghavan and Yun 2008; Abdel et al. 2013). The deleterious effects of organic and inorganic pollutants on ecosystems are well known, and much expenditure is devoted to industrial treatment methods to prevent or limit such discharges. Various physio-chemical and eco-friendly methods such as ion exchange (Dabrowski et al. 2004), chemical precipitation (Charerntanyarak 1999), electrokinetics (Yuan and Weng 2006) and membrane processing (Qdais and Moussa 2004) have been implemented for the treatment of such pollutants. However, some pollutants are persistent in ecosystem, because they cannot be destroyed or degraded (Park et al. 2010; Ahmed et al. 2017; Barrios-Estrada et al. 2018). Such pollutants become a core issue around the world. Therefore, unique treatment methods are required to remove such potentially toxic, hazardous and persistent pollutants from the environments. Such toxic pollutants can be efficiently removed by biosorption process, which is a safe and eco-friendly approach (Bilal et al. 2018).

In biosorption process, biomass is used as a sorbent material for selective removal of toxic pollutant from aqueous solutions to the desired low levels. The earliest applications of biosorption techniques involved sewage and waste treatment (Ullrich and Smith 1951). Biosorption approach was also investigated in renovating wastewater generated by the chemical industry (Stasiak 1969). Biomass possess a wide spectrum of desired properties, It can be both live and dead organisms and found to be promising biotechnological tool for the removal of toxic pollutants (Gadd 2009). Recent research studies have directed attention to various biosorbent materials where algae, fungi, agricultural and forestry-based materials have proved to be eco-efficient and environmentally friendly sorbent materials. The abovementioned advantages make biosorption process as significant approach in the field of environmental biotechnology (Dhankhar and Hooda 2011; Ibrahim et al. 2016).

9.2 Biosorption

In biosorption, the prefix “bio” stands for a biological entity (live or dead) and suffix “sorption” is a term used to describe both adsorption and absorption (Salam 2019). Biosorption is a reversible sorption process which involves binding of sorbate to the surface of biosorbent (Mrvcic et al. 2012). This process entails microorganisms, plant-derived materials, agriculture wastes or any material of biological origin as biosorbent for the successful removal of recalcitrant pollutants. The pollutant can be inorganic or organic in nature and may be present in soluble or insoluble forms in the environment. These pollutants bind with the functional groups present at the surface of biosorbent by means of various interactions. Researchers suggest biosorption as an ideal alternative for the treatment of metal or dye containing effluents (Davis et al. 2003; Chojnacka 2010).

Biosorption is a complex mechanism and not fully understood. The key role in this physico-chemical process includes mechanisms such as absorption, adsorption, chelation, ion exchange and precipitation (Volesky 2007). The microbial biomass which receives various pollutants, primarily absorbing these chemicals on the cell surface and then uptake them by active or passive transport (Blazquez et al. 2011). Biosorption is viable in a wide pH and temperature range. Biosorption has fascinating advantages over conventional methods for waste water treatment (Sheng et al. 2007; Izabela et al. 2013). Some of these are listed below:

- *Cheap*: The biosorbent cost is very low since they are obtained from waste biological material and they can be produced in simple nutrient medium.
- *Metal/dye selective*: The sorption performance of different biomass can be more or less selective for different solutes. By physico-chemical treatment of biomass, multiple heavy metals can be removed at a time in sorption process.

- *Recovery of metals/solutes*: In case of metals, it can be recovered from the biomass by treating the biomass with various desorption agent.
- *Regenerative*: Biosorbent can be reused for the sorption process, once the metal/ pollutant is recovered from the biomass.
- *Reduced volume of waste or toxic material production*: No secondary problems of sludge generation occur with biosorption process.
- *Broad spectrum*: Biosorption is functional over wide range of conditions including temperature, pH, presence of other metal ions, etc.

9.3 Biosorbent

A biosorbent can be defined as any biological material which has the sorption capacity for a variety of sorbate material. A wide range of biological material has been employed as biosorbent, which can be living or non-living in nature such as algal biomass, fungi, bacteria, agricultural waste, etc. Generally biomass selected for biosorption process should be rich in organic ligands or functional groups (Jinsong and Paul 2014). An ideal biosorbent should be easily available, non-toxic in nature, must have high biosorption capacity, large-scale usability and reusability (Bilal et al. 2018). Biosorbent can be categorized as living biosorbent and non-living biosorbent which are as follows:

9.3.1 Living Biosorbent

9.3.1.1 Bacteria

Bacteria are prokaryotic unicellular living microorganism having a variety of morphology and able to sustain different environmental condition. A bacterium cell possesses different organelles such as cell wall, capsule, cell membrane and slime layer which helps in biosorption process (Jinsong and Paul 2014; Abdia and Kazemia 2015; Laxmi et al. 2018). Bacterium cell wall is an impermeable barrier to the small substrate and provides rigidity to cell. Bacterial cell wall has anionic group which attracts metal ion and internalized inside the cell in biosorption process. Similarly, capsule, slime layer has various functional groups such as amino, carboxyl, phosphate, and sulphate which are responsible for uptake of metal and other pollutants (Abdia and Kazemia 2015; Shamim 2018; Laxmi et al. 2018). A scientific report shows that filamentous Gram-positive bacteria actinomycetes remove cadmium with about 95% removal capacity (Zouboulis and Matis 1998).

9.3.1.2 Fungi

Fungus are ubiquitous in nature. Fungal cell wall components such as chitins, mannans and glucan has various functional groups such as carboxyl, phosphate, uranic acids, proteins, etc. which are responsible for solute uptake (Abdia and Kazemia 2015). Generally metal ions are taken up by fungal cells through ion exchange, complexation and physical adsorption process. *Saccharomyces cerevisiae* is known for biosorption process in free living, immobilized form and genetically engineered from. Similarly mushrooms uptake metal ions by their fruiting bodies, mycelia and sporocarps (Shamim 2018). White root fungi belonging to group *Basidiomycota* remove mixed pollutants from the discharged effluent (Yakup and Bayramoglu 2005). However, certain fungi existing in symbiotic relationship with plant and animal showed biosorption process in in situ condition (Abdia and Kazemia 2015).

9.3.1.3 Algae

Algal cell is an ideal biomass for the biosorption due to its high uptake capacity, low cost production and abundance presence of algal biomass in oceans. On the basis of evolutionary pathway, algae are classified as microalgae (green algae), macroalgae (brown algae) and red algae. The basic difference in algae is present in cell wall structure of algal cell, which is a major site for biosorption. Algal cell wall consist of cellulose, alginic acid, polymers and polysaccharide which basically contains sulphydryl, hydroxyl, phosphate, sulphate, imidazole, amine and carboxyl group. Biosorption by algal biomass depends on ion exchange process or complexation process (Jinsong and Paul 2014; Shamim 2018). Amongst various groups, brown algae play an important role in biosorption as they contain higher amount of acidic functional group in cell wall such as polymer of mannuronic acid and guluronic acid, which is responsible for metal uptake. There is a report on cadmium and lead biosorption by *Sargassum* biomass, due to the presence of carboxylic functional group in cell wall (Davis et al. 2003). When pH of process solution is greater than 10, hydroxyl group of polysaccharide becomes negatively charged, which participate in biosorption process of positively charged solutes (Abdia and Kazemia 2015). Algae cell produces phytochelatin in the extracellular environment, which may take part in metal chelation process (Shamim 2018). In few experiments, encapsulation of algal biomass by polyvinylalcohol, chitosan, agar, alginate, polyurethanes, polyacrylamide and surface modification by acid, base and aldehyde showed significant improvement in biosorption process (Alhakawati and Banks 2004; Bayramoglu and Yakup 2009; Lopez et al. 2002; Mata et al. 2008; Sheng et al. 2008; Yang et al. 2011).

9.3.1.4 Genetically Modified Organisms as Biosorbent

In genetic modification, a process is designed to manipulate microorganism according to our need. In case of biosorption process, organisms are designed such that higher solute uptake is achieved in harsh environmental condition (Bae et al. 2000). A recombinant strain of *Escherichia coli* have metallothionine gene, showed more than 75% biosorption capacity of cadmium within first 20 min of experiment (Gadd 2009). Phytochelatins contain repeating units of γ Glu-Cys which has higher metal binding capacity. Increasing the repetitive metal binding motif of (Glu-Cys) increases Cd^{+2} and Hg^{+2} metal ion uptake in the process of biosorption (Bae et al. 2000). Some Gram-positive bacteria also preferred for genetic modification process as it has only one layer, i.e. peptidoglycan layer which is less sensitive to shear forces. The recombinant strains of *Staphylococcus xylosus* and *Staphylococcus carnosus* express chimeric proteins containing polyhistidyl peptides which significantly improve Ni^{+2} binding capacity and help in nickel removal from the industrial effluents (Patel and Chandel 2015).

9.3.2 Non-living Biosorbent

9.3.2.1 Agricultural Waste

Corn cobs, soya/bean hulls, cotton seeds hulls, rice straw, wheat straw, etc. are example of few lignocellulosic agricultural waste. These agricultural wastes contain phenolic or carboxylic functional groups which exhibit ion exchange mechanism and help in biosorption process (Shamim 2018). Sawdust and bark produced as a waste in the forest industry possesses high absorption capacity have advantage of low cost and easy availability. Sawdust contains lignin, cellulose and hemicelluloses and is highly utilizable in biosorption of synthetic dye. Fly ash exhibits negative surface charge in alkaline condition, which involves in mechanism of precipitation and electrostatic interaction for metal biosorption (Izabela et al. 2013).

9.3.2.2 Biopolymers

Alginate is the most common and important biopolymer in the field of biotechnology. The polymeric form of alginate, i.e. calcium alginate, showed higher capacity to remove copper and lead (Jinsong and Paul 2014). Another biopolymer is chitin, composed of chitosan, due to the low cost and higher absorption capacity for all metal ions, chitosan is widely used in wastewater treatment. Chitosan showed higher biosorption capacity for metal ions because, structure of chitosan has flexible polymer chain and large number of hydroxyl and amino groups (Ramachandra et al. 2005).

9.3.2.3 Peat Moss

Peat moss is generally lignin- and cellulose-containing soil material. It is a good adsorbent, cheap and easily available in nature. The highly porous nature of peat moss imparts metal binding capacity. It can bind a variety of heavy metals due to the presence of carboxylic, phenolic and hydroxylic functional groups (Ramachandra et al. 2005).

9.4 Biosorption Technique and Mechanism

The process of biosorption involves a solid phase as biosorbent and a liquid phase containing a sorbate molecule. The binding mechanism of sorbate onto biosorbent is a complex process and likely to depend on the cell wall or the surface of the biomass. In case of any live biomass used, the composition of the cell wall has great importance in biosorption process. The cell wall of biomass is mainly composed of polysaccharides, proteins and lipids, which contains a number of functional groups like hydroxyl, carboxyl, amino, ester, sulfhydryl, carbonyl-terminal end, etc. These chemical/functional groups attract or sequester pollutants and play a key role in the biosorption of pollutants from aqueous solutions (Izabela et al. 2013).

In biosorption process, many types of biosorbent are derived from various forms of biomass which includes bacteria, fungi, yeasts, and algae. The complex structure of biomass suggests that there are many techniques or mechanisms, by which biosorbent can remove pollutants from the waste water. The various mechanisms by which biological materials accumulate heavy metals and other pollutants from wastewater include: adsorption, chelation/complexation, ion exchange, surface precipitation, etc. (Bilal et al. 2018). These mechanisms or techniques involved in biosorption process are as follows:

9.4.1 Ion Exchange

Ion exchange is considered as the principle mechanism of biosorption, which is the process of functional groups present on the surface of biomass. Cell walls of microorganisms contain polysaccharides where metal ions exchange with the counter ions of the polysaccharides (Chojnacka 2010; Vijayaraghavan and Balasubramanian 2015). Alginate plays a key role in biosorption by brown algae; ion-exchange takes place between metals when binding to alginate. In the cell wall of brown algae alginates present as salts of K^+, Na^+, Ca^{2+} and Mg^{2+}. These ions exchange with counter ions such as CO^{2+}, Cu^{2+}, Cd^{2+} and Zn^{2+}, in biosorption process of heavy metals. Macrophytes function as natural ion exchangers where monovalent ions (H^+, Na^+/K^+) present at the surface of biomass are involved in ion exchange process (Verma et al. 2008). There are also reports on biosorption of copper by fungi *Ganoderma lucidum* and *Aspergillus niger*, where the metal is taken up by ion exchange mechanism (Muraleedharan and Venkobachar 1990).

9.4.2 Coordination or Complexation

The combination of cations with molecules or anions containing free electron pair is termed as coordination or complex formation. The heavy metal cation is bound to central atom and the anions or molecules with which it forms a coordination compound termed as ligand. When a ligand is composed of several atoms with basic or nucleophilic nature, the ligand is termed the ligand atom. When a base containing more than one ligand atom is termed as multidentate complex, then the complex formation with multidentate ligands is termed as chelation (Abdia and Kazemia 2015). Complexation or coordination is the result of electrostatic attraction between a metallic ion chelating agent and a polymer that can be excreted by a microorganism. Complexation or coordination can be caused by: biosurfactants, polysaccharides, proteins and nucleic acids. These chelating agents contain pairs of electrons that present electrostatic attraction. Metal uptake by sulphated polysaccharides (fucoidan) present in algal cell wall is observed due to complexation process (Veglio and Beolchini 1997; Davis et al. 2003). In *Pseudomonas syringae* complexation mechanism is responsible for the accumulation of calcium, magnesium, cadmium, zinc, copper and mercury. The organic acids (e.g., citric, oxalic, gluonic, fumaric, lactic and malic acids) produced by microorganisms may chelate toxic metals and results in the formation of metallo-organic molecules. A scientific report shows that alginic acid extracted from *Laminaria digitata* is effective in metal-ion binding ability in solution containing Pb^{2+}, Cu^{2+}, Cd^{2+}, Ba^{2+}, Sr^{2+}, Ca^{2+}, CO^{2+}, Ni^{2+}, Mn^{2+} and Mg^{2+} metals. Metals may be biosorbed or complexed by carboxyl groups found in microbial polysaccharides and other polymers (Abdia and Kazemia 2015). Aksu (1992) reported that biosorption of copper by *C. vulgaris* and *Z. ramigera* takes place through adsorption and coordination between metal ions and amino and carboxyl groups of cell wall polysaccharides.

9.4.3 Physical Adsorption

It is a process of adhesion of atoms, ions or molecules on the surface of adsorbent from a gas, liquid or dissolved solid in a solution. This process creates a film of the adsorbate on the surface of the adsorbent. Physical adsorption takes place with the help of electrostatic interactions, Van-der Waals forces, covalent bonding, redox interaction and biomineralization. This process is independent of metabolism and is very promising especially for treating large volumes of wastewater (Ahluwalia and Goyal 2007; Kuroda and Ueda 2010; Nishitani et al. 2010). In physical adsorption, metal ions are attracted by the negative charge on the surface of biosorbent, which suggest that adsorption process is dependent on the pH of process solution. It is observed that pH range of 4–8 is found to be favourable for the biosorption of heavy metals. There is also report on biosorption of uranium, cadmium, zinc, copper and cobalt by dead biomasses of algae, fungi and yeasts through electrostatic interactions (Borro and Fein 2005; Wang and Chen 2006; Machado et al. 2010). The extracellular polymeric substances (EPS) produced by bacteria also remove heavy metals as a result of adsorption process (Gupta et al. 2005).

9.4.4 Precipitation

In case of precipitation, metal ions precipitate with the functional groups present on the surface of biosorbent and remain intact or penetrate into the microbial cell. The process of precipitation can be dependent or independent of the cellular metabolism and the metal precipitates formed can be organic or inorganic metal precipitates. Generally, the extracellular polymeric substances produced by the microorganisms are normally involved in organic precipitate formation. Biosorption of uranium and thorium by non-living fungal biomass is a good example of precipitation (Jayaram and Prasad 2009). Precipitation mechanism was also reported for the removal of Cr, Cu, Zn, Pb, Fe and Mn, by using agricultural waste like soybean meal, watermelon rind and green tomato husk (Liu et al. 2012; Garcia-Mendieta et al. 2012; Witek-Krowiak and Reddy 2013).

9.4.5 Oxidation-Reduction (Redox)

A variety of oxido-reductive transformations alter metal specification and lead to increased deposition of metals in and around cell walls (Cima-Mukul et al. 2019). Microorganisms can mobilize or immobilize metal ions, metalloid and organo-metal compounds by promoting redox processes. Microorganisms can oxidize metals such as Mn^{2+}, Fe^{2+}, CO^{2+}, Cu^{2+}, AsO^{2-}, SeO and ${SeO_3}^{2-}$ or reduce metals such as Mn^{4+}, Fe^{3+}, CO^{3+}, ${AsO_4}^{2-}$ and ${SeO_4}^{2-}$ and obtain energy from these reactions (Gavrilescu 2004). In this process, acidic and basic natures of the functional groups that are present on the biomass surface decide the nature of redox reaction and the bond that is involved in biosorption process (Pistorius et al. 2009; Michalak et al. 2013). In reduction process, metal ion interacts with the functional groups like carboxyl and gets reduced which leads to biosorption process. Many organisms remove Cr (VI) by reducing them into Cr(III) in the aqueous solution (Park et al. 2005).

The abovementioned mechanisms are the major techniques by which a biosorbent can efficiently remove pollutants from the discharged industrial waste water. However, apart from these, few other mechanisms may involve in biosorption process. The metal transport systems of cell membrane may involve in heavy metal transportation across microbial cell membranes. In such process, initially metals are bound to the cell walls, and then an intracellular uptake transports metal across the cell membrane (Costa and Leite 1991; Gadd and DeRome 1988; Huang et al. 1990; Nourbakhsh et al. 1994). In case of biomethylation, microorganisms transform metal ions from a more toxic to a less toxic form. Heavy metals such as Hg, As, Cd, Se, Sn, Te and Pb can be methylated by a variety of bacteria, filamentous fungi and yeasts. Biomethylation results in increased mobility and suitability of the metals, which is a favourable condition for biosorption process by a living microbial species (Roane and Pepper 2001; Gadd 2004). Sometimes microbial cell when exposed to toxic concentrations of heavy metals, expression of cysteine-rich peptides occurs. These peptides form complexes with divalent metals and ultimately remove the metal ions from the outer environment (Bae et al. 2000).

9.5 Kinetics of Biosorption

Biosorption kinetics studies provide the possible information about the mechanism involved in the biosorption process. Biosorption kinetics plays a crucial role in the selection and design of reactor systems as well as in operations for the treatment of industrial effluents. Biosorption kinetics also demonstrates the rate of solute bonding on the biosorbent surface (Izabela et al. 2013).

To study biosorption kinetics, the quality of a biosorbent must be determined. The quality of a biosorbent is judged by determining the solute uptake/sorption capacity of a biosorbent, i.e. sorbate concentration that has been removed by the biosorbent from the bulk solution during experimental condition. Generally, the sorption capacity is determined by taking different initial quantities of solutes in a biosorption experiment (Ahalya et al. 2003; Abbas et al. 2014). In biosorption experiment, solute/sorbate uptake by a biosorbent is calculated using following equation:

$$q = \frac{V(C_{\mathrm{i}} - C_{\mathrm{e}})}{M} \tag{9.1}$$

Here,

q = Amount of sorbate biosorbed by biomass (mg/g)
C_{i} = Initial concentration of sorbate (mg/L)
C_{e} = Concentration of sorbate (mg/L) at equilibrium
V = Volume of the experimental solution (L)
M = Mass of adsorbent (g)

To study the sorption performance of a biosorbent, biosorption isotherm models are studied in detail. In biosorption isotherm, solute concentration is varied in a biosorption experiment while other parameters like temperature, pH and ionic strength are kept constant. A variety of models are studied to characterize biosorption isotherm which includes Langmuir model, Freundlich model, Tempkin model, D-R (Dubinin–Radushkevich) model, etc. Amongst them, Langmuir model and Freundlich model are studied normally to understand biosorption isotherm (Izabela et al. 2013).

9.5.1 Freundlich Model

The Freundlich isotherm is a nonlinear sorption model. This model describes a monolayer sorption to a heterogeneous surface (i.e., surfaces having adsorption sites of varying affinities) by interactions between adsorbed molecules. This model is expressed by the following equation (Jalali-Rad et al. 2004; Abdia and Kazemia 2015):

$$q_e = k_f \cdot {C_e}^{1/n} \tag{9.2}$$

Here, k_f and n are the Freundlich constants.

The logarithmic form of Eq. (9.2) is:

$$\log q_e = \log k_f + 1/n \log C_e \tag{9.3}$$

The curve of this equation shows intercept $\log(k_f)$ and the slope $1/n$.

Here, k_f and n are Freundlich constants. k_f is related to the sorption capacity, and n is related to the sorption intensity. The value of constant n greater than 1.0 shows that the sorption is favourable physical process (Jalali-Rad et al. 2004; El-Sikaily et al. 2011).

9.5.2 Langmuir Model

Langmuir model is generally studied for describing gas or liquid adsorption on solid material. The Langmuir model represents monolayer sorption on a homogeneous surface of the sorbent without interaction between adsorbed molecules. This model evaluates the maximum adsorption capacity of a sorbate on a sorbent material (Abdia and Kazemia 2015).

The Langmuir model is described by following equation:

$$q_e = \frac{q_{\max} b c_e}{1 + b c_e} \tag{9.4}$$

Equation (9.4) can be linearized as follow:

$$\frac{c_e}{q_e} = \frac{1}{q_{\max} b} + \frac{c_e}{q_{\max}} \tag{9.5}$$

Here,

q_e = Amount of solute removed (mg/g)
c_e = Equilibrium concentration (mg/L)
b = Langmuir constant related to affinity
OR
Equilibrium adsorption constant related to the affinity of binding sits (L/mg)
$q_{\max}$ = Maximum solute uptake under the given conditions (mg/g)

The Freundlich and Langmuir constants have been calculated from the corresponding plots. These models are widely studied by scientist to understand the biosorption kinetics. These models are two-parameter models which describe equilibrium state for adsorption of metal ions in experimental work (Abbas et al. 2014). By studying biosorption kinetics, it was observed that biosorption process is faster for the uptake of cationic contaminants than that of anionic contaminants in the standard experimental conditions (Pavasant et al. 2006; Yang and Chen 2008; Ibrahim 2011).

9.6 Application of Biosorption

The awareness in environment concern led in search of a new waste treatment technology which is inexpensive and capable of treatment of polluted wastewaters. Thus, in search of new treatment technology, lots of efforts have been made on biosorption to treat effluent containing industrial waste. Biosorption process has the capacity to remove various pollutant materials such as metals, dyes, fluorides, phthalates, pharmaceuticals, etc. from the industrial effluent. However, the process of biosorption is mostly focused for toxic metal ion removal and can also be used in the recovery of valuable metals such as silver and gold (Davis et al. 2003; Veglio and Beolchini 1997).

9.6.1 Biosorption of Cations/Anions

Microorganisms i.e. bacteria, fungi, yeasts, cyanobacteria and algae have been widely reported for the biosorption of heavy metals. The research on biosorption is mostly applied for the removal of cations, which includes Cr(III), Pb(II), Cd(II), Zn(II), Cu(II), etc. (Izabela et al. 2013). Research showed that various agro-industrial waste and natural biosorbents have been applied for the removal of Cu (II) and other ions i.e. Zn, Cr, Na, Ca, K from electroplating waste with almost 77–95% biosorption efficiency for Cu(II) ions (Das et al. 2008). The research on anion biosorption is also studied. This studies show that biosorption of anion is highly dependent on chemical conditions such as pH of the solution. Anionic species like TcO^{-}_{4}, $PtCl_4^{3-}$, CrO_4^{2-}, SeO_4^{2-} and $Au(CN)_2^{-}$ showed increased biosorption at low pH values (Garnham et al. 1992).

9.6.2 Biosorption of Dye

Various biosorbent materials such as bacteria, algae and fungi are also used for the biosorption of broad range of textile dyes. The interaction between dyes and biomass depends on the functional group at the surface of microbial biomass and chemical structure of dye (Maurya et al. 2006). Apart from chemistry between dye and biomass, solution pH markedly affects the biosorption process. Solution pH affects surface charge of biosorbent, availability of dye and degree of ionization. Maximum biosorption of anionic and cationic dye was obtained at pH 2.0 and pH 10, respectively. Anionic textile dyes i.e. RR239, RBB and DB85 are effectively removed by waste beer yeast slurry as biosorbent at optimum pH 2. In another report, algal biosorbent *Cosmarium* removes contaminant malachite green dye with biosorption efficiency of 89.1% (Saraf and Vaidya 2015; Castro et al. 2017).

9.6.3 Biosorption of PAH (Poly Aromatic Hydrocarbon)

The decreases rate of biodegradation of PAH and it's adverse effect on environment requires immediate removal of these pollutant. Biosorption of PAH by live or dead biomass is an effective remediation technology for the removal of such pollutant. In a research biosorption of PAH by *Phanerochaete chrysosporium*, transfer PAHs from solution to fungal biomass. Here, biosorption of PAH was observed by both live and dead mycelium pellet. The study also shows that, rate of PAH biosorption was higher by living mycelial pellet of *Phanerochaete chrysosporium*. In another study, it was found that *Klebsiella oxytoca* PYR-1 effectively removed phenanthrene with almost 85.7% biosorption efficiency (Jie et al. 2013; Zhang et al. 2018).

9.7 Factors Affecting Biosorption Process

A successful biosorption requires optimum performance of biosorbent in the discharged industrial effluent. However, the performance of biosorbent depends on several operating parameters/factors which effect biosorption efficiency by altering mass transfer coefficient, biosorbent capacity, biomass surface charge, metal uptake rate and metal speciation. These operating parameters/factors that affect biosorption process include solution pH, process temperature, biosorbent concentration, agitation rate, etc. These factors are discussed in detail as follows:

9.7.1 Solution pH

The surface of microbial biomass contains polysaccharides, amino acids and lipids, which possess functional groups such as amino, carboxylic, sulphydryl, amide, hydroxyl, phosphate and thiol groups. These functional groups provide specificity in binding with metal ions (Ting and Mittal 2002; Laxmi et al. 2018; Salam 2019). Solution pH is an important factor in biosorption process as pH influences metal precipitation, metal speciation and availability of metal for biosorption, chemistry of functional group hence affect the overall uptake of sorbent (Ting and Mittal 2002; Patel and Chandel 2015). A change in solution pH causes protonation and deprotonation of the functional group (Salam 2019). At low pH, excess H^+ ions associate with ligands and exhibit competition with sorbant for binding site. As pH increases, ligands such as carboxyl, phosphate, imidazole, and amino groups, exposed and carry net negative charges which attract positively charged metal ion and increases biosorption process. However, solution pH above 7 creates precipitate and hydroxide anionic complex which ultimately decreases metal uptake. In a different case, metal precipitation was observed at $pH > 5$ for Pb, $pH > 6.7$ for Ni, $pH > 6$ for Cu, $pH > 7$ for Cr and $pH > 8$ for Cd (Gadd 2009; Salam 2019). The optimum pH for biosorption process also depends on the metabolism of organism. A report shows that increase in pH from 1 to 4 increases biosorption of Cr(IV) from waste water by *Saccharomyces cerevisiae* (Laxmi et al. 2018). In another report, biosorption of Au(III) was decreased when pH changed from 1.9 to 0.9 and maximum sorption was observed at pH 1.9–3.8 (Rudzinski and Plazinski 2010).

9.7.2 Temperature

Temperature deals with kinetic energy and thermodynamic process of metal ion adsorption (Ali et al. 2014; Laxmi et al. 2018). An endothermic sorption process increases with increase in temperature while in case of exothermic sorption process, a decrease in temperature causes increase in biosorption process (Bilal et al. 2018). Generally, biosorption process is carried out between temperature range of 20 and 35 °C (Shamim 2018). Higher temperature enhances biosorption efficiency by increasing surface activity and kinetic energy of biosorbent. However, higher temperature also disrupts physical structure of biosorbent material (Abdia and Kazemia 2015). An increase in temperature increases biosorption of Cr(III) and Cu(II) by *Aspergillus flavus*. It may be due to increased collision frequency between sorbate and sorbent, and maximum biosorption of Cr(III) and Cu(II) was obtained at temperature 40 °C (Azhar and Iram 2014; Abdia and Kazemia 2015; Bilal et al.

2018; Laxmi et al. 2018). In another study, optimum temperature for maximum Cd biosorption was observed at 40 °C by *Saccharomyces cerevisiae* (Laxmi et al. 2018). Biosorption of Pb(II) by green algae was increased with an increase in temperature, which may be due to the endothermic nature of the process. Similarly, in biosorption of dye, increase in temperature causes increase in biosorption which may be due to the increase in movement of dye molecules (Safa and Bhatti 2010; Saltabas et al. 2012; Bilal et al. 2018).

9.7.3 Contact Time

Biosorption process is also affected by contact time between biosorbent and sorbate molecule. Optimum contact time to reach process equilibrium depends on the nature of biosorbent and sorbate molecule (Ali et al. 2014). It was reported that initial increase in contact time results in increased biosorption process, because 90% of binding sites on biosorbent surface are vacant for binding sorbate molecules. However, further increase in contact time does not increase in biosorption process due to the saturation of active site of biosorbent (Laxmi et al. 2018; Bilal et al. 2018). In biosorption process of dye by algae, a rapid increase in biosorption was observed at initial 15 min and reaches to equilibrium at about 75 min. In fungal biosorption of Ni^{+2}, equilibrium was achieved after 180 min of biosorption process (Ali et al. 2014). In case of *Bacillus cereus* and *Pseudomonas aeruginosa*, biosorption equilibrium for Zn biosorption was obtained at contact time of 30 min (Laxmi et al. 2018).

9.7.4 Agitation Speed

Agitation of process suspension enhances mass transfer of solute molecule from fluid to biosorbent. An optimum agitation speed develops homogeneity of process suspension which results in higher uptake rate of biosorption. However, higher agitation speed develops vortex which results in loss of homogeneity and disturbs the physical nature of biosorbent, which leads to decrease in biosorption rate. Optimum agitation speed for Cd and Zn biosorption by *Aspergillus niger* was obtained at 80 rpm with biosorption efficiency of 65%. In case of Cr(IV) removal by *Rhizopus nigricans*, maximum removal was observed at 120 rpm (Ramachandra et al. 2005; Abdia and Kazemia 2015; Laxmi et al. 2018; Bilal et al. 2018; Salam 2019).

9.7.5 Initial Concentration of Sorbate Molecule

Initial concentration of sorbate molecule provides positive driving force to overcome mass transfer resistance between solid and liquid phases (Shamim 2018). However, a higher initial sorbate molecule concentration increases biosorption rate till process equilibrium. In a biosorption experiment, at initial Cd concentration of 25 mg/L, biosorption rate of 86.8% was observed by *Hypnea valentiae*. In case of acid green dye, an increase in biosorption efficiency of 94–98% was obtained when initial dye concentration was taken from 30 to 90 mg/L in the biosorption process (Ting and Mittal 2002; Jaikumar and Ramamurthi 2009; Laxmi et al. 2018; Bilal et al. 2018).

9.7.6 Biomass Concentration

Biomass concentration is crucial for biosorption process as it determines the capacity of sorbent and provides solute binding site. A higher biomass concentration increases biosorption due to the availability of higher surface area for solute uptake (Jaikumar and Ramamurthi 2009; Ali et al. 2014). In case of Cd and Pb biosorption by *Anabaena sphaerica,* metal uptake was increased with biosorbent dose from 0.025 to 0.25 g/100 ml. However, further increase in biosorbent dose does not enhance metal uptake due to the formation of biomass aggregates (Laxmi et al. 2018). In another study of biosorption of azo dye in aqueous media, maximum biosorption was achieved at dosage of 0.5 g/L of biosorbent (Safa and Bhatti 2010). Similarly, Bueno et al. (2008) reported increased metal uptake rate of Pb(II), Cr(III) and Cu(II) with an increased biomass concentration of *R. opacus* from 0.5 to 1 g/L.

9.8 Desorption and Recovery

Generally, metal ions are recovered from the biosorbent after biosorption process, which is known as desorption of metal from biosorbent. In desorption process, some chemical agents were used to treat the treated biosorbents, which include mineral acids (HNO_3, H_2SO_4, HCl), organic acids (acetic acid, citric acid) and complexing agents (thiosulfate, EDTA). A desorption agent does not damage the physical properties of biosorbent, so that biosorbent sorption efficiency must remain in its original state. However, sometimes the treatment of chemical agent can improve sorption capacities of a biosorbent (Ahalya et al. 2003; Alluri et al. 2007; Ahemad and Kibret 2013).

Desorption of dye-loaded biomass can be done by some organic solvents such as methanol, ethanol or surfactants (Aksu 2005). Boudechiche et al. (2016) used H_2O, HCl, NaCl and NaOH as desorption agent for the removal of methylene blue dye from the lignocellulosic biomass (*Luffa cylindrica*). In case of pesticides and phenolic compounds, distilled deionized water, $CaCl_2$ and NaOH can be used as desorption agent. Desorption process in advantageous from the economic point of view, as it enables re-use of the biomass, and recovers containment of sorbed materials, which were otherwise lost in discharged effluent (Aksu 2005).

9.9 Conclusion

A number of conventional methods have been developed for the treatment of environmental contaminants. However, biosorption is found to be a modern concept and effective biotechnology of living or dead biomass for cleaning the environment. This method is a cheaper alternative approach which is easier to apply in the industrial scale. The implementation of biosorption process requires fundamental research and detailed knowledge of biosorbents, kinetic models and biosorption mechanisms. The mechanism of biosorption suggest that pH of the process solution is most important operational parameters, which activate functional group on biomass surface and decide the metal uptake. In order to be a more economic approach, biosorption process needs further research in selective desorption approach, comprehensive modelling for kinetic studies and complex biosorption systems.

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Chapter 10

Synergistic and Antagonistic Effects of Microbial Co-culture on Bioremediation of Polluted Environments

Elham Khanpour-Alikelayeh and Ali Partovinia

Contents

Abstract The release of organic and inorganic pollutants into the soil, groundwater, and surface water has become one of the major worldwide concerns. The remediation of contaminated ecosystems could be carried out by different methods, such as physicochemical and biological approaches. Bioremediation has been receiving

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D. G. Panpatte, Y. K. Jhala (eds.), *Microbial Rejuvenation of Polluted Environment*, Microorganisms for Sustainability 26, https://doi.org/10.1007/978-981-15-7455-9_10

increasing attention from researchers because of its relatively low cost, simplicity, environmental friendliness, and ability to convert contaminants to harmless end products. However, this technology currently confronts many challenges for the bioremediation of recalcitrant compounds. Multi-species microbial consortia have enormous potential for degradation of hazardous environmental pollutants such as petroleum hydrocarbons. Until now, different microbial consortia including bacterial, fungal, fungal–bacterial, and yeast–bacterial, depending on the contaminants structure and microorganisms capability, have been applied. Performance of co-cultures is strongly influenced by environmental factors such as pH, temperature, and moisture that need to be given careful consideration. There are some studies about bioremediation of pollutants using mixed culture of microorganisms, but few of them focus on microbial interactions and influencing factors for effective biodegradation. Therefore, great attention needs to be placed on investigation of factors affecting co-culture performance. Therefore, in this chapter, synergistic and antagonistic effects of microbial co-culture on bioremediation of polluted environments have been studied.

Keywords Biodegradation · Bioremediation · Microbial co-culture · Microbial consortia · Organic pollutants · Synergistic effect

10.1 Introduction

Hazardous pollutants in the natural ecosystem are a serious threat to human health and other creatures, which are caused by a wide range of industrial activities such as petrochemical and metallurgical processes as well as the production of paint, textile, and insecticide (Vivienne et al. 2013; Wang et al. 2018).

There are various physico-chemical and biological methods for removing these pollutants from the aqueous and terrestrial environment. These conventional treatment methods, including chemical oxidation, reverse osmosis, ion exchange, and filtration, have usually several drawbacks like limited effectiveness, high cost, and production of more toxic and harmful by-products (Kok Kee et al. 2014).

In the last few years, bioremediation has received more scientific attention as an eco-friendly and cost-effective alternative approach in which living microbial cells play key roles (Bidja Abena et al. 2019; Paradelo and Barral 2009). Bioremediation is a relatively new treatment technique that converts the pollutants to non-toxic substances, which are carbon dioxide, biomass, and water. Microorganisms are ubiquitous in the environment and can use organic pollutants as only carbon and energy sources (Kumar et al. 2011). To enhance bioremediation efficiency, there are different strategies such as bio-augmentation and bio-stimulation (Bidja Abena et al. 2019).

Bio-augmentation is the addition of pure culture or a microbial consortium to biologically clean up a specified contaminated area, such as sediment, soil, or water (Sharma et al. 2018). Typically, bio-augmentation is used when indigenous microorganisms are not capable of degrading recalcitrant toxic compounds such as petroleum hydrocarbons (Qiao et al. 2014). Hydrocarbon biodegradation in the soil can be limited by various forms of nutrients and electron acceptors, such as nitrogen, phosphorus, oxygen, or carbon. Bio-stimulation is based on the addition of nutrients, oxygen, or other electron donors and acceptors to polluted sites to encourage the growth of the indigenous microbial populations, consequently improving the biodegradation process (Adams et al. 2015; Fulekar et al. 2012). Degradation of complex and recalcitrant compounds usually requires the presence of more than a single species of microorganisms (Ayaz and Gothalwal 2014). The cooperation of various microbes as a consortium has great potentiality in bioremediation of hazardous chemicals, and synergistic effects between strains of the culture may improve their efficacy under diverse environmental conditions (Birolli et al. 2019; Wang et al. 2017).

10.2 Co-culture Classifications

In bioremediation technology, various microorganisms (i.e., yeast, fungi, and bacteria) remove the toxic compounds from contaminated sites (Kumar et al. 2011). Each of these biological agents can usually degrade a wide range of contaminants. But since some pollutants are a combination of different components, individual microorganisms are not capable of degrading and eliminating them from the environment. For example, crude oil is a complex mixture with recalcitrant chemical structures composed of saturated hydrocarbons, aromatic hydrocarbons, resins, and asphaltenes (Bao et al. 2012). Despite a wide variety of microorganisms capable of metabolizing petroleum hydrocarbons, none of them can degrade all petroleum components. To overcome this problem, a number of researchers have used mixed cultures of microorganisms (Andersson et al. 2003; Li and Li 2011). Additionally, in most studies, the general approach of bioremediation is to use microorganisms capable of degrading target compounds. While, it is essential to identify the specific intermediate compounds generated during the biodegradation process, because some of these metabolites mainly involve the degradation pathway and have inhibitory effects on microbial activities (Partovinia and Naeimpoor 2014). Therefore, the use of diverse microbial populations capable of consuming intermediate metabolites along with the target contaminant-degrading microorganisms can lead to successful bioremediation. Different microbial strains can collaborate and form a consortium depending on the type of contaminants. Microbial co-cultures are classified as follows.

10.2.1 Bacterial Consortium

Complete degradation of many recalcitrant and complex pollutants such as PAHs requires the action of a co-culture of bacteria. Microorganisms in a bacterial consortium can attack contaminants at different positions and by sequential degradation, mineralize them to harmless products (Kumar et al. 2017; Singh et al. 2014). Members of the consortium may improve bioremediation efficiency in a variety of ways, such as oxidation of the compounds, production of surfactants, and utilization of intermediate metabolites (Baker and Herson 1990). Prpich and Daugulis (2005) have used a mixed microbial population consisted of two *Pseudomonas* sp., and two *Acinetobacter* sp., for the bioremediation of phenol via a polymer-mediated TPPB (two-phase partitioning bioreactors) system. Their results showed that the bacterial consortium was more capable of degrading high concentrations of phenol (2000 mg/L), with decreased lag phase time (10 h), and an increased specific rate of phenol degradation (0.71 (g phenol)(g cell $h-^{1}$) compared to a single pure strain (Prpich and Daugulis 2005). Guo et al. (2017) have investigated the bacterial consortium for bioremediation of PAH-contaminated soil (pyrene and benzo[a]pyrene) in the presence or absence of hydroxypropyl-b-cyclodextrin (HPCD). They observed that PAH mineralization was enhanced after 10 weeks, particularly in the presence of HPCD, which increased the bioavailability of PAHs (Guo et al. 2017). Abraham et al. (2014) have studied biodegradation of pesticides mixture by a bacterial consortium comprised of ten microorganisms. They reported that the bacterial consortium was capable of degrading the pesticide mixture into non-toxic metabolites (Abraham et al. 2014). Accordingly, it would appear that the microbial consortium can be more effective compared to the pure culture (Guo et al. 2017; Ma et al. 2018). Table 10.1 highlights the bioremediation of some pollutants by bacterial consortium used in previous researches. In general, recent studies have shown that bacterial consortium has resulted in improved biodegradation capacity.

10.2.2 Fungal Consortium

Fungi can produce lignin-modifying enzymes, such as laccase and manganese peroxidase that enable them to degrade high molecular weight, complex, or more recalcitrant compounds, including aromatic structures (Chen et al. 2010; Hassan 2014; Zhou et al. 2014). The fungal mycelial networks and hyphal growth allowed fungi to extend the location of their biomass in search of growth substrates and thus overcome motility restrictions in soil and enhanced the degradation efficiency (Ma et al. 2018; Vivienne et al. 2013). A study carried out by Kumari and Naraian (2016) to investigate the efficacy of fungal co-culture (*Pleurotus florida* (PF) and *Rhizoctonia solani* (RS)) in decolorization of synthetic brilliant green carpet industry dye. They reported that employed co-culture removed 98.54% of the dye at concentration 2% (w/v) during 12 days in submerged fermentation, while it was higher than

Table 10.1 Bioremediation of some pollutants using bacterial consortium

Co-cultures	Species	Contaminant	Type of pollutant	Temperature (°C)	Initial concentration	pH	Medium	Bioremediation outcomes	References	Duration
Bacterial	*BF1* and *BF2* and *Pseudomonas putida*	Dye	Chrysoidine and Procion Brilliant Red	28 ± 2	20–100 μg/ml	9–10.5	Aqueous	80% of degradation	Senan and Abraham (2004)	3 days
Bacterial	*Bacillus*, *Pseudomonas*, *Acidobacteria*, sulfur-reducing bacteria	Crude oil	Petroleum Sludge		1% (w/v)	7.5	Sludge	44.01% removal of total petroleum hydrocarbons (TPH)	Devi et al. (2011)	30 days
Bacterial	*Pseudomonas putida* (NII 1117), *Klebsiella* sp. (NII 1118), *Pseudomonas stutzeri* (NII 1119), *Pseudomonas aeruginosa* (NII 1120)	Pesticide	Chlorpyrifos	37	500 mg/kg	7	Soil	65.87% removal	Sasikala et al. (2012)	20 days
Bacterial	*Bacillus subtilis* DNS4, *Variovorax* sp., *Arthrobacter* sp. DNS10, and *Arthrobacter* sp. DNS9	Herbicide	Atrazine	30	100 mg/L		Soil	Partial metabolization	Zhang et al. (2012)	48 h
Bacterial	*Ochrobactrum* sp. N1, *Brevibacillus parabrevis* N2, *B. parabrevis* N3, and *B. parabrevis* N4	Crude oil	Paraffin oil	25	0.5% (w/v)	7.0–7.2	Aqueous	51.1% removal	Bao et al. (2012)	10 days

(continued)

Table 10.1 (continued)

Co-cultures	Species	Contaminant	Type of pollutant	Temperature (°C)	Initial concentration	pH	Medium	Bioremediation outcomes	References	Duration
Bacterial	*Mesorhizobium* sp., *Alcaligenes* sp., and *Bacillus* sp.	PAH		28	9362.1 mg/kg	6.4	Soil	20.2% and 35.8% of total PAHs were removed	Mao et al. (2012)	56 days
Bacterial	*Actinobacteria* and *gamma-proteobacteria phyla*	Petroleum hydrocarbon				7.8	Soil	TPH was decreased from 63.4 mg g^{-1} to 2.5 mg g−1	Gargouri et al. (2014)	30 days
Bacterial	*10 microorganisms*	Pesticide	Chlorpyrifos, monocrotophos and endosulfan	37	300 mg/L of chlorpyrifos, 1000 mg/L of monocrotophos, 1000 mg/L of endosulfan	6.8–7.0	Aqueous	Chlorpyrifos, monocrotophos, and endosulfan were degraded after 2, 3, and 4 days of incubation, respectively	Abraham et al. (2014)	4 days
Bacterial	*Ochrobactrum* sp., *Stenotrophomonas maltophilia*, *P. Ochrobactrum* sp., *Stenotrophomonas maltophilia*, and *P. aeruginosa*	Crude oil		37	3% v/v	7.2	Aqueous	83.49% (C8–C35) removal	Varjani et al. (2015)	75 days
Bacterial	*Bacillus licheniformis (KU297878, KU297879, KU297880*, and *KU297881)*	Crude oil		45, 50, 55	13 g/ L		Aqueous	77.70%, 58.19%, and 51.90%	García-Alcántara et al. (2016)	11 days

Bacterial	*Cupriavidus*, *Achromobacter*, and *Pseudomonas*	Pesticide	Carbofuran	25	50–200 mg/L	6.5	Aqueous	Removal of 100 mg/L of CBF at a HRT of 23 h	Castro-Gutiérrez et al. (2016)	23 h
Bacterial	*Viridibacillus arenosi B-21*, *Sporosarcina soli B-22*, *Enterobacter cloacae KJ-46*, and *E. cloacae KJ-47*	Heavy metals	The mixture of Pb, Cd, and Cu	30	2 mM of heavy metal mixture	8.5	Soil	98.3% for Pb, 85.4% for Cd, and 5.6% for Cu	Kang et al. (2016)	48 h
Bacterial	*Burkholderia*, *Nitratireductor*, *Nevskia*, and *Sulfuritalea*	PAH	Pyrene, benzo [a]pyrene	(25 ± 0.5)	200.0 μg/g of pyrene and 100.0 μg /g of benzo[a]pyrene	4.51	Soil	76% removal	Guo et al. (2017)	10 weeks
Bacterial	*Arthrobacter sulfonivorans*, *Variovorax soli* and *Advenella* sp.	Herbicide	diuron	20 ± 1	10 mg/L		Aqueous	98.8% mineralized	Villaverde et al. (2017)	20 days
Bacterial	*Achromobacter xylosoxidans strain APZ*, *Klebsiella pneumoniae strain AHM*, and *Bacillus mannanilyticus strain AVS*	Dye	Azoic-cum-sulfonic textile mill effluent	25		6.6	Aqueous		Kumar et al. (2017)	
Bacterial	Indigenous bacterial consortium and exogenous *Bacillus subtilis*	Crude oil		30	1% v/v	7.0–7.2	Aqueous	85.01%	Tao et al. (2017)	7 days

(continued)

Table 10.1 (continued)

Co-cultures	Species	Contaminant	Type of pollutant	Temperature (°C)	Initial concentration	pH	Medium	Bioremediation outcomes	References	Duration
Bacterial	Aboriginal Bacterial consortium from sediments collected from the Penglai 19-3 oil platform, Bohai Sea, China	Crude oil		30	2% (w/v)		Aqueous	43.56% for TPH and 51.29% for sediments	Wang et al. (2018)	28 days
Bacterial	*Brevibacterium frigoritolerans*, *Bacillus aerophilus*, and *Pseudomonas fulva*	Pesticide	Phorate	37 ± 1	100, 200, 300 mg/kg	7.61	Soil	97.65–98.31%	Jariyal et al. (2018)	42 days
Bacterial	*Averyella* sp. *4 L*, *Bacillus* sp. *CBMAI 2051*, *Bacillus* sp. *CBMAI 2065*, *Bacillus* sp. *CBMAI 1837*, *Bacillus* sp. *5G*, *Bacillus* sp. *4T*, *Bacillus* sp. *6E*, *Curtobacterium* sp. *CBMAI 1834* and *Pseudomonas* sp. *3F*	Pesticide	Pyrethroid (±)-lambda-cyhalothrin	32	100 mg/L		Aqueous	3.7–43.1% of biodegradation	Birolli et al. (2019)	5 days

Bacterial	Bacterial consortium (BDAM)	Herbicide	Bispyribac sodium		2–5 mg/kg	7.1	Soil	96–100%	Ahmad et al. (2019)	40–60 days
Bacterial	*Raoultella ornithinolytica*, *Bacillus subtilis strain BJ11*, *Acinetobacter lwoffii strain BJ10*, *Serratia marcescens strain PL*, and *Acinetobacter pittii strain BJ6*	Crude oil		30	49,300 mg/kg	8.03	Soil	94% removal	Bidja Abena et al. (2019)	10 days

individual microbial cells (82.12% with PF and 68.89% with RS) (Kumari and Naraian 2016). Chen et al. have examined biosorption and biodegradation of polycyclic aromatic hydrocarbons in aqueous solutions by a live and heat-killed consortium of white-rot fungi. Linear and non-competitive sorption isotherms, indicating the primary mechanism of bio-sorption is the partitioning of PAHs into fungal biomass. They reported that in 1 week, phenanthrene (70–80%) and pyrene (90%) were degraded by live white-rot fungi (Chen et al. 2010).

10.2.3 Fungal–Bacterial Consortium

Many contaminants such as long-chain alkanes and petroleum aromatic hydrocarbons (PAHs) with low bioavailability, hydrophobicity, and high molecular weight often faced with mass transfer limitation (Boonchan et al. 2000; Cheng et al. 2017). Simultaneous use of bacteria and fungi may increase the bioremediation process. Fungi can transfer bacteria in soil and, thus, increase bacterial access to the otherwise inaccessible contaminants (Ellegaard-Jensen et al. 2014). Some fungus species are also able to degrade different PAHs. Examples of different fungal–bacterial consortia used for different contaminants are summarized in Table 10.2.

Yuan and co-workers have used indigenous bacterial consortium and exogenous fungus *Scedosporium boydii* for bioremediation of crude oil. Their results showed that crude oil biodegradation rate was enhanced from 61.06% to 81.45% when the inoculation ratio of bacteria to fungi was 3:1. The evenness, relative abundance, and diversity of bacteria were also increased observably in the defined co-culture (Yuan et al. 2018). Cheng et al. (2017) have investigated the performance of fungal–bacterial consortium in biodegradation of mono-chlorobenzene (CB) at the initial concentration of 220 mg L^{-1}, and they affirmed that a microbial consortium composed of bacteria and fungi performs better than a single microorganism.

But it should be noted that bacteria and fungi may also exhibit antagonistic interactions (Ellegaard-Jensen et al. 2014(. Andersson et al. (2003) in their research have observed that in bioremediation of PAH-contaminated soil, the inoculation with the white-rot fungi *Pleurotus ostreatus* had a substantial adverse effect on the indigenous soil microorganisms. While, in the soil inoculated with brown-rot fungi, *Antrodia vaillantii* metabolites accumulated, and adverse effects were not observed on the indigenous microorganisms. Similarly, Kim et al. have examined separately the function of two fungi *Penicillium* sp. and *Aspergillus terreus* with bacteria *Rhodococcus* sp. for bioremediation of PAH-polluted soil. The co-culture of *Penicillium* sp. and *Rhodococcus* sp. was efficient for the removal of different PAHs from contaminated soil as well as the toxicity reduction of soil. But the co-culture of the fungi *A. terreus* and *Rhodococcus* sp. did not show any synergistic interactions (Kim and Lee 2007). Therefore, it can be concluded that by selecting a proper set of microorganisms as co-culture, the effective bioremediation can be achieved.

Table 10.2 Summary of studies on fungal–bacterial consortia

Co-cultures	Species	Contaminant	Type of pollutant	Temperature (°C)	Initial concentration	pH	Medium	Bioremediation outcomes	References
Bacterial–fungal	*Stenotrophomonas maltophilia*, *Penicillium janthinellum*	PAH	Benzo[a] pyrene	25	250 mg/L	6	Aqueous/ soil	25% mineralization	Boonchan et al. (2000)
Bacterial–fungal	Bacterial strain *Rhodococcus* sp. IC10 and two fungi *Aspergillus terreus* and *Penicillium* sp.	PAH	Snthracene, phenanthrene, and pyrene	25		6.8	Soil	Pollutants were totally biodegraded by days 68, 54, and 64 days	Kim and Lee (2007)
Bacterial–fungal	Fungi *Cen. echinulata* and bacteria *Vibrio rumoiensis*	PH		28	10.2 g/kg	6.7	Sediment	60% removal of TPH	Li and Li (2011)
Bacterial–fungal	*Pseudomonas aeruginosa* and *Aspergillus nicer*/ *Phanerochaete chrysosporium*	Dye	Distillery effluent	25			Aqueous	87.8% decolorization	Pal and Vimala (2012)
Bacterial–fungal	Bacteria (*Sphingomonas* sp. SRS2, *Variovorax* sp. SRS16, and *Arthrobacter globiformis* D47) and fungi (*Mortierella* sp. LEJ702 and LEJ703)	Herbicide	Diuron		100 μg/kg	7	Aqueous	Mineralizing 32.2 ± 5.7%	Ellegaard-Jensen et al. (2014)

(continued)

Table 10.2 (continued)

Co-cultures	Species	Contaminant	Type of pollutant	Temperature (°C)	Initial concentration	pH	Medium	Bioremediation outcomes	References
Bacterial–fungal	*Sphingobacteriia*, *Flavobacteriia*, *Bacteroidia*, *Nitrospirales*, and *Phycisphaerae*/*Geotrichum candidum* and *Candida pseudolambica*	Dye	Reactive Red	25	120 mg/L	7	Aqueous	80% decolorization	Zhou et al. (2014)
Bacterial–fungal	Bacteria *S. marcescens* L-11, *actinomycetes*, *S. rochei* PAH-13 and white rot fungus, *P. chrysosporium* VV-18	PAH	Fluorene, anthracene, phenanthrene, and pyrene	30 ± 1	200 μg/ml	6.8 ± 0.3	Soil	83.5–100%	Sharma et al. (2016)
Bacterial–fungal	Indigenous bacterial consortium (*Paraburkholderia* sp. and *Paraburkholderia tropica*) and exogenous fungus *Scedosporium boydii*	Crude oil		30	1% v/v		Aqueous	81.45%	Yuan et al. (2018)

10.2.4 Yeast–Bacterial Consortium

In contrast to white-rot fungi, the applications of eukaryotic microorganisms such as yeast in the bioremediation processes have not been fully explored (Walls et al. 2019). While the capability of some yeast species in the mineralization of xenobiotic organic compounds (e.g., azo dyes), petroleum hydrocarbons (PAHs), and phenol has been reported (Chen et al. 2015; Ehrhardt and Rehm 1985; He et al. 2004). Also, the nitrogen and phosphorus contents of yeast (10% and 3–5% of a yeast cell dry weight, respectively) suggest that yeasts may be capable of removing nutrients from wastewaters (Walls et al. 2019). Yeast, like bacteria and fungi, is found in a myriad of environments and can have antagonistic or synergistic interactions with other microorganisms (Wang et al. 2009). The presence of yeasts can inhibit the growth of white-rot fungi due to their good growth at pH 5–6 in carbohydrate-based media and their higher growth rates compared with filamentous fungi (Šlosarčíková et al. 2017). But many bacteria and yeasts can help each other to degrade some toxic intermediate metabolites produced during the bioremediation process (Chen et al. 2015). The appropriate combination of yeast and bacteria has been shown more powerful potential in the treatment relative to pure culture systems (He et al. 2004). In a study by Zhang et al. (2014), the effects of the bacterial consortium, yeast, and yeast–bacterial co-culture on bioremediation of oil-contaminated soil were compared. They observed that after 48 days, the initial heavy petroleum contamination level (TPH) was reduced 56%, 40.1%, and 37.7% in yeast–bacterial, bacterial and yeast treatments, respectively. Also, the maximum PAH degradation rate occurred in yeast–bacterial co-culture (32.0%), whereas 25.3% and 11.7% were observed with treatments by using of yeast and yeast–bacterial, respectively (Zhang et al. 2014). Chen et al. (2015) found the significant potential of a consortium consisting of the bacterium *Pseudomonas* sp. MO2A and the yeast *Debaryomyces maramus* CW36 for enhancing degradation and detoxification of polychlorinated biphenyls (PCBs) in the aqueous phase. During 14 days of incubation, in the pure culture of yeast and bacterium, the degradation efficiencies of total PCBs were 57.0% and 27.8%, respectively. While the co-culture of the bacterium and the yeast showed promoted PCB degradation (69.6%). Their results indicated that the co-culture of bacteria-yeast was more effective for PCB degradation than any single culture due to their complementary role in degradation of toxic intermediates (Chen et al. 2015).

10.2.5 Microalgae-Bacterial Consortium

Although bacteria, fungi, and yeast have mainly been identified as the major microorganisms that remediate polluted environments, many algal species also have the ability of consuming a broad category of pollutants including nitrates, phosphates, phenol, black oil, heavy metals (HMs), and benzopyrene (Maza-Márquez et al. 2017; Mondal et al. 2019). Microalgae are ubiquitous photosynthetic microorganisms that live in both marine and freshwater (Mondal et al. 2019). They can use sunlight, water, and carbon dioxide (or inorganic carbon) as energy and carbon sources and convert them to algal biomass and exogenous oxygen (O_2). Given that the most important requirement of aerobic bacterial is oxygen, the co-culture of bacteria and microalgae can be an efficient, cost-effective, and straight forward solution for the removal or biotransformation of nutrients and pollutants from surface water, as well as wastewater (Mujtaba et al. 2017). Oxygen consumed by aerobic bacteria converts to carbon dioxide, the carbon source of microalgae. Also, bacteria play an essential role in the growth of algal by the release of vitamins and phytohormones. All of the above, plus the ability of biofilm formation on the solid surfaces immersed in aqueous media by microalgae and bacteria, leads to the establishment of a sustainable consortium (Liu et al. 2017).

Ji and co-workers have investigated the ability of two microalgae-bacteria consortia (*Chlorella vulgaris-Bacillus licheniformis* and *Microcystis aeruginosa-Bacillus licheniformis*) for the removal of nutrients from synthetic wastewater. They observed that on the tenth day, the *Chlorella vulgaris-B. licheniformis* system removed 86.55%, 80.28%, and 88.95% of soluble chemical oxygen demand (sCOD), total dissolved phosphorus (TDP), and total dissolved nitrogen (TDN), respectively. But, the *Microcystis aeruginosa-B. licheniformis* system only removed 65.62%, 70.82%, and 21.56% of sCOD, TDP, and TDN, respectively (Ji et al. 2018). In another study, Fito and Alemu (2018) studied the potential of native microalgae–bacteria consortium (*Chlorella* sp., *Chlamydomonas* sp., and *Scenedesmus* sp. and naturally existing municipal wastewater bacteria) to eliminate nutrients and organic pollutants from primary-treated municipal wastewater. They reported that the maximum removal of TKN 69%, TP 59%, PO_4^{3-}, P 73%, COD 84%, and BOD_5 85% was observed in the algae consortia and wastewater-borne bacterial combined treatment system, whereas for bacteria stand-alone system, the maximum removal of TKN 31%, TP 56%, PO_4^{3-}, P 50%, COD 44%, and BOD_5 52% was recorded (Fito and Alemu 2018).

10.2.6 Other Microbial Consortia

In addition to the microbial consortia mentioned above, the researchers have used other co-cultures such as yeast, algae, yeast–algae, and algae–fungi consortia in their studies. A study carried out by Kamyabi et al. (2017) investigated the capability of yeast consortium (*Sarocladium* sp. and *Cryptococcus* sp.) as compared to their individual cultures in surfactant production and oil degradation. They affirmed that oil removal and biomass production in the co-culture were about 28% and 35% higher than individual cultures of *Sarocladium* sp. and *Cryptococcus* sp., respectively. Also, the most efficient bio-surfactant production was achieved in the case of a co-culture (Kamyabi et al. 2017).

Walls and co-workers have used a native co-culture of microalgae (*Scenedesmus* sp.) and wild yeast for simultaneous municipal wastewater treatment and bioethanol production in non-sterile, heterotrophic bioreactors. Based on their results, the microalgae and yeast co-cultures achieved a high level of nutrient removal (96% nitrate, 100% TAN, and 93% orthophosphate) in 3 days. Also, yeast provided the additional advantage of aerobic fermentation, possibly allowing simultaneous wastewater treatment and bioethanol production (Walls et al. 2019).

Studies conducted by Kulkarni et al. (2014) have shown the effectiveness of *lichen Permelia perlata* (fungi that live in association with phototrophic algae) for biotransformation and detoxification of toxic textile dye Solvent Red 24 (SR24). They reported that the algae–fungal consortium is the beneficial biological system for bioremediation technology (Kulkarni et al. 2014).

In another study, López-Pacheco et al. (2019) used a microalgae consortium consisting of *Arthrospira maxima* and *Chlorella vulgaris* for removal and biotransformation of 4-nonylphenol. Their results indicate that *C. vulgaris* is more resistant to 4-NP than *A. maxima* (cell growth inhibition by 4-NP of 99%), and this microalgae consortium reduced up to 96% of 4-NP in water in the first 48 h of culture (López-Pacheco et al. 2019).

10.3 Application of Microbial Consortium in Bioremediation

The microbial co-cultures can be employed in the removal of various pollutants from contaminated environments. In recent years, numerous investigations have confirmed that the different microbial consortia, including bacterial, fungal, fungi–bacteria, and yeast–bacteria, are capable of degrading and mineralizing organic pollutants.

10.3.1 Organic Pollutants

Increased levels of organic pollutants by anthropogenic activities are a global concern because these compounds are toxic and persistent in the environment and can cause an imbalance in the ecosystem by adversely affecting flora and fauna. Many different types of microorganisms such as fungi and bacteria are constantly at work in nature to degrade organic compounds, but the effectiveness of bioremediation processes in the detoxification of hazardous organic pollutants directly depend on chemical structure and concentration of pollutants, the availability of nutrients, and above all the biodegradation ability of the microorganisms (Adams et al. 2015; Bidja Abena et al. 2019; Cerniglia 1993). Therefore, the selection of suitable species is of great significance to succeed in bioremediation.

10.3.1.1 Polycyclic Aromatic Hydrocarbons (PAHs)

Polycyclic aromatic hydrocarbons (PAHs) are highly toxic and hazardous compounds with potential carcinogenicity and mutagenicity that released into the environment through both natural and human processes (Mao et al. 2012; Perelo 2010; Borràs et al. 2010). Low water solubility and high adsorption coefficient result in their accumulation in soils and sediments (Kim and Lee 2007; Perelo 2010). The Environmental Protection Agency (EPA) has introduced 16 PAHs, including pyrene, naphthalene, anthracene, fluorene, and phenanthrene as priority pollutants of the aquatic and terrestrial ecosystems (Sharma et al. 2016). One of the major challenges facing the bioremediation of petroleum aromatic hydrocarbon-contaminated sites is the failure to remove high-molecular-weight PAHs (Boonchan et al. 2000). Some different bacterial strains, including species of *Pseudomonas*, *Alcaligenes*, *Mycobacterium*, *Rhodococcus*, *Burkholderia*, and *Cycloclasticus* are efficient in utilizing and degrading lower molecular weight PAHs (Kim and Lee 2007) while high-molecular-weight PAHs could be better degraded by the mixed cultures of white-rot fungi like *Phanerochaete chrysosporium* and bacteria (Borràs et al. 2010; Sharma et al. 2016). As an example, Guo and co-workers have observed that mixed microbial cultures appear to be more advantageous than pure cultures in the biodegradation of PAHs (Guo et al. 2017). A list of biodegradation of PAHs using different microbial consortium is given in Table 10.3. Among the microbial consortium studied, bacterial consortia and bacterial–fungal consortia have been most widely used by many researchers in the bioremediation of PAH-polluted environments.

Kim and Lee (2007) have studied the degradation of PAHs in soil by mixed microbial co-culture, which consists of fungal and bacterial species of *Penicillium* sp. and *Rhodococcus* sp. IC10, respectively. Individual strains and a mixed consortium were tested for their ability to remove PAHs from the soil. At the end of the incubation period, *Rhodococcus* sp. IC10, *Penicillium* sp., and the consortium removed 32%, 45%, and 66.7% of anthracene, 10%, 15%, and 16% of fluoranthene, 58%, 64%, and 72.8% of phenanthrene, and 20%, 46.5% and 68.4% of pyrene, respectively. According to their results, the consortium had better performance over single strains for the removal of different PAHs (Kim and Lee 2007).

10.3.1.2 Pesticides

Pesticides are substances or a mixture of substances for preventing, destroying, repelling, mitigating the pests, and increasing agricultural production that is classified by their target species into subcategories of herbicides, insecticides, fungicides, bactericides, and others. In recent years, pesticides have been widely used in agricultural applications which led to the diffusion of these pollutants in the environment. Pesticides have adverse effects on human health and can pose a threat to the safety of ground and surface water (Golding 2006). Most of the pesticides and their

Table 10.3 Biodegradation of petroleum hydrocarbons using microbial consortium

Co-cultures	Species	Contaminant	Type of pollutant	Temperature (°C)	Initial concentration	pH	Medium	Bioremediation outcomes	References	Duration
Bacterial–fungal	*Stenotrophomonas maltophilia*, *Penicillium janthinellum*	PAH	Benzo[a] pyrene	25	250 mg/L	6	Aqueous	25% mineralization	Boonchan et al. (2000)	49 days
Yeast–bacterial	*Bacillus subtilis*, *Bacillus megaterium*, *Achromobacter xylosoxidans*, *Pseudomonas fluorescens*, *Candida tropicalis*, and *Rhodotorula dairenensis*	PH		30	21.5% (w/w, dry weight basis)	7.2	Oily sludge	Reducing 92.5% of aliphatics, 79.3% of aromatics, 48.6% of NSO-containing compounds, 31.8% of asphaltenes, and 80.6% of TPH	He et al. (2004)	1-year microcosm experiment
Fungal	White-rot fungi *(CW-1)*	PAH	Phenanthrene and pyrene	25 ± 0.5	1.0 mg/L phenanthrene 0.1 mg/L pyrene		Aqueous	Phenanthrene (70–80%) and pyrene (90%)	Chen et al. (2010)	7 days
Bacterial–fungal	*Fungi Cun. Echinulata* and *bacteria Vibrio rumoiensis*	PH		28	10.2 g/kg	6.7	Sediment	60% removal of TPH	Li and Li (2011)	50 days
Bacterial	*Mesorhizobium* sp., *Alcaligenes* sp., and *Bacillus* sp.	PAH		28	9362.1 mg/kg	6.4	Soil	20.2% and 35.8% of total PAHs were removed	Mao et al. (2012)	56 days
Bacterial	*Actinobacteria* and *gamma-proteobacteria phyla*	PH				7.8	Soil	(TPH) was decreased from 63.4 mg g^{-1} to 2.5 mg g^{-1}	Gargouri et al. (2014)	30 days

(continued)

Table 10.3 (continued)

Co-cultures	Species	Contaminant	Type of pollutant	Temperature (°C)	Initial concentration	pH	Medium	Bioremediation outcomes	References	Duration
Yeast–Bacterial	*Bacillus subtilis*, *Pseudomonas fluorescens*, *Streptococcus faecalis*, and *Candida tropicalis*	PAH		25	21,552 mg/kg	8.2	Soil	56% for total petroleum hydrocarbon and 32% for polycyclic aromatic hydrocarbons	Zhang et al. (2014)	48 days
Bacterial–fungal	bacteria *S. marcescens L-11*, *Actinomycetes*, *S. rochei PAH-13*, and white-rot fungus, *P. chrysosporium VV-18*	PAH	Fluorene, anthracene, phenanthrene, and pyrene	30 ± 1	200 μg/ml	6.8 ± 0.3	Soil	83.5–100%	Sharma et al. (2016)	30 days
Bacterial	*Burkholderia*, *Nitratireductor*, *Nevskia*, and *Sulfuritalea*	PAH	Pyrene, benzo [a]pyrene	25 ± 0.5	200.0 μg/g of pyrene and 100.0 μg/g of benzo[a] pyrene	4.51	Soil	76% removal	Guo et al. (2017)	10 weeks

metabolites are too persistent in the environment, and bioremediation can be an effective method for the elimination of their residues from contaminated areas (Birolli et al. 2019). Since some individual strains are only capable of degrading partially of a particular pesticide, a bacterial consortium can assist in the complete mineralization of the contaminant. In a study by Abraham et al. (2014), complete degradation of organophosphorus and organochlorine pesticides contacting 300 mg/L of chlorpyrifos, 1000 mg/L of monocrotophos, 1000 mg/L of endosulfan was observed within 24 h of incubation by a bacterial consortium comprised of 10 microorganisms. Castro-Gutiérrez et al. (2016) similarly reported that consortium of bacteria *Cupriavidus*, *Achromobacter*, and *Pseudomonas* were capable of degrading high concentrations of carbofuran (CBF) and also other carbamates such as aldicarb, methiocarb, and methomyl in batch bioreactors. Nonetheless, compared with mixed cultures, the single strains could not degrade all the tested carbamates (Castro-Gutiérrez et al. 2016).

Furthermore, the bacterial–fungal consortium increases bacterial access to the pollutants in the contaminated soil, especially in heterogeneous soil environments. In a mechanism referred to as the "fungal highway," bacteria extend their living area and disperse along fungal mycelium. In the study conducted by Ellegaard-Jensen et al. (2014) on diuron herbicide, several fungal–bacterial consortia were investigated by combining different diuron-degrading bacteria and fungi. The fastest mineralization of diuron was obtained in the sand with an added microbial consortium consisting of both degrading bacteria and fungi (*Mortierella* LEJ702, *Variovorax* SRS16, and *A. globiformis* D47), whereas the single bacterial strains or other consortium degraded only about almost 10% of the diuron (Ellegaard-Jensen et al. 2014). Therefore, it can be concluded that microbial consortia have shown superior efficiency in pesticides biodegradation.

10.3.1.3 Dyes

Textile, printing, and dyeing industries discharge large amounts of highly colored wastewater in their nearby water resources (Lalnunhlimi and Krishnaswamy 2016; Senan and Abraham 2004). Synthetic dyes and their intermediates causing environmental concern because of their color, recalcitrant compounds, and potential toxicity on the animal and human health (Kumari and Naraian 2016). Physicochemical treatment techniques of dye wastewater like filtration, adsorption, and photolysis have disadvantages of being highly expensive and the emission of toxic substances (Kumar et al. 2017; Senan and Abraham 2004). On the contrary, bioremediation using the natural degradation capacity of the indigenous and native microorganisms (bacteria, yeast, fungi, etc.) has shown the most viable and cost-effective technology. The microbial consortium is a potential strategy for the improvement of bioremediation. He et al. (2004) have used a microbial consortium consisting of a white-rot fungus and a *Pseudomonas* bacterium for decolorization of azo dye (Direct Fast Scarlet 4BS) under static and shaking culture. Their results show that the extracellular enzyme-producing rate of white-rot fungus is increased due to the synergistic reaction with *Pseudomonas*, and consequently the decolorization rate of 4BS is improved remarkably that led to the complete mineralization. Based on their observation *Pseudomonas* could not completely degrade 4BS, which indicated that decomposition of 4BS needs the synergistic reaction of versatile enzymes coming from different individual strains (He et al. 2004).

10.3.2 Inorganic Pollutants

Many inorganic pollutants including metals compounds, heavy metals, cyanides, nitrates, sulfates, and industrial waste are causing acute negative impacts on aquatic organisms as well as on terrestrial creatures (Shekhar et al. 2020). Most of the inorganic wastes are non-biodegradable that allow them to persist in the environment. But, under anaerobic conditions and in the absence of oxygen, various inorganic compounds such as Fe(III), Mn(IV), nitrate, and sulfate can be excellent electron acceptors to the improvement of organic contaminants bioremediation (Devi et al. 2011; Lee et al. 2012). Since there have been few microorganisms in nature that are capable of degrading inorganic contaminants, they should be used according to their efficiency for the type of contaminant (Dixit et al. 2015).

10.3.2.1 Heavy Metals

The accumulation of heavy metals (Cd, Cr, Cu, As, Pb, and Hg) in aquatic and terrestrial environments caused by mining, industrial, and agricultural activities led to serious environmental problems (Kang et al. 2016; Shekhar et al. 2020). Heavy metals are non-biodegradable as they can inhibit microbial growth and activities. However, there are numerous microorganisms in nature that rely on varying amounts of heavy metals as essential micronutrients for growth and survival, consequently can easily convert them into non-toxic forms (Dixit et al. 2015). A study carried out by Kang et al. (2016) showed the effectiveness of a bacterial consortium on the bioremediation of a mixture of Pb, Cd, and Cu in soil. Based on their results, the consortium including four bacterial strains (*Viridibacillus arenosi* B-21, *Sporosarcina soli* B-22, *Enterobacter cloacae* KJ-46, and *E. cloacae* KJ-47) showed significantly higher growth rate and more efficiency for the remediation of heavy metals compared to the single strain cultures. They reported 98.3%, 85.4%, and 5.6% remediation of Pb, Cd, and Cu, respectively, after 48 h by the bacterial mixture. Compared with single-strain cultures, the bacterial mixtures exhibited a considerably higher growth rate, urease activity, resistance to heavy metals, and also higher heavy metal bioremediation capacity than individual cultures (Kang et al. 2016).

10.4 Factors Affecting Consortium Performance

Bioremediation efficiency using microbial consortium can be limited by many factors such as environmental variables, microbial competitions, and different species of microorganisms in a consortium (Cheng et al. 2017; Hibbing et al. 2010). Hence, the object of this section is to briefly describe the environmental factors affect the microbial consortium activity.

10.4.1 Environmental Factors

Various environmental factors, including pH, moisture, and temperature, can directly affect the microbial activities (Adams et al. 2015; Ayaz and Gothalwal 2014). Optimization of these variables has an important role, providing better conditions for microbial growth and thus can provide more efficient bioremediation (Varjani et al. 2015).

10.4.1.1 pH

The pH of aquatic and terrestrial environments can change by both natural and anthropogenic processes, and the resulting pH variation may have direct and indirect effects on the degradation ability of microbial populations (Wu et al. 2017). Generally, extreme pH conditions have a negative impact on bacterial diversity and microbial activities (Rahman et al. 2002). Fungi are much more resistant to acidic conditions than bacteria. The optimal conditions for fungal growth vary between pH values of 3 and 7 depending on the species, while studies have shown most bacteria grow best in neutral and alkaline conditions (pH > 7) (Mani and Kumar 2014; Walse et al. 2011). The pH also strongly influences both abiotic (i.e., carbon availability, nutrient availability, and the solubility of metals) and biotic factors (i.e., biomass composition of fungi and bacteria) in contaminated soil (Rousk et al. 2009). The effect of pH on the decolorization of textile dye using bacterial consortium RVM 11.1 was studied by Moosvi et al. (2005). They reported that the rate of decolorization increased with an increase in pH value from 6 (1.47 mg/l/h) to 8.5 (2.41 mg/l/h). The maximum rate of decolorization was gained between pH 7 and 8.5, and when the initial pH of the medium was below 5.5, no decolorization was observed (Moosvi et al. 2005). Gou et al. (2009) have reported that the optimum pH was at 3 for Reactive Brilliant Red X-3B decolorization by a fungal–bacterial consortium comprising of *Penicillium* sp. QQ and *Sphingomonas xenophaga* QYY. Whereas, in the same study, optimum pH for *Penicillium* sp. QQ was observed at 4 or 5. In another study conducted by Lu et al. (2008), the optimal pH for decolorization of 1-aminoanthraquinone-2-sulfonic acid by *Sphingomonas xenophaga* QYY was 6–7. Also, Qu et al. (2005) affirmed that in decolorization of bromoamine acid by

Sphingomonas xenophaga QYY, the most suitable pH was different, 6.5 for growing cells and 8.5 for resting cells, which meant that the optimal pH of a consortium is not necessarily the mean pH values of the consortium members and can be more or less than the optimum pH of individual strains in the consortium or average pH. Therefore, it is noteworthy that in the application of microbial consortium, pH should be considered as an influencing factor.

10.4.1.2 Temperature

Temperature is an important factor that directly affects the microbial activity and, consequently, the rate and extent of bioremediation (Adams et al. 2015; Mani and Kumar 2014). The optimal temperature differs among species, but in general, biochemical reaction rates to an extent rise with increasing temperature and slows with decreasing temperature (García-Alcántara et al. 2016; Ijoma and Tekere 2017). As reported by Ayaz and Gothalwal (2014) for successful biodegradation of complex hydrocarbons by a microbial consortium (Qs1, Qs2, and Qs5), the temperature must be higher than 25 °C. Their results also showed that the growth rate of the bacterial consortium and individual bacterial increased with increasing temperature, and the highest growth rate was observed at 35 °C (Ayaz and Gothalwal 2014). In another study, Chaudhari and Kodam (2010) have examined the optimum temperature for thiocyanate biodegradation at initial concentration of 2500 mg/L by the co-culture (*Klebsiella pneumoniae* and *Ralstonia* sp.). The consortium was able to degrade the maximum thiocyanate in the temperature of 37 °C and could also maintain thiocyanate removal efficiency in the temperature range 30–40 °C (Chaudhari and Kodam 2010). However, different optimum temperatures have been observed for individual *Klebsiella pneumoniae* and *Ralstonia* sp. in the other previous studies. For example, in a study by Ali et al. (2018), the optimum temperature for kerosene biodegradation by *Klebsiella pneumoniae* sp. was observed at 35 °C (Ali et al. 2018) and in another study on ethanethiol degradation by *Ralstonia* sp., Sedighi et al. (2013) reported that the optimal growth temperature was 30 °C (Sedighi et al. 2013). Therefore, it can be generally inferred that the optimum temperature of a consortium can be different from the optimum temperatures that are obtained by the pure microbial culture. However, more investigation is required about temperature effect to improve biodegradation capacity of microbial consortium.

10.4.1.3 Moisture

Moisture is another essential factor that influences the rate of microbial growth and biochemical activity. The optimum presence of water in the contaminated soils (12%–25%) enables the diffusion of nutrients and oxygen supplies during the degradation process (Adams et al. 2015; Piakong and Nur Zaida 2018). Both high and low moisture contents can have a strong negative impact on bacterial and fungal growth. Excessive soil moisture due to the poor aeration is unfavorable to aerobic bacteria, and droughts often result in a decrease in the microbial populations and activity, especially for fungus (Borowik and Wyszkowska 2016; Schimel et al. 1999). Enzymes in the soil are also influenced by moisture content because they need water to sustain their vital operations (Borowik and Wyszkowska 2016). The study conducted by Piakong and Nur Zaida (2018) investigated the effect of various parameters including pH, temperature, and moisture content in the bio-augmentation of oil sludge contaminated soil by single strains and microbial consortium at two different concentration levels (5% and 10%). Based on their report, the soil moisture of treated soil in both concentrations studied was in the range of 5.21–23.15%. They reported that at 5% oil sludge, the moisture content was the lowest by 3.05-fold as compared to 10% concentration, and consequently the microbial activity in single strains and microbial consortium at 5% concentration of oil sludge was lower. Their finding suggested that the watering process has to be done regularly to achieve the optimum soil moisture content for the hydrocarbon degradation process (Piakong and Nur Zaida 2018).

10.4.1.4 Initial Pollutant Concentration

The growth rate and yield of microorganisms as well as the enzyme activity are sensitive to high contaminant concentrations (Raj et al. 2007; Yu et al. 2019). For instance, the high concentration of organic pollutants like petroleum hydrocarbons (PH) can have inhibitory effects on microbial populations (Speight and El-Gendy 2018). Furthermore, the initial concentration of compounds affects the rates of uptake and mineralization of many organic compounds (Sathishkumar et al. 2008). In the study conducted by Rahman and co-workers, the effect of various oil concentration (1%, 2.5%, 5%, 7.5%, and 10%) on the biodegradation of Bombay High (BH) crude oil was investigated by a mixed bacterial consortium (*Micrococcus* sp. GS2–22, *Corynebacterium* sp. GS5–66, *Flavobacterium* sp. DS5–73, *Bacillus* sp. DS6–86, and *Pseudomonas* sp. DS10–129). They observed that an increase in crude oil concentration (1–10%) caused a decrease in the percentage of degradation (from 78% to 52%) (Rahman et al. 2002). Similarly, Lahel et al. (2016) have studied the effects of pollutant concentration (in the range of 5000–15,000 mg/kg-soil) on the bioremediation of diesel contaminated soil by mixed microbial consortia. They reported that the favorable diesel concentration for the bioremediation of diesel-contaminated soil was approximately 10,000 mg/kg-soil, and the toxicity of diesel on microorganism was observed with increasing diesel concentration (Lahel et al. 2016).

Based on the results of previous researches, since in a mixed culture, the populations are different from one another, in terms of media conditions, optimization of various factors (pH, temperature, moisture, and initial pollutant concentration) involved in bioremediation efficiency is probably required to obtain a stable culture and a satisfactory result (Cao et al. 2019; Del Panno et al. 2005; Wu et al. 2017).

10.4.2 Microbial Interactions

Microbial species under mixed culture conditions invariably interact with each other as well as with the abiotic part of their environment (Fredrickson and Stephanopoulos 1981). Microorganisms in most ecosystems often face limited space and a constant battle for resources, which these conditions give rise to conflict. Competition for a limiting resource may be classified as antagonistic, neutral, or beneficial for the microbes (Ijoma and Tekere 2017; Stubbendieck and Straight 2016).

10.4.2.1 Synergistic Effect

The synergistic relationship between different species in a consortium is very important for the optimal bioremediation and other industrial fermentation. Many microorganisms gain benefits while being a close association with other species (Ijoma and Tekere 2017). For example, as each strain has its own metabolic activity, it may produce toxic intermediate metabolites during the biodegradation process that can be utilized by other strains (Bidja Abena et al. 2019; Guo et al. 2017; Piakong and Nur Zaida 2018). In a study by Kamyabi et al. (2017), the co-culture ability of two yeast (*Sarocladium* sp. and *Cryptococcus* sp.) was investigated in surfactant production and oil degradation. According to their observation, the synergistic effect of co-culture resulted in 28% and 35% increase in oil degradation and biomass production, respectively, compared to the individual cultures (Kamyabi et al. 2017). Furthermore, in the degradation of a particular contaminant, one species is able to metabolize some compounds, and other compounds are metabolized by the other members in the consortium (Tao et al. 2017; Yuan et al. 2018). The interaction between members of an atrazine degrading consortium named DNC5 has been researched by Zhang et al. (2012). Based on their findings, the consortium DNC5 degraded all of the atrazine within approximately 32 h, and a synergistic effect was observed between consortium members. Their experiments showed that each community member improves the biodegradation of atrazine by playing a significant role. *Arthrobacter* sp. DNS10 was the only strain capable of mineralizing atrazine to cyanuric acid. Then *Bacillus subtilis* DNS4 and *Variovorax* sp. DNS12 utilized cyanuric acid during the atrazine degradation process, and finally, the last strain *Arthrobacter* sp. DNS9 was involved in reducing isopropylamine that inhibited the atrazine degrading species (*Arthrobacter* sp. DNS10) (Zhang et al. 2012). In another study carried out by Bidja Abena et al. (2019), the potential of five bacterial strains for crude oil degradation was evaluated individually and as a mixed consortium. Their findings showed that single strains (*Raoultella ornithinolytica* strain PS, *Bacillus subtilis* strain BJ11, *Acinetobacter lwoffii* strain BJ10, *Acinetobacter pittii* strain BJ6, and *Serratia marcescens* strain PL) achieved 50.0–83.5% of degradation, while the consortium comprising the above five strains degraded more than 94.0% of crude oil after 10 days of incubation. They affirmed that these strains as a consortium have a good potential of application in the remediation of crude oil-contaminated environments (Bidja Abena et al. 2019).

10.4.2.2 Antagonistic Effect

A consortium could be ineffective as a result of antagonistic interaction among members of the consortium. A microbial population by producing substances that have inhibitory or toxic effects on other microorganisms can negatively impact their growth and activity. Liang et al. (2018) have investigated the potential antagonism between members of a microbial consortium composed of *Donghicola* sp. CT5, *Bacillus* sp. CT6, *Alcaligenes* sp. CT10, and *Pseudomonas* sp. ZS1. They demonstrated that ZS1 growth is antagonized by other strains and ZS1 also exhibited antagonistic effects against CT5 and CT6. Co-growth analysis and plate inhibitory assay showed that CT10 antagonized against ZS1. Their results indicated that CT10 produced several antimicrobial compounds including cyclodipeptide c-(L-Pro-L-Phe), which was known to inhibit the growth of *Pseudomonas* sp. (Liang et al. 2018). Interactions between members of a microbial consortium can also be competitive; this would mean that different microbial populations compete for access to nutrients and other limiting resources of the environment (Hibbing et al. 2010). In a study by Piakong and Nur Zaida (2018), the potential of single and microbial consortium consisting of *P. aeruginosa*-BAS-Cr1, *S. paucimobilis*-ReTOS-Cr1, and *S. maltophilia*-RAS-Cr1 was examined to remediate oil sludge-contaminated soil. Based on their observation, the single strain *P. aeruginosa*-BAS-Cr1 has the highest oil-degrading capacity compared to microbial consortium. They expressed that the inefficiency of microbial consortium might be due to the nutrient stress and competition between three single strains (Piakong and Nur Zaida 2018). In another study, Borràs et al. investigated the effect of bacteria *Pseudomonas aeruginosa* and *Rhodococcus erythropolis* on growth, biochemistry, and biodegradation efficiency of two model species of white-rot fungi capable of PAH degradation. Their results represented a significant decrease in the degradation of total PAHs in the presence of bacteria. Also, live bacteria reduced the laccase levels in the soil about five times, but they did not affect the capability of the two fungal organisms to colonize soil and did not influence the fungal growth yields (Borràs et al. 2010).

10.4.3 Same/Different Strains in Culture Populations

Different strains participating in a synthetic consortium can be of entirely different species or can be from closely related strains of the same species. Despite many advantages of the microbial consortium in comparison with monocultures, there are still challenges associated with using different species for constructing the consortium (Jawed et al. 2019). For instance, since the growth rates of different species will not be identical, it results in competition for the same growth resources such as nutrients and oxygen, and the faster-growing species eventually take over the culture (Roell et al. 2019). Also, toxic substances that are produced by some bacterial species can inhibit the other members of the microbial community (Hibbing et al. 2010). In the case of closely related species, it is generally easier to form a stable system due to similar growth conditions. However, there are many examples that a mixture involving different species have successfully collaborated (Goers et al. 2014).

10.4.4 Free/Immobilized Microbial Consortium

One way to increase the effectiveness of microorganisms in bioremediation processes is the immobilization of microbial cells on/in carrier materials (Bayat et al. 2015; Maqbool et al. 2012). In general, cell immobilization refers to restricting cellular mobility within or throughout a matrix (Yanez-Ocampo et al. 2009). Among various immobilization techniques (adsorption, binding on a surface, flocculation, entrapment, and encapsulation), cell entrapment is widely used because of the characteristics of low cost and easy to apply (Bayat et al. 2015; Chen et al. 2017; Dzionek et al. 2016). Immobilization of microbial cells can provide a high cell density, greater tolerance to substances toxicity, and stable long-term operation (Chen et al. 2017; Gan et al. 2019). Some immobilized microbial consortia used in previous studies are summarized in Table 10.4. He et al. (2004) have studied the capacity for rapid decolorization of Direct Fast Scarlet 4BS by a free and immobilized microbial consortium consisting of a white-rot fungus and a *Pseudomonas*. They reported 99% of color removal after 6 h by the immobilized consortium, whereas for free cells, only 90% of color removal was achieved, and it took 24 h. Based on their results, immobilized microbial consortium has the ability to survive in wide ranges of pH and temperature of practical dyeing wastewater (He et al. 2004). In another study, Partovinia and Naeimpoor (2013) have investigated phenanthrene (PHE) biodegradation by freely suspended cell and immobilized microbial consortium in polyvinyl alcohol cryogel beads. Their results showed that the immobilized cell system was capable of the maximum PHE removal of 400 ppm at an initial PHE concentration of 750 ppm, whereas, under these conditions, freely suspended cell removed 310 ppm of PHE (Partovinia and Naeimpoor 2013).

Wide range of natural (chitosan, agar, alginate, carrageenan, wood chips, and wheat) and synthetic carrier materials (polyacrylamide, polyethylene glycol, polyurethane, polyvinyl, and resins) have utilized for bioremediation applications (Angelim et al. 2013; Bayat et al. 2015; Kurade et al. 2019; Wahla et al. 2019). The selection of the appropriate carrier for cell immobilization can influence the success of bioremediation. Yanez-Ocampo and co-workers have tested the removal of two organophosphate pesticides (methyl-parathion (MP) and tetrachlorvinphos (TCF)) by a bacterial consortium immobilized with two supports consisting of alginate and tezontle. They observed that the percentage of MP removed by the immobilized consortium was significantly greater than that removed by the

Table 10.4 Examples of consortia immobilization in/on different carriers

Co-culture	Type of strains	Contaminant	Carrier	References
Bacteria–fungal	*Fungus 8–4* and *bacterium 1–10*	Azo dye (Direct Fast Scarlet 4BS)	Polyvinyl alcohol (PVA)	Fang et al. (2004)
Bacteria–fungal	White-rot fungus and a *Pseudomonas*	Azo dye 4BS (Direct Fast Scarlet)	Polyvinyl alcohol (PVA) and Ca alginate	He et al. (2004)
Microbial consortium	Azo dye-resistant microorganisms	Azo dye	Alginate beads	Steffan et al. (2005)
Consortium		Carbendazim and 2,4-dichlorophenoxyacetic acid	Loofa sponge	Nagase et al. (2006)
Fungal	*Merulius aureus syn. Phlebia* sp. and an *unidentified* genus	Pulp and paper mill effluent	Nylon mesh	Malaviya and Rathore (2008)
Bacteria	Bacterial consortium	Methyl-parathion (MP) and tetrachlorvinphos (TCF)	Alginate/tezontle	Yanez-Ocampo et al. (2009)
Bacteria	Hydrocarbon-degrading bacterial consortium	Crude oil	Peanut hull powder	Xu and Lu (2010)
Bacteria	*Bacillus* sp. culture	Anthraquinone, thiazine, and vat dyes	Saw dust with sodium alginate	Saratale et al. (2010)
Bacteria	(Consortium I): *Achromobacter denitrificans*, *Acinetobacter baumannii*, *Aeromonashydrophilacaviae*, *Pseudomonas fluorescens*, *Pseudomonas stutzeri*, *Rahnellan aquatilis*, and *Stenotrophomonas maltophilia* (Consortium II): *Pseudomonas alcaligenes*, *Ochrobactrum intermedium*, *Klebsiella oxytoca*, *Sphingobacterium multivorum*, *Pseudomonas putida*, *Chryseobacterium massiliensis*, and *Stenotrophomonas maltophilia*	Diesel oil/phenol	Expanded clay pellets/polymeric ladders/PVC rings/cellulose-based carrier	Ławniczak et al. (2011)

(continued)

Table 10.4 (continued)

Co-culture	Type of strains	Contaminant	Carrier	References
Microbial consortium plant	*Sesbania cannabina* and microbial consortium	Petroleum hydrocarbons	Ca alginate	Maqbool et al. (2012)
Microbial consortium	Phenol-oxidizing organisms	Phenanthrene	Polyvinyl alcohol cryogel beads	Partovinia and Naeimpoor (2013)
Bacteria	*Streptomyces* consortium	Lindane	Cloth sachets	Saez et al. (2014)
Bacteria	Bacterial consortium and *Pseudomonas* sp. AY762360	Pulp and paper mill effluents	Polyurethane foam (PUF), sodium alginate (SA), polyacrylamide, and agar	Hoskeri et al. (2014)
Bacteria	*Burkholderia cepacia* GS3C (EU2821101), *Pandoraeapnomenusa* GP3B (EU233279), and *Sphingomonas* GY2B (DQ139343)	Petroleum-contaminated acid soil	Sawdust	Li et al. (2016)
Fungal	*Cladosporeum perangustum*, *Penicillium commune*, *Paecilomyces lilacinus*, and *Fusarium equiseti*	Tannery wastewater	Nylon mesh	Sharma et al. (2016)
Bacteria	Four *metagenomic clones* and *Bacillus subtilis* strain CBMAI 707	Oil	Chitosan beads	Dellagnezze et al. (2016)
Bacteria	*Gordonia alkanivorans* CC-JG39 and *Rhodococcus erythropolis* CC-BC11	Petroleum hydrocarbon	Polyurethane-polyurea co-polymers, alginate, and activate carbon	Chen et al. (2017)
Bacteria–microalgae	*Pseudomonas putida* and *Chlorella vulgaris*	Nutrients and COD	Ca-alginate	Mujtaba et al. (2017)
Bacteria	Bacterial consortium MB3R	Herbicide (Metribuzin (MB))	Biochar	Wahla et al. (2019)
Bacteria	*Oceanobacillus* sp., *Nesiotobacter* sp., *Ruegeria* sp., *Photobacterium* sp., *Enterobacter* sp., *Haererehalobacter* sp.,	Crude oil using	Self-immobilized	Ganesh Kumar et al. (2019)

	Exiguobacterium sp., *Acinetobacter* sp., and *Pseudoalteromonas* sp.			
Bacteria–yeast	Bacteria (*Brevibacillus laterosporus*) and yeast (*Galactomyce sgeotrichum*)	Remazol red and textile industry effluent	Calcium alginate, polyvinyl alcohol, stainless steel sponge, and polyurethane foam	Kurade et al. (2019)

suspension culture (41%, 72%, and 66% with the suspended, alginate immobilized, and tezontle immobilized consortium, respectively). Also, the viability of the consortium immobilized in alginate and tezontle supports was significantly higher (11 and 13 days, respectively) than consortium in suspension (6 days). However, alginate beads and tezontle showed almost similar performance (Yanez-Ocampo et al. 2009).

Similarly, Hoskeri et al. (2014) compared biodegradation of chloroaromatic pollutants by bacterial consortium immobilized in various matrices, including polyurethane foam (PUF), sodium alginate (SA), polyacrylamide, and agar. Based on their observation, the freely suspended cells of bacterial consortium showed a lower rate of degradation as compared to immobilized cells. Also, they affirmed that the PUF immobilized cells of bacterial consortium showed more tolerance to pH and temperature changes than freely suspended cells (Hoskeri et al. 2014).

10.5 Conclusion and Future Prospects

Rapid industrialization and urbanization have been accompanied by environmental contamination, including widespread pollution of water, soil, and sediment. Bioremediation using microbial consortium and co-culture is one of the most promising strategies to clean up contaminated sites. The case studies in this chapter illustrate that microbial consortia are generally more effective in bioremediation of different pollutants compared to single microorganisms. For example, bacterial–fungal consortium increases bacterial access to the pollutants via fungal highway in the contaminated soil, especially in heterogeneous soil environments. In the other case study, extracellular enzymes producing the rate of white-rot fungus are increased due to the synergistic reaction with *Pseudomonas* bacteria. Moreover, many bacteria and yeasts can help each other to degrade some toxic intermediate metabolites produced during the bioremediation process. However, it is important to note that the effect of various factors involved in bioremediation strategies improvement are needed to be addressed in future studies.

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Chapter 11
Enzyme-Oriented Strategies to Mitigate Polluting Agents from Environment

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D. G. Panpatte, Y. K. Jhala (eds.), *Microbial Rejuvenation of Polluted Environment*, Microorganisms for Sustainability 26, https://doi.org/10.1007/978-981-15-7455-9_11

Abstract Deterioration of environment quality and equilibrium by rampant industrial development, urbanization, and an exponential increase in population growth is the most important environmental issue, around the world. Environmental contamination by a vast array of toxic polluting agents such as dyes, heavy metals, pesticides, pharmaceuticals, industrial wastes, and personal care products released from natural or anthropogenic activities has a direct adverse consequence on human health and living entities. Therefore, it is of utmost meaningful for scientists and researchers to find solutions in effective mitigation and addressing these pollution problems for a sustainable environment. Though various biological, physical, and chemical approaches have been advocated to transform contaminants from the polluted water, these remediation methodologies are either inefficient or restricted due to techno-economic limitations. In this juncture, enzyme-oriented strategies are rapid, eco-sustainable, and socially acceptable and thus have been intensely examined for the mitigation and transformation of a vast array recalcitrant organic contaminants. In this chapter, an effort has been made to present an overview of the microbial-derived peroxidases (lignin peroxidase, manganese peroxidase, chloroperoxidase), and laccases in degrading toxic, mutagenic, carcinogenic, and hazardous environmental contaminants. The screening of enzyme-catalyzed degradation intermediates/by-products and enzyme immobilization is briefly discussed. Finally, the contribution is concluded along with future visions to move forward in this exciting era of research.

Keywords Bioremediation · Environmental contaminants · Biocatalysis · Enzyme immobilization

11.1 Introduction

Contamination of water, soil, and air by a variety of different pollutants such as dyes, pesticides, esters, hydrocarbons, heavy metals, polychlorinated biphenyl compounds (PCBs), and petroleum products are one of the foremost environmental problems (Sharma et al. 2018). All these contaminants generated from various agricultural and industrial resources are highly venomous and carcinogenic. Massive buildups of these chemicals become perilous to the ecosystem (Fig. 11.1) (Liu et al. 2019; Morsi et al. 2020). Textile industries produce substantial wastewater by consuming an enormous amount of water from the different steps of dyeing and finishing processes. The industrial wastewater contains color, residues of reactive dyes, chemicals, and different complex compounds including alkaline and acidic contaminants (Chatha et al. 2017; Rasheed et al. 2019; Ali et al. 2020; Parra-Saldivar et al. 2020). Dyes are heterocyclic aromatic compounds, which are carcinogenic and highly challenging to decompose. So contemporary attention is directed toward

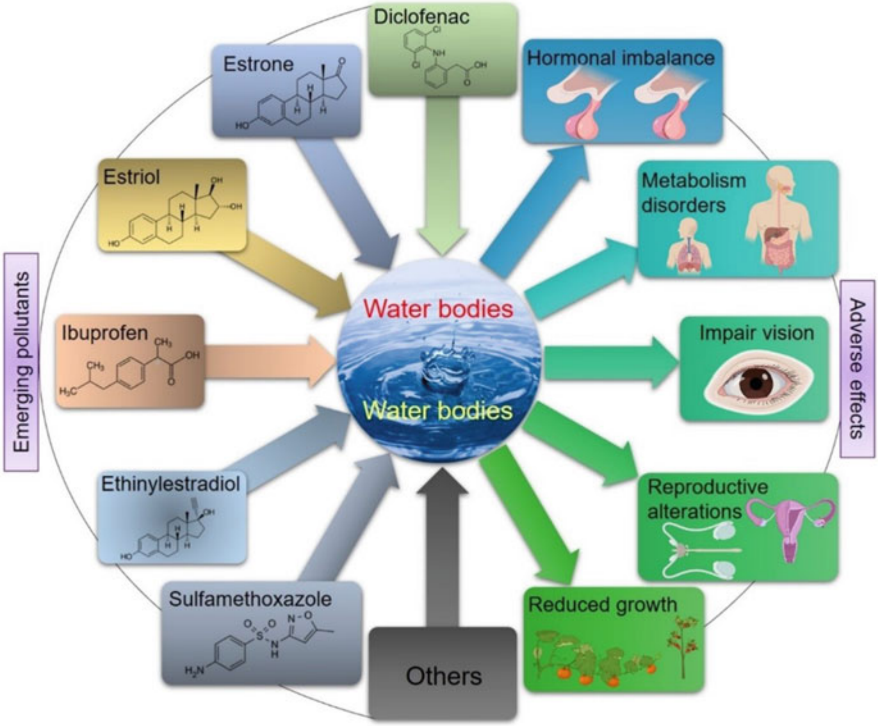

Fig. 11.1 Notable adverse effects of numerous emerging contaminants. (Source: Morsi et al. 2020)

the effective and economic removal of these carcinogenic compounds from textile-generated wastewater.

Even though physical, chemical, and physicochemical methods are widely used, and these methods can work effectively, they have several potential limitations, such as overall high cost, ineffectiveness, production of high sludge, and formation of toxic side products. Hence, it is well accepted that there is a dire need to find better, novel, and more environmentally safe approaches for wastewater remediation. Biological decolorization of dyes by using different microorganisms and their enzyme armory is an eco-friendlier and cost-efficient substitute to the chemical methods for degrading various kinds of organic pollutants and considered a promising area of research in water treatment (Al-Maqdi et al. 2018). The use of ligninolytic enzymes seems an excellent strategy for degrading recalcitrant polluting agents and synthetic dyes (Bilal et al. 2017a, b). In this study, an effort has been made to present an overview of the microbial-derived peroxidases (LiP, MnP, chloroperoxidase) and laccases in disintegrating toxic, mutagenic, carcinogenic, and hazardous environmental contaminants. After a brief portrayal of the screening of enzyme-catalyzed degradation intermediates/by-products and enzyme immobilization, the contribution is concluded along with future visions to move forward in this exciting era of research.

11.2 Bioremediation: A Sustainable Tool for Environmental Cleanup

Biological degradation and transformation of different organic pollutants and pesticides in the soil and other environmental matrices are generally referred to as the bioremediation process. Recently, mounting research consideration has been devoted to developing new, low-cost, eco-friendly, and sustainable approaches for the degradation and cleaning of contaminated pollutants in the atmosphere and lithosphere. The existence of an enormous magnitude of pesticides and a mixture of diverse pollutant substances in the situation for a longer duration may be due to the persistent nature and absence of pollutant degrading microorganisms. Bioremediation is a biological process that is involved in immobilizing, decontamination, changing, abolishing, or detoxifying various types of petrochemicals, industrial complexes, agricultural practices, and recycling wastes from the environment through the all-inclusive action of bioremediators (Xiong et al. 2016). To date, different bioremediation technologies based on bioaugmentation, biodegradation, and biostimulation have been applied to restore the auto-depuration abilities, soil quality, and characteristics of the environment. These techniques implicate microorganism (such as bacteria, fungi, or yeasts)-mediated transformation or hydrolysis of toxic pollutants into nontoxic or less-toxic compounds. The efficiency of these technologies depends upon various factors such as concentration, physical, and chemical nature of the toxic compounds and environmental physicochemical characteristics (Narayanan et al. 2013). Microbes have the potential to reduce the significant effect of recalcitrant pollutant compounds by eradication and degradative capabilities. The degradation rate of pollutants can be increased by genetically manipulating metabolic pathways to enhance the regulatory steps into bacterial strains (Mallavarapu et al. 2011; Iqbal and Bilal 2020). Different factors such as temperature, availability of nutrients, aerobic and anaerobic conditions, pH, the concentration of nutrients, type of soil, and environmental condition affect microbial population and concentration of contaminants in a particular environment. In biodegradation, the microorganisms utilize the pollutant as a substrate and induce enzymes, then the pollutants are enzymatically converted into smaller molecules that are usually less toxic (Ahmed et al. 2017). Biodegradation processes have many advantages compared to the physiochemical techniques as they are safer, less disruptive, less expensive, require lower energy employment, considered as green catalysis process, and can be used with pollutants having very low concentrations which cannot be achieved using physiochemical techniques (Holanda et al. 2019). The major drawback of biological treatments is that they require a longer time, and the microorganisms may not be able to grow and survive under adverse environmental conditions (Al-Maqdi et al. 2018).

11.3 Enzyme-Assisted Degradation: A Green Biocatalytic Process for Environmental Cleanup

Enzymes are robust and most efficient biological entities, which offer many advantages over chemical catalysts. The use of enzyme-based treatments offer numerous benefits such as the aptitude to be operational at high and low concentrations of pollutants, reduced amount of sludge generation, work in a catalytic manner, can be applied over a wide range of pollutants, low energy input, and many others (Aslam et al. 2016; Unuofin et al. 2019). Although enzymatic remediation has many advantages, some challenges are needed to address such as the high cost of catalytic enzymes, inability to re-use the enzyme, possibility of having changes in the conformation of the enzyme under harsh environmental conditions (i.e., enzymes may lose their stability under harsh environmental conditions such as high temperatures or high and low pH values) and the possibility of forming hazardous soluble by-products (Pandey et al. 2017). However, most of these issues can be deciphered by immobilizing the enzyme on different carrier matrices.

Various microbial strains possess enzyme systems that have the ability for the breakdown of several aliphatic and aromatic toxic substances. Ligninolytic enzymes comprise laccases and peroxidases like LiP, versatile peroxidase, and manganese peroxidase. All these enzymes have enormous environmental, textile, biotechnological, and pharmaceutical applications due to their hidden biotechnical potential. These enzymes involved in different catabolic reactions have the ability to degradation and augmentation due to their specific and nonspecific binding affinity with the substrate. Different microbial strains produced various enzymes that have the capabilities to bioremediation efficiency, reduce the deleterious effect of heavy metals, biodegradation of pollutants, and detoxification diverse physical and chemically hazardous waste. This mechanism is effective in such a condition where natural environmental parameters favored for microbial development and enhance the degradation process at a quicker rate (Bonugli-Santos et al. 2015). Oxidation-reduction reactions assist to oxidize the contaminants and converting into non-hazardous and harmless compounds.

Oxidoreductases are the most widely investigated class of enzymes for the bioremediation of wastewater. These enzymes catalyze the oxidation-reduction-mediated biotransformation of various classes of hazardous organic pollutants including cresols, phenols, chlorinated phenols, herbicides, pesticides, dioxins, synthetic textile dyes, PPCRs, and many others (Bilal et al. 2018, 2019a, b). Oxidoreductases include oxidases, peroxidases, dehydrogenases, and oxygenases. Among oxidoreductases, peroxidases and laccase (oxidase enzymes) are the most commonly used enzymes for the enzymatic-remediation studies due to their high ability to degrading different organic contaminants. These enzymes form radicals that degrade the parent pollutant into smaller products that are more biodegradable and exhibit minimal toxicity (Unuofin et al. 2019; Bilal and Iqbal 2020).

11.3.1 Laccase: A Choice Candidate for Environmental Cleanup

Laccase is a multi-copper-containing blue oxidase enzyme and belongs to oxidoreductases. The induction, formation, and secretion of extracellular laccase varies in the presence of different physical and nutrient growth conditions like pH, temperature, moisture, aeration, nutrients, mediators, and inhibitors. It is revealed that copper plays a role in the induction of laccases by most of the laccase producers (Berry et al. 2014). Laccases can be extracted from fungi, bacteria, plants, and insects. Nevertheless, laccases from microbial origins, particularly, from wood-decaying fungi, have gathered incredible interest owing to great oxidation ability to multiple compounds and a wider spectrum of substrate specificity. It drives the oxidative cleavage of a diversity of phenolic compounds, diamines, aromatic amines, and electron-rich substrates accompanied by simultaneous mono-electronic reduction of molecular oxygen to water (Fig. 11.2) (Bilal et al. 2019b). Laccases enhance the conversion of phenoxyl radicals to the ketone, demethoxylation, and cleavage of carbon in phenolic structures. Oxidation of non-phenolic structures of lignin is also carried out by laccase in the presence of different mediators. Laccases are responsible for the

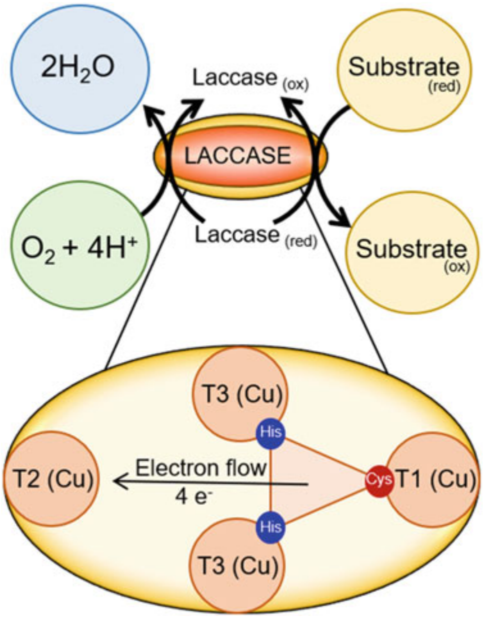

Fig. 11.2 A simplified schematic illustration of the catalytic cycle of laccase. (Source: Bilal et al. 2019b)

degradation of organic pollutants including organochlorines, polychlorinated biphenyls, 2,4,6-trinitrotoluene, polyaromatic hydrocarbons, and different wood preservatives (Pointing 2001; Bilal and Iqbal 2019a). In the last two decades, the use of laccase for the bioremediation of xenobiotics such as endocrine-disrupting compounds (EDC), for decolorizing azo dyes and bleaching has been explored (Bilal et al. 2019c). Different types of synthetic dyes has been used in pharmaceutical, food, printing, cosmetics, and paper industries. Several environmentally related emerging contaminants such as dyes, cosmeceuticals, and pharmaceutically active residues, antibiotics, and others are potentially carcinogenic and produce toxic effects once released into the environment (Narkhede et al. 2013; Bilal et al. 2020a, b; Rasheed et al. 2020).

11.3.1.1 Dye Degradation by Laccases

Wastewaters produced from different industries like paper industry, fiber industry, refineries, paints, dye industry, pig ranches, and tanneries pose genuine water contamination because dye chemicals and harmful substances are present. Two main types of sources of dyes that are secreted in the environment are from textile and fiber color treating industries as industrial discharges. Almost 10–15% of dyes have vanished in sewerage during dyeing treatment (Chen et al. 2008; Robinson et al. 2001). To keep the natural environment unaffected, these sewerages must be processed first. If the dyes are not properly treated, they create a slurry of mud with high concentrations (Alam et al. 2009). Though physical or chemical treatments are effective for the removal of dyes, they are a very expensive, and unnecessary use of toxic chemicals may also cause some other type of pollutions. Laccases produced by white-rot fungi have a significant effect on the degradation of sulfonated polymeric, heterocyclic, and azo dyes and detoxify recalcitrant substances. A newly isolated laccase from *Oudemansiella canarii* fungus led to 80% decolorization of Congo red (50 mg/L) within a reaction duration of 24 h at pH 5.5 and 30 °C. Characterization analyses revealed that the laccase not only breaks the chromophoric group of the dye but also catalyzed the cleavage of various covalent linkages resulting in efficient dye molecule disintegration. It also significantly reduced the toxicity and thus might be valuable in the mitigation of azo dyes and EDC (Iark et al. 2019; Bilal et al. 2019d). Table 11.1 summarizes recent studies on the degradation of recalcitrant environmental pollutants by laccases from various microbial strains.

11.4 Emerging Contaminants

Emerging contaminants are a new class of organic chemicals that are found in water bodies. These are man-made/synthetic chemicals or naturally occurring materials that are found in the natural environment without being monitored or regulated in most cases and can affect the health of living beings significantly (Sauvé and

Table 11.1 Degradation of recalcitrant environmental pollutants by laccases from various microbial strains

Enzyme	Source	Target pollutant	Degradation (%)	References
Laccase	*Trametes versicolor*	Triclosan	100	Sun et al. (2019)
Laccase	*Trametes versicolor*	Congo red	96	Zhang et al. (2020)
Laccase	Genetically modified *Aspergillus*	Direct Red 23	>75	Kashefi et al. (2019)
Laccase	Genetically modified *Aspergillus*	Acid Blue 92	>75	Kashefi et al. (2019)
Laccase	White rot fungi	2,4-dichlorophenol	87	Wu et al. (2019)
Laccase	*Trametes versicolor*	Diclofenac	90	Apriceno et al. (2019)
Laccase	*Trametes versicolor*	Carbamazepine in spiked water	76	Simón-Herrero et al. (2019)
Laccase	*Trametes versicolor*	Carbamazepine in secondary effluent	74	Simón-Herrero et al. (2019)
Laccase	*Trametes pubescens*	Bisphenol A	99	Lassouane et al. (2019)
Recombinant laccase	*Streptomyces ipomoeae* CECT 3341	Reactive Black 5	94.11	Blánquez et al. (2019)
Recombinant laccase	*Streptomyces ipomoeae* CECT 3341	Indigo carmine	98.4	Blánquez et al. (2019)
Recombinant laccase	*Streptomyces ipomoeae* CECT 3341	Orange II	88.86	Blánquez et al. (2019)
Laccase	*Aspergillus*	Prometryn	66.2	Chen et al. (2019)
Laccase	*Aspergillus*	Mefenacet	66.9	Chen et al. (2019)
Laccase	*Aspergillus*	Prochloraz	88.4	Chen et al. (2019)
Laccase	*Aspergillus*	Bensulfuron-methyl	69.8	Chen et al. (2019)
Laccase	*Pycnoporus sanguineus* CS43	diclofenac	68	García-Morales et al. (2018)
Laccase	*Pycnoporus sanguineus* CS43	Acetaminophen	>90	García-Morales et al. (2018)
Laccase	*Trametes versicolor*	Acetaminophen	80	Pulicharla et al. (2018)
Laccase	*Trametes versicolor*	Carbamazepine	95	Naghdi et al. (2018)

(continued)

Table 11.1 (continued)

Enzyme	Source	Target pollutant	Degradation (%)	References
Laccase	*Trametes sanguineus laccase expressed in Trichoderma atroviride*	Phenanthrene	97	Balcázar-López et al. (2016)
Laccase	*Trametes sanguineus laccase expressed in Trichoderma atroviride*	Benzo[α]pyrene	99	Balcázar-López et al. (2016)
Laccase	*Trametes versicolor*	Diclofenac	100	Xu et al. (2015)
Laccase	*Trametes versicolor*	Diclofenac	99	Lloret et al. (2013)
Laccase	*Myceliphthora termophila*	Diclofenac	100	Lloret et al. (2010)

Desrosiers 2014). They encompass a broad array of various toxic compounds and their degraded intermediates: antibiotics, pesticides, analgesics, pharmaceuticals, hormones, textile dyes, and personal care products (Lapworth et al. 2012). They are mainly detected in wastewater treatment plants (WWTPs), pharmaceutical production plants, hospitals, graveyards, household products, landfills, aquatic environment, industrial effluents, and municipal sewage (Ahmed et al. 2017). These are suspected to cause serious ecological threats such as interfering with the endocrinal system, reproductive impairments, physical abnormalities, congenital disorders in some species, feminization of some fish species, and many others (Belhaj et al. 2015). A study in 2011 concluded that the occurrence of perfluorinated chemicals in serum could be associated with the risk of breast cancer in women. Due to their ability to cause undesirable and deleterious effects on human health and to the ecosystem, they have become the main focus of many academic research groups. More than 1000 different types of emerging contaminants have been identified, such as PCPs, pesticides, pharmaceuticals, and hormones.

11.4.1 Pharmaceutical Products and Xenobiotics

Pharmaceutical products are released openly by pharmaceutical manufacturers or in hospital wastewater and have profound health-related concerns. Nonsteroidal anti-inflammatory drugs contain various chemical components of medications used for the treatment of many diseases and inflammation in animals and humans. Various sources of xenobiotics such as discharge of industries contain aromatic and aliphatic hydrocarbon, phenol and phenolic derivatives, paints, plastic, polymers, dyes, fertilizers, insecticides, pesticides, and landfill leachate (Ben Younes et al. 2013; Bilal et al. 2019e). In a very recent study, laccase drives the dehydrochlorination of an insecticide, lindane, to form non-toxic and environmentally friendlier by-products

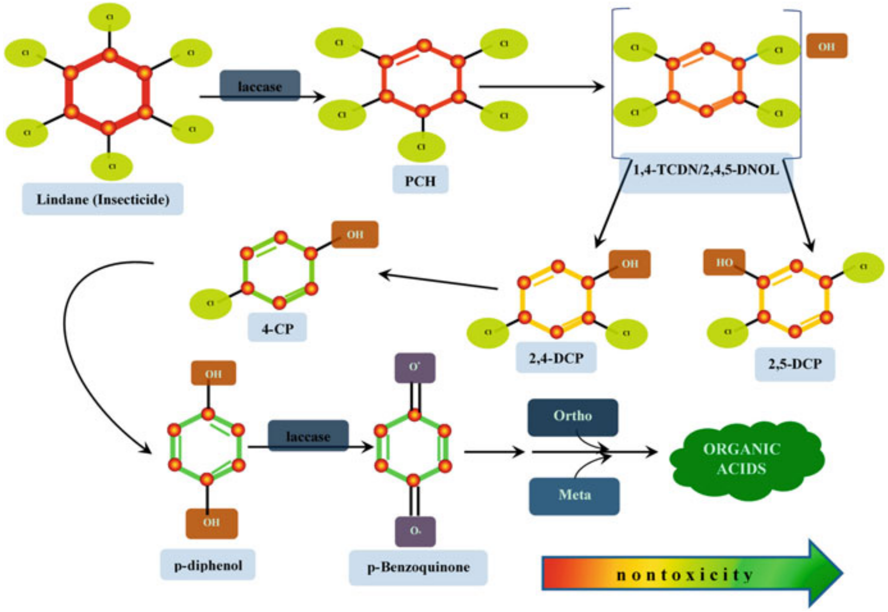

Fig. 11.3 Proposed degradation pathway of an insecticide, lindane, to form non-toxic organic acids. (Source: Unuofin et al. 2019)

(Fig. 11.3) (Unuofin et al. 2019). A favorable aspect of laccase functions is that they can cleave various substrates without using an external source of H_2O_2 or Mn^{2+} or any other co-factor that is necessitated when some peroxidases such as LiP or MnP are used (Unuofin et al. 2019). Lloret et al. (2010) demonstrated the capability of laccase to breakdown different estrogens into resulting products that have lower or no estrogenic activity. The potentiality of a novel *Pycnoporus sanguineus CS43* laccase for biotransformation of different pharmaceutical micropollutants was appraised. Using syringaldehyde as a redox mediator, a removal efficacy of 40%, 80%, and 100% was recorded for ciprofloxacin, amoxicillin, and sulfamethoxazole antibiotics, respectively, within 3 h of reaction time (Guardado et al. 2019).

11.4.2 Polycyclic Aromatic Hydrocarbons Degradation by Laccase

Effluents that are released by textile industries contain dyes and also other components with different concentration such as salts, chelating agents, detergents, precursors, metabolites, and by-products produced interference in decolorization efficiency. Textile effluent that released industries into the environment even in small proportion causes water pollution and environment and public health risk. In the last few decades, researchers especially concentrated on removing baleful compounds from textile effluents. The ligninolytic enzyme can degrade and mineralize polycyclic aromatic hydrocarbons (PAHs), and it is believed that they performed the same processes as in lignin degradation. Various PAHs are mutagenic and carcinogenic (Pozdnyakova 2012). Oil fractions contain a high concentration of hydrocarbons, cycloalkanes, and paraffin that are mostly used in gasoline and fuel oil making. Diesel, tar, and heating oils are mixed with high molecular weight alkanes, asphaltenes, and aromatic compounds to obtain heavy fractions (Asif et al. 2017). For effective degradation of PAHs including anthracene, phenanthrene, benzo(*b*) fluoranthene, and benzo(*a*)anthracene, Xu et al. (2019) proposed a laccase micelles system. The supreme bio-activity of laccase was obtained at 30 °C and pH 4.2 using 60 mmmol/L KCl. The reactive regions of the PAHs degradation were also predicted and simulated. Crude enzyme extracts obtained from *Ganoderma* strains result in differential degradation of PAHs with a degradation efficacy of 9–67%, 11–64%, and 34–73% of phenanthrene, fluorine, and naphthalene, respectively, without the involvement of redox mediators.

11.5 Peroxidases: An Ecofriendly Strategy for Environmental Cleanup

Peroxidases are heme-containing proteins that utilize H_2O_2 or organic hydroperoxides as a co-substrate to mediate the oxidative cleavage of a broad range of organic and inorganic substrates (Fig. 11.4). Well-known sources of fungal enzymes are *Trametes versicolor*, *Pleurotus ostreatus*, *Lentinula edodes*, *Aspergillus* spp., *Coriolus hirsutus*, *Pleurotus eryngii*, and *Pleurotus pulmonarius* (Asgher and Iqbal 2013). The fungal enzyme has several benefits like substrate non-specificity and explicit oxidation of numerous xenobiotics utilizing atomic oxygen as the final acceptor of an electron rather than H_2O_2 leading to an eco-friendlier biocatalytic process (dos Santos Bazanella et al. 2013). These enzymes produced from different sources vary regarding their level of glycosylation, atomic weight, and kinetic properties (Adebayo et al. 2012). In the past, fungi like *Phanerochaete chrysosporium* were studied for the biodegradation of dyes and other pollutants by using its whole culture, crude enzymes, and purified enzymes. Nowadays, the research emphasizes on methods in which bioconversion of dyes from contaminated wastewater by using pure ligninolytic enzymes. Peroxidases produced by WRF show promising results for pollutant degradation due to their higher enzyme efficiency. VP, MnP, and LiP are among the important peroxidases. The activity of heme peroxidases, i.e., LiPs and MnP that uses the presence of hydrogen peroxidase and manganese, respectively, is the most widely investigated biocatalysts for bioremediation of recalcitrant substances. The multistep catalytic reactions of LiP involve H_2O_2-dependent oxidation of lignin-type compounds like phenolic, non-phenolic, and aromatic compounds with high redox potential. Since non-phenolic compounds

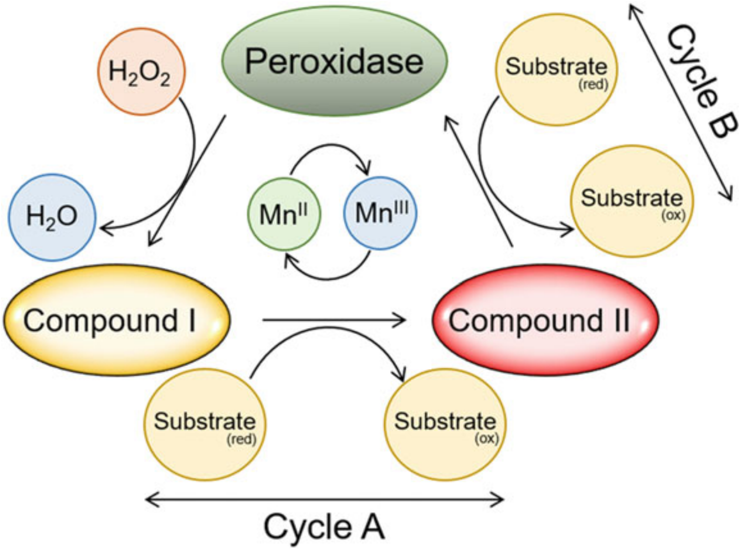

Fig. 11.4 A simplified schematic illustration of the catalytic cycle of peroxidases. (Source: Bilal et al. 2019b)

resemble lignin, e.g., veratryl alcohol, therefore can be easily depolymerized by LiP. Basidiomycetes like *P. ostreatus, Phanerochaete chrysosporium*, *Phlebia subserialis*, and *C. subvermispora* that secrete a huge quantity of peroxidases have an efficient aptitude for lignin degradation (Silva Coelho et al. 2010). Ligninolytic enzymes give the potential to WRF to detoxify partially or completely organic pollutants and xenobiotic compounds by mineralization (Rothschild et al. 2002). Table 11.2 summarizes recent studies on the degradation of recalcitrant environmental pollutants by lignin peroxidase from various microbial strains. Table 11.3 summarizes recent studies on the degradation of recalcitrant environmental pollutants by manganese peroxidase from various microbial strains.

Peroxidase from many strains of WRF has been proposed for the degradation of various effluents and textile (synthetic) dyes. Singh et al. (2013) have evaluated the potential of various *Pleurotus* species for the discoloration of direct Blue 14. Among the tested species, *P. flabellatus* displays the highest discoloration (90.39%) within 6 h, while three other *Pleurotus* species took more time for the degradation of dye. The rate of discoloration of direct blue dye solution through crude enzymes extracted from *P. flabellatus* seemed very fast. The presence of a powerful enzymatic mechanism of *P. flabellatus* efficiently degraded the recalcitrant and toxic dyes, and the enzyme can be recycled simply by immobilization techniques. Jamal et al. (2013) found that Ca-alginate beads entrapped peroxidase removed the color of dyes up to 90.6% of the mixture of dyes solution and the entrapped enzyme was repeatedly used in two reactor batch systems. The entrapped enzyme seemed to be efficaciously reusable for ten continuous cycles of dye degradation. Alneyadi and Ashraf (2016) reported the degradation of 2-mercaptobenzothiazole (MBT) that is widely detected

Table 11.2 Degradation of recalcitrant environmental pollutants by lignin peroxidase from various microbial strains

Enzyme	Source	Target pollutant	Degradation (%)	References
Lignin peroxidase	*Ganoderma lucidum*	Remazol Brilliant Blue R	>90	Bilal and Iqbal (2019b)
Lignin peroxidase	*Pichia methanolica*	Tetracycline	100	Guo et al. (2019)
Lignin peroxidase	*Pichia methanolica*	Dibutyl phthalate	100	Guo et al. (2019)
Lignin peroxidase	*Pichia methanolica*	5-Chlorophenol	100	Guo et al. (2019)
Lignin peroxidase	*Pichia methanolica*	Phenol	100	Guo et al. (2019)
Lignin peroxidase	*Pichia methanolica*	Phenanthrene	79	Guo et al. (2019)
Lignin peroxidase	*Pichia methanolica*	Fluoranthene	73	Guo et al. (2019)
Lignin peroxidase	*Pichia methanolica*	Benzo(a)pyrene,	65	Guo et al. (2019)
Lignin peroxidase A45	*Bjerkandera adusta* strain CX-9	Remazol Brilliant Violet 5R	15	Bouacem et al. (2018)
Lignin peroxidase A45	*Bjerkandera adusta* strain CX-9	Remazol Brilliant Blue Reactive	89	Bouacem et al. (2018)
Lignin peroxidase	*Pleurotus ostreatus* (PLO9) and *Ganoderma lucidum* (GRM117)	Remazol Brilliant Blue R	>50	Oliveira et al. (2018)
Lignin peroxidase	*Streptomyces griseosporeus*	Remazol Brilliant Blue Reactive	18	Rekik et al. (2019)
Lignin peroxidase	*Schizophyllum commune*	Sandal Fix Foron Blue E2BLN	89.71	Sofia et al. (2016)
Lignin peroxidase	*Schizophyllum commune*	Sandal Fix Turq Blue GWWF 165%	95.43	Sofia et al. (2016)
Lignin peroxidase	*Schizophyllum commune*	Reactive T Blue GWF	69.86	Sofia et al. (2016)
Lignin peroxidase	*Phanerochaete chrysosporium*	Bisphenol A	90	Gassara et al. (2013)
Lignin peroxidase	*P. ostreatus*	Remazol Brilliant Blue R	≥50	Oliveira et al. (2018)
Lignin peroxidase	*Ganoderma lucidum*	Sandal-fix Red C4BLN	93	Shaheen et al. (2017)

(continued)

Table 11.2 (continued)

Enzyme	Source	Target pollutant	Degradation (%)	References
Lignin peroxidase	*Ganoderma lucidum*	Sandal-fix Black CKF	70	Shaheen et al. (2017)
Lignin peroxidase	*Ganoderma lucidum*	Sandal-fix Golden yellow CRL	80	Shaheen et al. (2017)

in the WWTPs and the aquatic environment. MBT is an organosulfur compound mainly used in manufacturing rubber items such as tiers. It can be degraded by two different peroxidases, which are SBP and chloroperoxidase (CPO). Table 11.4 summarizes recent studies on the degradation of recalcitrant environmental pollutants by chloroperoxidase from various microbial strains. SBP was able to degrade 100% of the MBT into smaller by-products effectively, while CPO degraded only 35% of MBT. Recently, Almaqdi et al. (2019) established a robust and rapid LC-MSMS-based strategy to monitor the degradability of 21 diverse kinds of emerging contaminants by applying five different peroxidases, namely manganese peroxidase, soybean peroxidase, lactoperoxidase, chloroperoxidase, and horseradish peroxidase. They reported that some of the tested environmental pollutants could be easily transformed by the catalytic activity of all peroxidases ascertained, while some are only susceptible to degradation by a particular peroxidase enzyme. However, some organic pollutants completely remained resistant to the degradative activity of the peroxidases even using a suitable redox mediator.

Oxygenases catalyze the degradation of aromatic, cycloalkanes, ethers, heterocyclic compounds, ammonification, desulfurization, dehalogenation, hydroxylation, reductive dechlorination, and biotransformation. Oxygenases catalyzed an oxidative dehalogenation reaction to give the corresponding labile products that endure additional chemical breakdown. Hydrolytic enzymes can degrade the main chemical linkages that present in noxious molecules resulting in a reduction in toxic effect. This methodology gives advantages for bioremediation of organophosphate, carbamate insecticides, and oil spilling. Synthetic insecticide compounds like organochlorine and heptachlor can retain in soil but easily degrade without the presence of oxygen in environments (Vasileva-Tonkova and Galabova 2003).

11.6 Screening of Enzyme-Catalyzed Degradation Intermediates and By-Products

The degradation and transformation of a vast array of environmental contaminants by different pathways result in the generation of various metabolic end-products and intermediates during the biocatalytic reaction. In the majority of the degradation studies, environmental scientists, and researchers mainly focus on the vanishing of

Table 11.3 Degradation of recalcitrant environmental pollutants by manganese peroxidase from various microbial strains

Enzyme	Source	Target pollutant	Degradation (%)	References
Manganese peroxidase BA30	*Bjerkandera adusta* strain CX-9	Remazol Brilliant Violet 5R	70	Bouacem et al. (2018)
Manganese peroxidase BA30	*Bjerkandera adusta* strain CX-9	Methyl Green	12	Bouacem et al. (2018)
Manganese peroxidase BA30	*Bjerkandera adusta* strain CX-9	Poly R-478	80	Bouacem et al. (2018)
Manganese peroxidase BA30	*Bjerkandera adusta* strain CX-9	Remazol Brilliant Blue Reactive	38	Bouacem et al. (2018)
Manganese peroxidase BA30	*Bjerkandera adusta* strain CX-9	Cibacet Brilliant Blue BG	77	Bouacem et al. (2018)
Manganese peroxidase BA30	*Bjerkandera adusta* strain CX-9	Acid Blue 158	91	Bouacem et al. (2018)
Manganese peroxidase BA30	*Bjerkandera adusta* strain CX-9	Indigo Carmine	42	Bouacem et al. (2018)
Manganese peroxidase TP55	*Trametes pubescens* strain i8	Remazol Brilliant Violet 5R	76	Rekik et al. (2019)
Manganese peroxidase TP55	*Trametes pubescens* strain i8	Direct Red 5B	66	Rekik et al. (2019)
Manganese peroxidase TP55	*Trametes pubescens* strain i8	Methyl Green	50	Rekik et al. (2019)
Manganese peroxidase TP55	*Trametes pubescens* strain i8	Poly R-478	88	Rekik et al. (2019)
Manganese peroxidase TP55	*Trametes pubescens* strain i8	Remazol Brilliant Blue Reactive	42	Rekik et al. (2019)
Manganese peroxidase TP55	*Trametes pubescens* strain i8	Cibacet Brilliant Blue BG	46	Rekik et al. (2019)
Manganese peroxidase TP55	*Trametes pubescens* strain i8	Acid Blue 158	95	Rekik et al. (2019)
Manganese peroxidase	*Ganoderma lucidum*	Triclosan	75	Bilal et al. (2017a, b)
Manganese peroxidase	*Ganoderma lucidum*	Nonylphenol	96	Bilal et al. (2017a, b)
Recombinant manganese peroxidase	*Ganoderma lucidum* 00679	Drimaren Blue CL-BR	92.8	Xu et al. (2017)
Recombinant manganese peroxidase	*Ganoderma lucidum* 00679	Drimaren Yellow X-8GN	90.2	Xu et al. (2017)
Recombinant manganese peroxidase	*Ganoderma lucidum* 00679	Drimaren Red K-4Bl	70.1	Xu et al. (2017)
Recombinant manganese peroxidase	*Ganoderma lucidum* 00679	Disperse Navy Blue HGL	93.4	Xu et al. (2017)
Manganese peroxidase	*Ganoderma lucidum*	Reactive Red 195A	>95	Bilal et al. (2016)
Manganese peroxidase	*Anthracophyllum discolor*	Anthracene	>65	Acevedo et al. (2010)

(continued)

Table 11.3 (continued)

Enzyme	Source	Target pollutant	Degradation (%)	References
Manganese peroxidase	*Anthracophyllum discolor*	Pyrene	>86	Acevedo et al. (2010)
Manganese peroxidase	*Anthracophyllum discolor*	Fluoranthene	>15.2	Acevedo et al. (2010)
Manganese peroxidase	*Anthracophyllum discolor*	Phenanthrene	<8.6	Acevedo et al. (2010)

Table 11.4 Degradation of recalcitrant environmental pollutants by chloroperoxidase from various microbial strains

Enzyme	Source	Target pollutant	Degradation (%)	References
Chloroperoxidase	*Caldaromyces fumago*	Tetrabromobisphenol	80	García-Zamora et al. (2019)
Chloroperoxidase	Commercial	Roxithromycin	25	Almaqdi et al. (2019)
Lactoperoxidase	Commercial	Roxithromycin	80	Almaqdi et al. (2019)
Chloroperoxidase	*Caldaromyces fumago*	17β-Estradiol	82.67	García-Zamora et al. (2018)
Chloroperoxidase	*Caldaromyces fumago*	Ketoconazole	99	García-Zamora et al. (2018)
Chloroperoxidase	*Caldaromyces fumago*	Diclofenac	94.87	García-Zamora et al. (2018)
Chloroperoxidase	*Caldaromyces fumago*	Sulfamethoxazole	>80	García-Zamora et al. (2018)
Chloroperoxidase	*Caldaromyces fumago*	Trazodone	25.19	García-Zamora et al. (2018)
Chloroperoxidase	*Caldaromyces fumago*	Naproxen	>80	García-Zamora et al. (2018)
Chloroperoxidase	*Caldaromyces fumago*	Tetracycline	>80	García-Zamora et al. (2018)

parental compounds than the inspection of biotransformation pathways, intermediate metabolites, and assessment of toxicity, mutagenicity, and estrogenicity of the degraded products. The determination of physicochemical properties and toxicity of transformed products have a profound concern following the degradation of venomous contaminants in the environment. Widely employed instrumental techniques to scrutinize enzyme-mediated transformation products include direct inlet-mass spectrometry, liquid chromatography with tandem mass spectrometry (Alneyadi and Ashraf 2016), GC-MS, and ^{1}H nuclear magnetic resonance (Hata et al. 2010). In addition, HPLC diode array detection EI-MS and liquid chromatography-electrospray time-off light mass spectrometry can also be used to detect compounds that are not easily identified by gas chromatography (Stadlmair et al. 2017). In a contemporary study, Lonappan et al. (2016) identified the transformation products by a rapid and newly established laser diode thermal desorption-mass spectroscopy.

11.7 Enzyme Immobilization: Expanding the Scope for Environmental Cleanup

Enzymes work impeccably under physiological conditions, and their functions are highly based on their conformations. Harsh and adverse environmental conditions that are usually experienced in effluent streams such as extreme temperatures, presence of inhibitors, high ionic strength, and very low or high pH and can affect the conformation of the enzyme, thus resulting in its denaturation. These issues can be overcome by immobilizing the enzyme on a solid support. Immobilization is the process in which the enzyme is attached to an insoluble support carrier, where it is held in a proper geometry resulting in an augmented steadiness of the biocatalyst and allows its reusability. The immobilization process converts the enzyme from its homogenous form to a heterogeneous catalyst (immobilized enzyme) to give an immobilized biocatalyst. Immobilized biocatalyst can be used for the continuous bioremediation of great volumes of effluent effectively (Bilal et al. 2019f). Immobilized enzymes have been successfully used for the degradation of different hazardous compounds due to their stability and repeated usability. Bilal et al. (2019f) reported the ability of free and immobilized laccase in degrading bisphenol A, which is an organic synthetic compound. In their work, laccase was covalently attached to chitosan beads and presented marked constancy, and it was capable of preserving 71.24% of its activity after ten cycles of treatments. Bisphenol A was almost completely degraded (more than 99%) by immobilized laccase after 2.5 h. Yang et al. (2017) investigated the capability of an immobilized laccase in the degradation of different antibiotics. The method that they used for the immobilization process is the cross-linking of enzyme aggregates (CLEAs) as they prepared laccase-M-CLEAs and utilized for the biodegradation of antibiotics. Results showed that laccase M-CLEAs was able to degrade more than 80% of tetracycline (TC) efficiently within 12 h. The degradation products of TC were detected using LC-TOF MS. Three degradation products were detected which are entitled TP 459, TP 431, and TP 396 that have elution time at 2.69, 6.01, and 6.35 minutes, respectively. An amino-functionalized MOF-based magnetic composites Fe_3O_4-NH_2@MIL-101(Cr) was fabricated to incorporate laccase by simple adsorption and covalent coupling (Fig. 11.5). The as-developed novel MOF–enzyme bioconjugate presented a quick removal of 2,4-dichlorophenol pollutants in the first hour of reaction and reached 87% after the complete reaction. Importantly, the insolubilized biocatalysts can be easily recovered from the complex reaction mixture solution by a magnet (Wu et al. 2019). Covalently coupled enzyme on functionalized polyimide aerogels contributed to 74% and 76% degradation of carbamazepine in

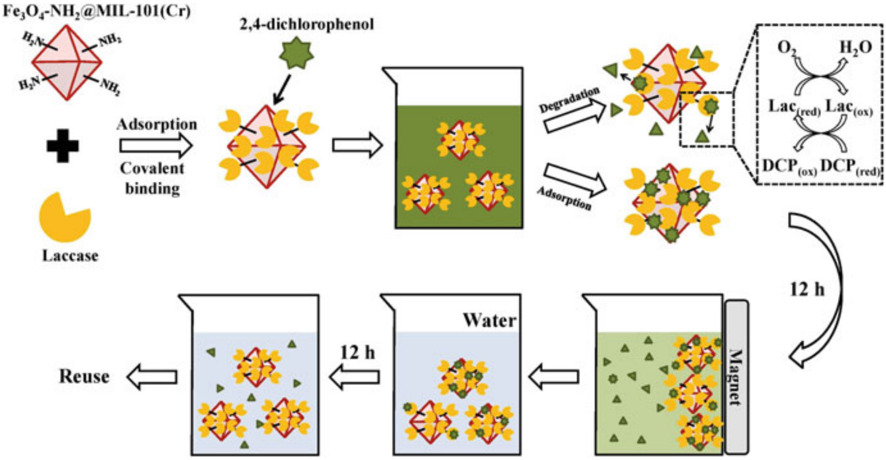

Fig. 11.5 Laccase immobilization on Fe_3O_4-NH2@MIL-101(Cr) and the application for the removal of 2,4-dichlorophenol. (Source: Wu et al. 2019)

secondary effluent and spiked water, respectively. The removal efficacy retained more than 65% and 50% for secondary effluent, and spiked water, respectively, even after seven repeated cycles (Simón-Herrero et al. 2019). Apriceno et al. (2019) reported the transformation of some widely used NSAIDs, including ketoprofen, diclofenac, and naproxen by applying a laccase-mediator biocatalytic system. To this end, *T. versicolor* laccase was directly attached on chitosan microspheres to obtain a biocatalytic system. Up to 90% of diclofenac was removed after 3 h reaction of optimal experimental conditions at pH 3.0 and an ABTS: drug ratio of 1:1 M. By using the laccase with an activity of 0.02 U, a diclofenac removal of achieved within 3 h, whereas about ~90% and 30% removal occurred for naproxen and ketoprofen, respectively, in 7 days at their elevated levels of 78.5, 98, and 108 mM, respectively.

Immobilized LiP from *P. methanolica* on Fe_3O_4@SiO_2@polydopamine nanoparticles revealed a high degradation efficiency leading to the complete removal of phenol, 5-chlorophenol, tetracycline, and dibutyl phthalate, whereas fluoranthene, phenanthrene, and benzo(a)pyrene were eliminated up to 73%, 79%, and 65%, respectively. On the other hand, the de-activated LiP showed adsorption of <25% of fluoranthene and phenanthrene pollutants (Guo et al. 2019). Very recently, Siddeeg et al. (2020) evaluated the efficacies of the MnP/Fe_3O_4/chitosan nanocomposite to eliminate two industrial dyes, namely Methylene Blue and Reactive Orange 16. Experimental results showed that the immobilized MnP biocatalyst exhibited a pronounced capacity to degrade both of the tested dyes, and led to a removal of 98% and 96% of Reactive Orange 16 and Methylene Blue, respectively. The developed biocatalytic system was reusable for up to five consecutive reaction cycles without the loss of any notable activity. In addition, plenty of reports have acknowledged the ability of immobilized enzymes to degrade different contaminants of emerging concern. It can be inferred that the immobilization of biocatalysts on different supports is an auspicious and ecologically friendly technique for the elimination of different polluting agents from wastewater and can be used for bioremediation of real textile wastewater and effluents.

11.8 Concluding Remarks and Outlook

With the rapid urbanization, industrial sectors, and intensified population growth, over the past few years, diverse types of organic contaminants, including dyes, pharmaceuticals, pesticides, and PCPs have been increasingly accumulated and detected in water bodies. Most of these emergent contaminants released from either domestic or industrial exoneration are unfortunately not eliminated by the present-day wastewater treatment techniques. Based on the extensive literature survey as stated above, this report highlighted that the biocatalytic approach has received an exceptional position in mitigating an array of emerging pollutants typically present in wastewater effluents. Many earlier studies have corroborated the applicability of a broad family of microbial enzymes to degrade different classes of organic pollutants. Enzyme immobilization appeared an effective way to overcome the challenges confronted by the free enzymes, as the supported/immobilized enzymes can be recovered after the process of degradation and reused. The forthcoming investigation should be concentrated to expand the prospects of enzymes under the actual treatment environments.

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Chapter 12
Nonaqueous Catalysis: A Way Forward for the Intermediation of Phenolic Environmental Pollutant Bisphenol A

Janki Trivedi, Urvish Chhaya, Yogesh Patel, and Darshan Rudakiya

Contents

Abstract Bisphenol A (4,4-propane-2,2-diyl) diphenol abbreviated as BPA is an important industrial chemical which is widely used to produce epoxy resin and polycarbonates. It evoked public interest in the last few years due to its toxic effects toward wildlife and human health. It is categorized as Endocrine Disrupting Chemical (EDC) and teratogen. Due to its aquaphobic nature, it is difficult to remediate BPA in aqueous system, thus nonaqueous catalysis is employed for the

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bioremediation. Catalysis in nonaqueous system using laccase enzymes offers certain advantages over aqueous system in case of BPA bioremediation, and those are increased activity, better stereo- and enantioselectivity, and increased thermo stability. Laccase encapsulated in reverse micelles has proven to be potential system for BPA removal, thus nonaqueous catalysis is a promising alternative for the intermediation of this hazardous micropollutant.

Keywords Bisphenol A · Bioremediation · Laccase · Nonaqueous catalysis · Reverse micelles

12.1 Introduction

Bisphenol A (4,4-propane-2,2-diyl) diphenol commonly known as BPA has been chemical of concern in last few years because of its detrimental effects on human health as well as on the aquatic wildlife. It is an important industrial chemical which was synthesized in 1891 as phenolic plasticizer of epoxy, polyester resin, and polycarbonates. These materials are extensively used in manufacturing of reusable bottles, baby bottles, dental sealants, various medical devices, thermal printing paper, CDs etc. (Mikołajewska et al. 2015). The global BPA consumption was estimated 7.7 million metric tons in 2015, and its expected compound growth rate is 4.8%, which means its consumption can reach up to 10.6 million tons in 2020. Asia Pacific has largest BPA market (53%), whereas Western Europe and USA are the second largest with 36% market share (Global Industry Analysts Inc. 2015; Industry Experts 2016).

BPA is reported as Endocrine Disrupting Chemical (EDC) which is one of the known Organic Micro Pollutants (OMPs). EDCs can imitate the biological activity of natural hormones, occupy the hormone receptors or interfere with the body's hormonal system and therefore cause various health-related issues in aquatic animals and humans (Fig. 12.1) (Kwak et al. 2001). BPA binds weakly to estrogen receptor and shows estrogenic effects on in vivo animal studies, and it shows teratogenic properties also (Rochester 2013). It has been detected in surface water, industrial run off, ground water, and landfill leachates (Crain et al. 2007). Humans are exposed to BPA through canned food, internal lining material of these cans possess BPA which leaches into food items. Moreover, fish and meat products are highly contaminated with BPA (Repossi et al. 2016).

High amount of BPA is related to numerous reproductive health issues in humans. BPA is detectable in human serum, urine, secretary body fluids like breast milk, and amniotic and follicular fluid. Research conducted on cohort undergoing infertility treatment showed that higher BPA is associated with poorer ovarian response. Studies on Asian-American male and female having high level of serum BPA showed that their fertilization probability reduces up to 55% (Braun et al. 2011).

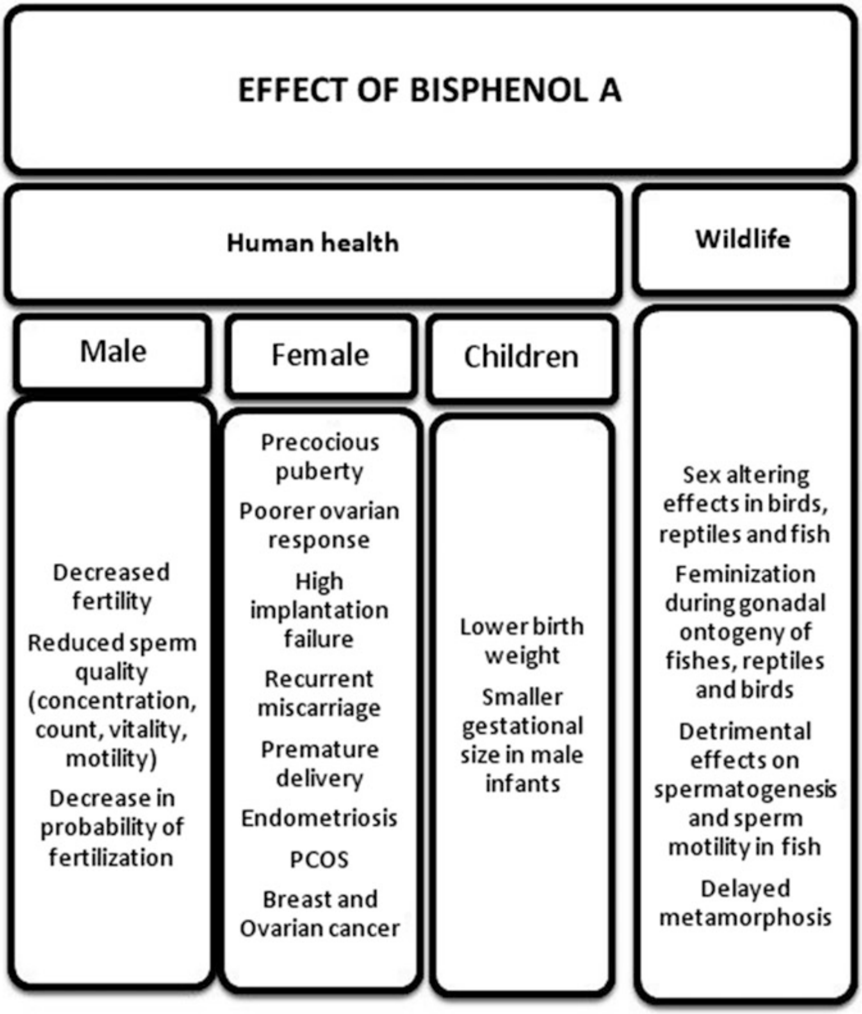

Fig. 12.1 Hazardous effect of bisphenol A

Kandaraki et al. (2011) reported that serum BPA concentration was higher in women with polycystic ovarian syndrome (PCOS) as compared to serum taken from normal female.

According to Sugiura-Ogasawara et al. (2005), total serum BPA content in women who experienced recurrent miscarriages was higher in comparison with healthy control women (Takeuchi et al. 2004). Women exposed to BPA during their pregnancy had babies with lower birth weight as compared to unexposed mother. It is also associated with higher implantation failure, premature delivery, and endometriosis in adult female (Ehrlich et al. 2012).

In males, higher urinary BPA is associated with decreased sexual function in dose-dependent manner. Men working at epoxy resin manufacturing companies showed high amount of BPA in urine as well as reduced sperm count, concentration, motility, and vitality (Li et al. 2010). It also increases the risk of erectile dysfunction and disturbs the function of Sertoli cells (Vijaykumar et al. 2017). BPA is also associated with insulin-dependent type 2 diabetes, obesity, and metabolic syndrome (Valentino et al. 2016; Cariati et al. 2019).

Aquatic organisms experiences maximum harmful effects of BPA due to direct exposure. BPA shows chronic toxicity toward fish, amphibian, benthos, plankton, mollusks, primitive sponges, and algae (Mihaich et al. 2018). BPA causes changes in gonadal and liver structure and its functions. During gonadal organogenesis, it can alter sex determination. It induces feminization in fishes, reptiles, and birds and mortality in some species of fishes at higher concentrations. It induces vitellogen production in mature male fishes and responsible for impairment of sex ratio (Crain et al. 2007).

Fishes (male) which are exposed to BPA show abnormality in spermatogenesis and reduced sperm motility. Studies conducted on adult male guppies reveal that sperm count declines by 40–70% after 21 days of 274–549 μg of BPA exposure, even lower BPA concentration also induces same effects in this fish. Overall fertility of males is compromised due to these effects (Haubruge et al. 2000).

BPA drastically affects metamorphosis in amphibians. Tadpoles exposed to 10 μmol/L of BPA concentration until metamorphosis showed delayed development, mouth malformations, reduced size of body, microcephaly, etc. (Canesi and Fabbri 2015). BPA also interferes with steroid hormone regulation because it directly interacts with its receptor to block or stimulate hormone production (Kwak et al. 2001).

Due to BPA associated health risks, the Food and Drug Administration (FDA) banned use of BPA in baby bottles and sippers in USA in 2012 (FDA n.d.). In fact, in 2017, the European Chemical Agency identified BPA as a substance of very high concern under European Unions' Registration, Evaluation, Authorization and Restriction of Chemicals (REACH) regulations. There is indeed a very strong movement from various countries toward bans of BPA. Industrialized countries like France, Canada, Belgium, Sweden, and Denmark also banned BPA. Major complications and diseases related to BPA reported in humans are shown in Fig. 12.2.

12.2 Nonaqueous Catalysis

It is possible to remediate BPA using various biological enzymes, but generally this enzymatic reactions processes take place in aqueous or polar environment because the catalyst is present and functional in that environment naturally. It is difficult to remediate BPA in natural aqueous system due to its hydrophobicity, thus switching to nonaqueous systems has potential to improve catalysis of hydrophobic substances

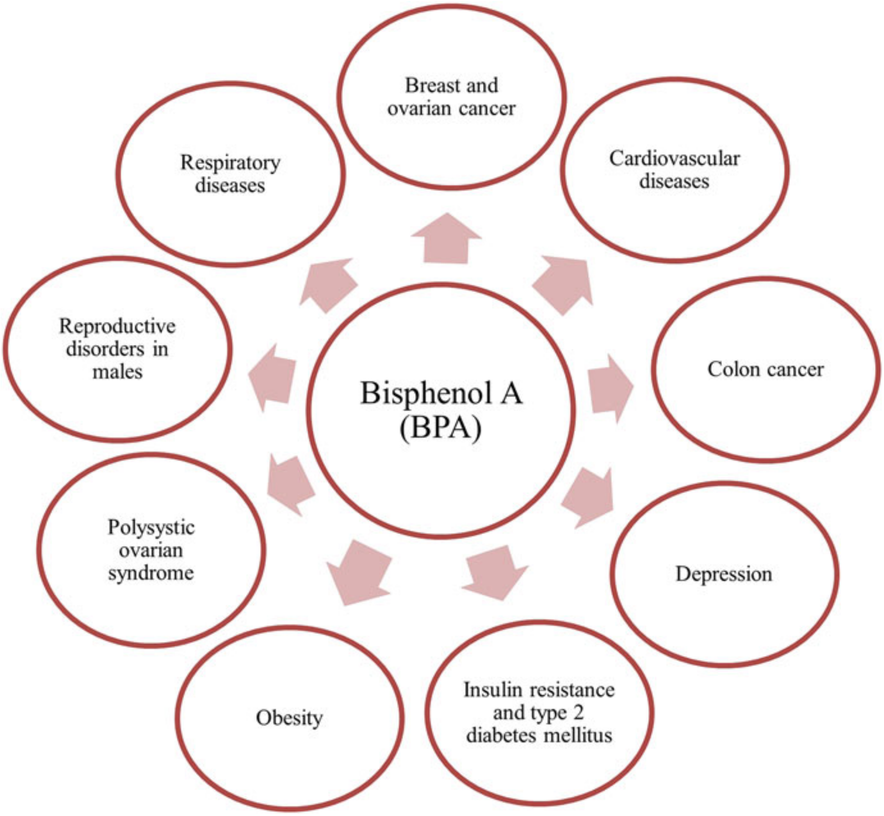

Fig. 12.2 Hazardous effect of BPA on human health. Adapted from (Bilal et al. 2019)

like BPA (Michizoe et al. 2001). Nonaqueous catalysis is advantageous over aqueous catalysis in so many ways as listed below:

1. Bioconversion and production of certain chemical (as discussed BPA) is constrained because low solubility in aqueous system can be easily taken care of in nonaqueous system.
2. Aqueous system gives rise to unwanted side reaction and has reverse thermodynamic equilibrium which is not the concern in nonaqueous system (Wang et al. 2016).
3. Furthermore, this catalysis provides enhanced technological utility of enzymes, better stereo-, regio-, and enantioselectivity (Klibanov 2001).
4. Higher product yields can be achieved by reducing substrate concentration and/or product inhibition, either indirectly by maintaining low concentration in aqueous microenvironment of the biocatalyst or by changing the interaction between the inhibitor and active site of the enzyme.
5. Application of low boiling point solvents will simplify the recovery of the product and biocatalyst.

6. Increased thermostability when micro aqueous reaction media are used (Chhaya and Gupte 2013).
7. Possibility of manipulation of enzyme in nonaqueous system is easier (Sakurai et al. 1988).
8. Enzymes acquire higher stability and unique behavior called molecular mimicry in nonaqueous system (Klibanov 2001).

There are four major categories of organic solvent reaction media for catalysis:

1. Biocatalyst directly suspended in solvent in dry state.
2. Two-phase system which consists of water and immiscible organic solvent in which dry biocatalyst is suspended, so-called micro aqueous organic solvent mixture.
3. Enzymes in supercritical fluid.
4. Reverse micellar system.

12.2.1 Enzyme Suspended in Organic Solvent

In this method, dry (lyophilized) enzymes are directly suspended in organic solvent. Enzymes behave differently in this medium and acquire some different characteristics in comparison with conventional aqueous systems (Zaks and Klibanov 1988).

The stability and activity of enzymes in nonaqueous systems will largely depend upon the solvent in which they are suspended. Partition co-efficient also known as log P value is the measure of hydrophobicity of the given organic solvent. Increase in log P value suggests increasing hydrophobicity. Water soluble or miscible solvent has log P value less than 1, whereas hydrophobic solvents has log P value greater than 4 (Broos et al. 1995).

It has been reported that flexibility of different enzyme changes in various solvents depending upon their log P value. Lipases from *Candida antarctica* (CALB) showed decrease in flexibility with respect to increase in log P value of organic solvent. Similar observation was made in case of subtilin enzyme from *Bacillus licheniformis*. Enzyme was less flexible in octane (log P: 4.183) in comparison with acetonitrile (log P: 0.344). It is evident that increasing hydrophobicity adversely affects flexibility of suspended enzymes (Trodler and Pleiss 2008; Sharma and Kanwar 2014).

Enzyme suspended in organic solvent has bell-shaped mechanism in terms of hydration dependency. It is evident that in very low water content, enzyme becomes very stiff, and in the presence of excess water, it loses its active configuration and starts to unfold. Ideal water content for enzyme to remain functional is around 10% w/w, in this condition biocatalyst behavior is similar to aqueous systems.

It was evident that molecular structure of organic solvent also affects the activity of suspended enzyme. Normally organic solvents having functional group at terminal carbon atom shows high enzyme inhibiting effects to that of solvents having functional group at internal carbon atom. These inhibitory effects might be due to the possible interaction between functional groups of solvent at terminal carbon and enzymes (Wang et al. 2016).

12.2.2 Enzymes in Biphasic System

The use of enzymes in organic systems normally results in a two-phase system as all water-soluble enzymes possess a considerable amount of water around them which is strongly bound to them, even when it is in an apparently dry state.

In any of the system the most basic and important thing is that enzyme must remain active and should be able to convert reactants into the product. For this to happen, there must be a small amount of reactant available in the microenvironment adjacent to enzyme which is aqueous. In this kind of systems, the reactants (substrate) normally have low water solubility. In biphasic system, enzymes' rate of reaction will largely be dependent on the thickness of unstirred layer (δ). Unstirred layer also known as δ, is the measure of thickness of aqueous layer microenvironment surrounding the enzyme. It is obvious that thickness of this layer is the most influential parameter because it will determine the availability of reactants for enzymes. If the enzyme is freely soluble, the unstirred layer (δ) will be very thin, and it will control the reaction rate by entry of reactants from more concentrated organic solvent phase through the solvent interphase boundary where reactant concentration is very low.

There are some conditions which will allow the optimization of two-phase system for enzyme catalysis. As discussed, log P value plays significant role by influencing solvent–aqueous interphase as well as transfer of the substrates and products.

1. The difference between the log P values of the interphase and reactants (substrate) should be minimum, whereas the amount of the reactant(s) should be much lower as compared to the organic phase. These situations will support and facilitate higher substrate concentration within the interphase, and as a result, a greater number of reactants are transferred from organic to aqueous phase.
2. Difference of log P value between formed product and organic phase should be minimum, and the quantity of product should be much higher as compared to organic aqueous interphase. It will positively affect the transfer of product from interphase to organic solvent after completion of the reaction.

The log P value of the solvent aqueous interphase will depend upon organic phase as well as surfactant and co-surfactant used. When surfactant and water both are in excess amount, multiple membranes of surfactant are formed which are concentric. It will form surfactant bilayer around the aqueous microenvironment.

In biphasic system, removal of water is possible by means of hydrolases. Control over water pool present around the enzyme was attained by molecular sieves (potassium aluminum silicate). Water dissolved in organic solvent can be removed using molecular sieves. Another method to remove water is vacuum distillation which is applicable if the solvent (organic phase) has higher boiling point than water. It is a very simple and efficient method applicable for wax manufacturing and lipase catalyzed esterification of fatty acids and alcohol.

12.2.3 Enzymes in Supercritical Fluids

Supercritical fluids (SCFs) are defined as the state of a compound or element above its critical temperature (Tc) and critical pressure (Pc). At this state they acquire many unusual properties, and they become inert and harmless system which facilitates many chemical processes. Critical parameters like temperature and pressure for such fluids will depend upon nature of substance being supercriticalized. Supercritical fluids have several advantages over conventional solvent system because of their selectivity and controllable reaction rates. Due to this, SCFs are employed for homogenous molecular catalysis and heterogenous catalysis. It was noted that in homogenous catalysis control over selectivity is higher as compared to heterogenous catalysis. In heterogenous solid catalysis, SCFs offer advantages like high rate of reaction and improved selectivity as compared to conventional systems, and problem of mass and heat transfer is also resolved in this system. In SCFs, gas–liquid phase transfer resistance is not observed, and it also intensifies the process (Wandeler and Baiker 2000).

In SCFs, phase behavior of fluid can be controlled using depressurization, and it facilitates separation of substates and products being utilized and formed during the process. The separated products will be free from harmful solvent residues. In comparison with solvents and liquids, diffusion rate is high in super critical fluids, and it speeds up homogenous and heterogenous reactions (Zhang et al. 2014). The properties of SCFs are often said to lie between those of a liquid and a gas, but it is important to note down that some of the SCF properties are similar to liquid. Moreover, slight change in temperature or pressure changes their properties significantly which make them tunable system. They are combination of more gas-like and more liquid-like properties which are suitable for chemical reaction and extraction (Jessop et al. 1995).

There are a variety of methods by which enzymes can be suspended in supercritical fluids. For the stabilization of enzymes in supercritical fluids, possible alternatives are preparation of sol gels, cross-linked enzyme aggregates (CLEAs), cross-linked enzyme crystals (CLECs), immobilized enzyme, lipid coated enzymes, and enzymes combined with surfactant that forms reverse micelles followed by microemulsion (Sheldon 2007).

Conventional nonaqueous technology deals with organic solvents which might be toxic and hazardous to environment. In this situation, supercritical fluids are eco-friendly approach to carry out various chemical reaction in benign way.

Supercritical carbon dioxide might be an ideal replacement medium for weakly polar or nonpolar chemical processes. It is just not a substitute, but it also changes the chemistry of process. There are relatively a smaller number of solvents utilized for supercritical fluid preparation particularly to catalyze reaction using enzymes because of enzymes' nature and their tendency to unfold and become inactive at higher temperature. Supercritical carbon dioxide (scCO_2) is a promising alternative to carry out enzymatic reaction. scCO_2 has become more popular due to its inert and nontoxic nature; in addition, it is readily available at cheaper rate. CO_2 forms supercritical fluid at relatively low temperature and thus suitable for catalysis using enzyme. Substances like ethene, ethane, and propane are not utilized for SCF preparation because of their high cost and flammability. Use of sulfur hexafluoride and xenon is also restricted because they are less cost effective and has very low solvent power. $scCO_2$ can be described as a "green" solvent because it replaces the toxic solvent system and does not produce any harmful by-product and enhances catalyst lifetime and regeneration properties. It is the only available solvent which is supercritical under condition where enzyme remains functional, and it is not a volatile organic compound (Hobbs and Thomas 2007).

12.2.4 Reverse Micelles as Potential Nonaqueous Catalytic System

Reverse micelles are tiny droplets of aqueous medium (radii in 1–50 mm) stabilized by surfactant in bulk of water immiscible organic solvent. Surfactants are amphiphilic material having both nonpolar hydrocarbon tails and polar head groups. When amphiphilic surfactant molecules are dispersed in polar solvents like water, they self-associate and form organized molecular assemblies which are known as micelles (Danielsson and Lindman 1981). The hydrophobic part of surfactant hydrocarbon chains form core of the micelles while polar heads are oriented toward the micelle–water interphase (Dominguez et al. 1997). If the surfactant molecules are dispersed in nonpolar solvents, they self-assemble into structure called reverse micelles in which the polar head groups are oriented toward the core part and solubilize water in it, whereas hydrophobic tails remain at the micelle–organic solvent interphase (Melo et al. 2001). In reverse micelles, enzymes are confined into water pool and isolated from organic solvent by single surfactant layer (Zaks and Klibanov 1988).

The sodium bis(2-ethylhexyl) sulfosuccinate (AOT)/isooctane/water reverse micellar system is widely used for enzyme immobilization because it mimics biological membrane in certain ways. AOT reverse micelles dispersed in organic solvent have similarity with lipid bilayer of cell membrane which has polar head and nonpolar tail; they also mimic properties of lipid bilayer and lipid rafts (Pike 2006). Isooctane (2,2,4-trimethylpantene) structure is similar to AOT tail structure and so that has best penetration into it. Sodium bis(2-ethylhexyl) sulfosuccinate (AOT) spontaneously forms reverse micellar structure in organic solvents like isooctane (Chang et al. 2000). AOT reverse micelles mostly possess spherical shape and have approximately $<10\%$ of surfactant, 0–10% of water and rest is organic solvent. These preparations have similar viscosity as organic pure solvents. These micelles collide with each other in a constant manner and as a result content present in these micelles keep on interchanging (by fusion of micelles, diffusion, and migration of solubilizate) in between as shown in Fig. 12.3 (Chhaya and Ingale 2016).

Reverse micelles, or water-in-oil microemulsions, have already been reported as an effective medium for enzyme immobilization (Xenakis et al. 2009). They have

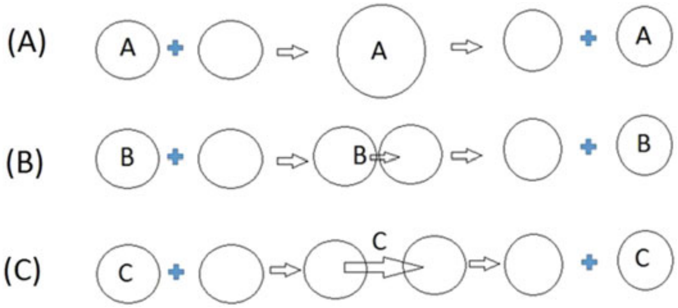

Fig. 12.3 Schematic representation of solubilizate exchange mechanism in reverse micelles: (**a**) Exchange mediated by fusion of two micelles which forms a dimer and then splitting into two different micelles. (**b**) Diffusion of solubilizate through the surfactant bilayer formed at the contact point of non-fusing reverse micelles. (**c**) Migration of solubilizate through the oil phase. Adapted from (Chhaya and Ingale 2016)

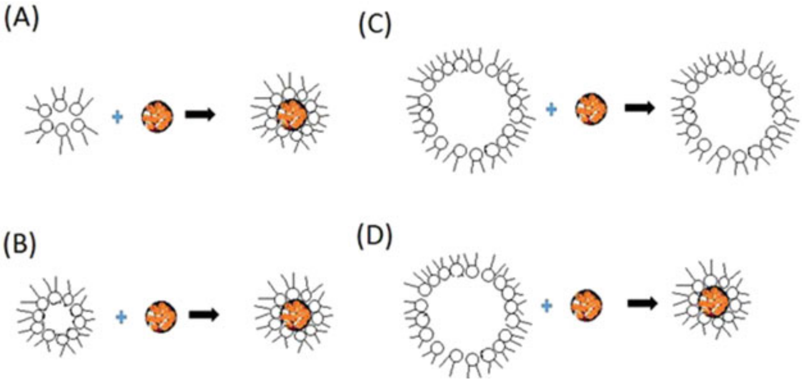

Fig. 12.4 Theoretical model showing the formation of the protein-containing micelles: (**a**) Creation of own micelles by protein according to the size equals to that of protein as an initial micelle is smaller than the protein molecule to be entrapped. (**b**) Protein solubilization occurs without noticeable change in the dimension and shape due to the equal size of micelles and protein. (**c**) No changes occur as initial micelles are larger than the protein. (**d**) Protein with anchoring groups interacts with the surfactant matrix even if initial micelle is large; hence, protein molecule creates its own micelle with a size equal to that of the protein. Adapted from (Chhaya and Ingale 2016)

been successfully used in several studies to improve reaction yields using lower amounts of biocatalyst and enhance enzymatic activity compared with conventional systems (Gonçalves et al. 2013). These structures forms thermodynamically stable and optically transparent liquid medium, in which large interfacial area provides an aqueous domain where hydrophilic enzymes can be hosted, an interface where the active site of enzymes can be anchored, and a nonpolar organic phase where the hydrophobic substrate or products may be dissolved (Fig. 12.4) (Buchholz and Klein 1987; Itabaiana et al. 2014).

12.2.4.1 Factors Affecting Activity of Enzyme Entrapped in Reverse Micelles

Activity of enzyme entrapped in reverse micelles is largely dependent upon three factors which are listed below:

Geometric Factor

Enzyme activity reaches maximum when protein fits properly into reverse micelles, which suggests that geometry of micelles influences enzyme activity (Vermue and Tramper 1995).

Hydration Ratio

Water and surfactant molar ratio ($W = [H_2O]/[\text{Surfactant}]$) greatly affect size of reverse micelles, and the diameter of reverse micelle is linearly proportional to amount of water incorporated. In micellar system, when only surfactant concentration was increased, it resulted in decreased micellar diameter. When both water and surfactants concentrations are increased simultaneously, it will increase reverse micelles concentration. Change in diameter of reverse micelles will affect biocatalyst present in the reverse micelles in terms of compressibility (Kamyshny et al. 2002).

Solvent

Both water activity and compressibility of protein in water pool are dependent upon the type of solvent used. Mostly nonpolar solvents are used in reverse micelles preparation because they limit enzyme in water pool, increase its thermo stability, as well as reduce product inhibition (Eicke et al. 1976; Chhaya and Ingale 2016).

12.3 Enzyme Immobilization Using Various Gels

Enzyme entrapped in reverse micellar system offers numerous advantages, but the major limitation of this system is biocatalyst present in this system is not reusable and separation of products from this micellar system is also difficult. To rectify this problem, the gelling of microemulsion by various gelling agent was introduced, in which biocatalyst retain their activity and handled in immobilized form, and in addition, it facilitates diffusion of various nonpolar or poorly soluble substrates and products (Blattner et al. 2006). Enzyme efficiently catalyzes nonpolar, polar

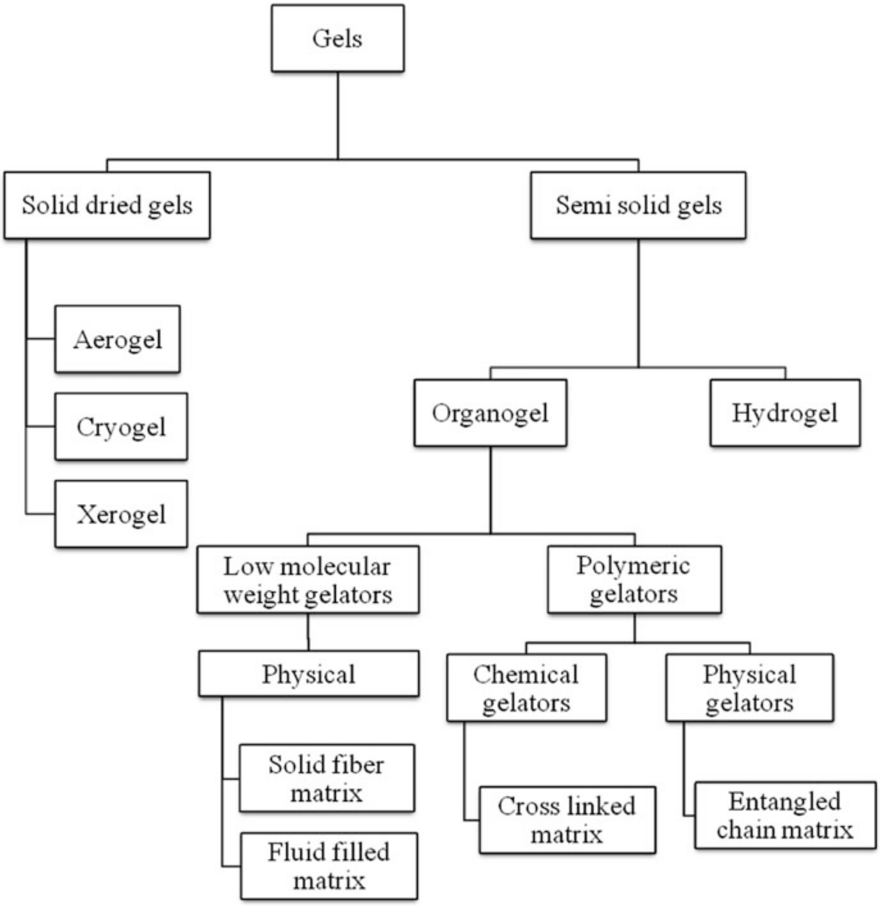

Fig. 12.5 Classification of gels. Adapted from (Mujawar et al. 2014)

and interfacially active substrates in such systems (Stamatis et al. 1993; Holmberg 1994; Chang et al. 2000). Classification of gels is given in Fig. 12.5.

12.3.1 Organogel

Organogel is defined as entrapment of organic liquid within a thermo-reversible, three-dimensional, cross-linked gel network which is viscoelastic in nature (Hughes et al. 2009). As described by Mehta et al. (2015), microemulsion-based organogel should have the following properties:

1. It should be nonreactive and compatible with other additives.
2. It should not support any kind of microbial growth.

3. It should not change characteristics of entrapped material.
4. It should be economic and easy to handle.
5. It should have high storage stability.

Organogels are principally classified based on nature of organic liquid used for its preparation and type of organogelators used for the purpose of cross-linking. These organogelators are broadly classified into polymeric organogelators (POG) and low molecular weight organogelators (LMOG) (molecular weight < 2000 g/mol, even smaller than 500 g/mol). Polymeric organogelator scan gel organic solvent by physical cross-linking. If the polymers are polypeptides, they will interact via hydrogen bond, and p-conjugated polymers interact by π-π stacking (Palomo et al. 2017).

Organogelators are also categorized into two different categories based upon their hydrogen bonding ability. Hydrogen bond forming organogelators are urea, amino acid, amide moieties, and carbohydrates. Non-hydrogen bond–forming organogelators include anthraquinone and steroid-based molecules (Plourde et al. 2005).

There are different low molecular weight organogelators which are widely used to solidify various organic solvent. The anthryl derivatives like 2,3-Bis-n-decyloxyanthracene (DDOA) has been successfully employed to gel alkanes, alcohol, nitrile and aliphatic amines. Organometallic compound such as mononuclear copper-β-diketonate gel hexadecane and dodecane by the formation of aggregates. Different gelator molecules, their characteristics, and application are listed in Table 12.1. Other than this, there are gelators which could form supramolecular structure by aggregating with different gelator and gel two-phase system. Two-component system of aminopyrimidine/dialkylbarbituric mixtures could form stable gels in cyclohexane, another example of two-component system is phenol/sodium bis(2-ethylhexyl) sulfosuccinate (AOT). AOT is an anionic surfactant, and it can self-assemble in solvent like isooctane. Sodium bis(2-ethylhexyl) sulfosuccinate (AOT) also forms ternary complex, in which major component of the system must be organic solvent and little amount of water is solubilized within AOT micelles, and it could be gelled using gelatin (Terech and Weiss 1997).

LMOG organogels are categorized based on their kinetic properties as strong organogels and weak organogels, and these gels have solid fiber network and fluid fiber network, respectively. Many of the natural molecules having complex structures like amino acid/small peptides, carbohydrates, cholesterol, and long hydrocarbon chains are potential LMOG because of their availability and continuous supply without extensive synthetic effort (Palomo et al. 2017).

12.3.2 Microemulsion-Based Organogel Preparation

Microemulsion-based organogels are prepared in three sequential steps as shown below (Fig. 12.6) (Madhav and Gupta 2011; Mujawar et al. 2014):

Table 12.1 Types of organogelators used in the formation of organogel, its properties, and application

No	Types of organogelators	Properties of gel formed	Application
1	4-Terbutyl-1-aryl cyclohexanols derivatives	Poor solubility in nonpolar solvent Forms solid gel at room temperature	Helps in thermoreversible organogel design (Garg et al. 2011)
2	Boc-Ala(1)-Aib (2)-β-(3)-OMe organogelators Boc-(tert-butoxycarbonyl) to protect amino terminal Ala-alanine amino acid Aib-α-aminoisobutyric acid OMe-methyl ester	Forms thermo-reversible transparent gel with nonpolar solvent like dichlorobenzene (Mehta et al. 2015)	Oil spill recovery (Jadhav et al. 2010; Mukherjee and Mukhopadhyay 2012; Basak et al. 2012; Ren et al. 2016)
3	Polymeric organogelators Poly(ethylene) Alkylated poly(glycerol methacrylate) (Bachl et al. 2015)	Colorless in nature Gelled structure formed due to precipitation of polyethylene molecules (Pawar et al. 2014)	Widely used as ointment base Pharmaceuticals (Mehta et al. 2015)
4	Low molecular weight gelators (Fatás et al. 2013) Lecithin (Kumar and Katare 2005) 12-Hydroxystearic acid 1,3:2,4-Dibenzaldehyde-D-sorbitol Bis-urea	Improved mechanical properties Some amphiphile at very low concentration (<2%) immobilize high amount of nonpolar solvent Some amphiphile has ability to self-assemble in the presence of polar solvent (Pawar et al. 2014)	Ointment with controlled antibiotic release Disposal of cooking oil Additive in cosmetics and dental material (Kirilov et al. 2014; Ohsedo 2016)

12.3.3 Preparation of Organogels

Organogels are prepared by two different mechanisms: fluid-filled fiber mechanism (Fig. 12.7) and solid fiber mechanism (Fig. 12.8).

12.3.4 Enzyme Immobilized in Various Microemulsion-Based Organogel (MBG)

Enzyme immobilized in MBGs retain their stable and active configuration for longer period, and thus their reusability also increases (Zoumpanioti et al. 2010). Moreover, it offers advantage of double immobilization first in the micellar microenvironment and second in the three-dimensional polymer network of gelator surrounding

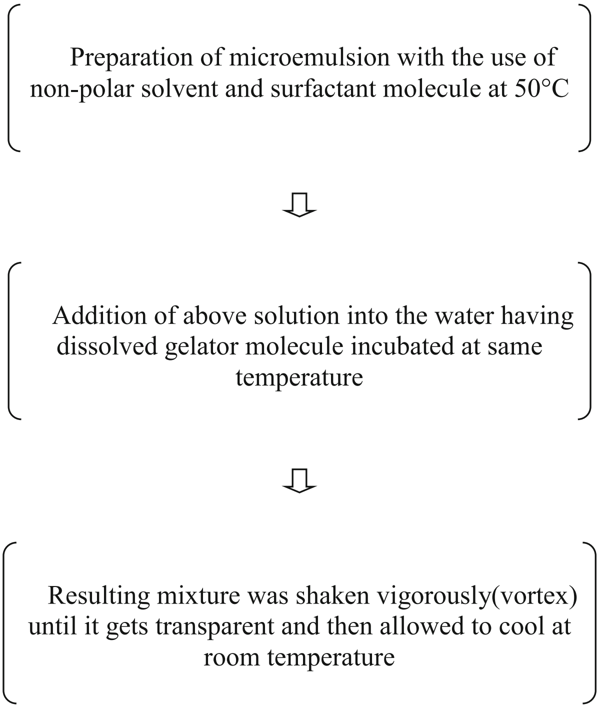

Fig 12.6 Preparation of microemulsion-based organogel

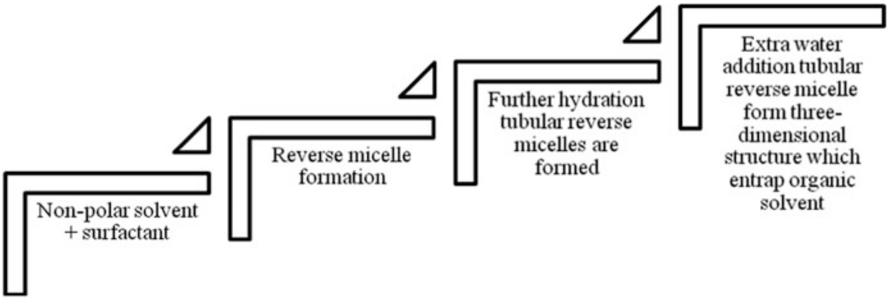

Fig. 12.7 Formation of organogel by fluid-filled fiber mechanism (Agrawal et al. 2004; Sahoo et al. 2011)

micelles (Rees et al. 1991; Gupta and Roy 2004). MBGs disperse enzyme at molecular level and various co-factors needed for catalyst can also be included in micellar system (Fadnavis and Koteshwar 1999). Enzymes hosted in MBGs (hydroxyl propyl methyl cellulose organogel) are able to catalyze reactions at 50 °C efficiently, and some of the organogels are stable at temperature higher than this (Raghavendra et al. 2014).

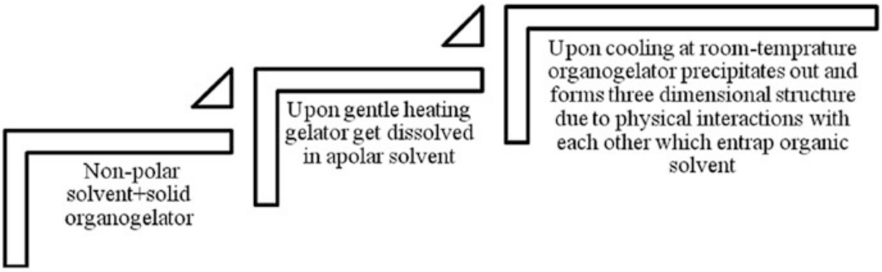

Fig. 12.8 Formation of organogel by solid fiber mechanism (Sahoo et al. 2011)

Lipases are enzymes of biotechnological importance because of their utility in preparation of fine chemicals, flavors, aromas, food supplements, etc. (Raghavendra et al. 2014). To maintain functionality of lipase, low water conditions are necessary. It utilized various nonpolar substrates which has high availability in organic solvent as compared to aqueous environment. Lipases are extensively used in microemulsion-based organogel systems (Xenakis and Stamatis 1999; Backlund et al. 1996; Zhang et al. 2015). Jenta and co-workers (1997) prepared lipase *Chromobacterium viscosum* (CV) immobilized microemulsion-based (AOT in isooctane) gelatin stabilized organogel to carry out condensation reaction of decanoic acid and n-octanol (esterification) to form octyl decanoate. This CV lipase organogel is found to have remarkable storage stability (−25 °C) and give higher product yield in repeated batches without any microbial contamination.

Lipase B from *Candida antarctica* (CaLB) has been encapsulated in AOT/isooctane microemulsion-based hydroxypropyl methyl cellulose (HPMC). These MBGs were used to catalyze esterification reaction of solketal and stearic acid. CaLB immobilized microemulsion-based organogel can be used to produce protected monoacylglycerol. As compared to conventional commercially immobilizes enzyme, MBGs give higher productivity, and their conversion yield was found to be 99% for this particular process. It could be utilized for 15 consequent cycles without activity loss. This esterification process was carried out at 45 °C which is relatively high, and it also converted substrates into desired product in lesser time (Itabaiana et al. 2014).

12.3.5 Case Study: Gelatin-Stabilized Microemulsion-Based Organogels

Microemulsions can be entrapped in the organogels using a gelator molecules; usually a biopolymer like agar, gelatin, or cellulose derivatives, to form microemulsion-based organogels (MBGs) (Soni and Madamwar 2001). It has been noted that MBGs are stiff and stable in different nonpolar or relatively polar organic solvents. The gel formation using various gelator molecules, for example gelatin, successfully retains active enzyme, surfactant, and water components, and it works as an immobilized carrier of enzyme. Organogel allows the diffusion of nonpolar substrates and formed products. In organogel, gel network is said to contain bicontinuous phase which comprises two immiscible liquid phases (water in oil microemulsion) retaining encapsulated biocatalyst (Itabaiana et al. 2014). Gelation of microemulsions is nano-gel formation where the number of gelatin molecules per droplet is two or more. If the gelator molecules are less than two molecules per droplet, then it will behave like random coil into the droplet. Microemulsion system retains its emulsion like properties at low concentration of gelator molecule, and their phase stability almost remains unchanged.

Usually 2–3% w/v gelatin concentration is used to form connecting structures between two dispersed phases. It will result in the formation of "fractal" clusters, which are responsible for the increase in viscosity of resulting gel significantly. Gelatin concentration higher than 2–3% w/v will form a three-dimensional semi-rigid structure which is a cross-linked structure called gel. It is "super-polymer" which can be employed to carry out various biotransformation processes like esterification and hydrolysis (Rees and Robinson 1993).

The structural and morphological characterization of gelatin-stabilized microemulsion-based organogel has been done by different authors (Atkinson et al. 1991; Capitani et al. 1988; Petit et al. 1991), and according to them, three different models of gel preparation are proposed, which are described below:

1. Gelatin molecules aggregate and thus form a rigid network that is surrounded by oil and water intertwining channels which are separated by surfactant zone (Capitani et al. 1988).
2. Gelatin aggregate forms rigid network that coexists with water and oil droplets stabilized using surfactant (e.g., AOT) (Atkinson et al. 1991).
3. In microemulsion, reverse micelles has aqueous phase inside them and some part of gelatin also, and these micelles connect to rest of the gelator in order to form helical structure (Petit et al. 1991).

12.4 Methods for Intermediation of Environmental Pollutant BPA

Several methods such as ozonation (Irmak et al. 2005; Gultekin et al. 2009), enzyme oxidation (Fukuda et al. 2001), sorption (Asada et al. 2004), membrane filtration (Dong et al. 2008), chemical oxidation (Yoshida et al. 2001; Ioan et al. 2007), solvent extraction (Fan et al. 2008), electrochemical process (Tanaka et al. 1999), and sonochemical degradation (Inoue et al. 2008) are introduced for the BPA removal from wastewater.

In addition to all previously described methods, another approach for BPA removal is used of nanotechnology. BPA removal from wastewater can be done with the use nanoparticles. Composite nanoparticles of Fe_3O_4/SiO_4 are best suited for BPA removal from aqueous system. Single-walled carbon nanotubes and multi-walled carbon nanotubes are also interesting system to carry out BPA intermediation. Multi-walled carbon nanotubes are better among them and remove BPA by absorptive mechanism, and it showed excellent selectivity for BPA molecule (Safabakhah and Pourzamani 2016).

Tursi and co-workers (2018) developed surface-modified cellulose fibers from Spanish broom (SB) and examined its potential to adsorb BPA from aqueous system. The functionalized fiber (FF) showed best absorptive efficiency at pH 5. The adsorption of BPA on the fiber was resulted due to hydrophobic interaction between them, and kinetic studies confirmed that it was a pseudo-second-order reaction. These FFs were reusable up to three cycles. It showed 77% BPA removal in ultrapure water and 64% in synthetic wastewater which suggest its high selectivity toward BPA.

All the information obtained from reported data suggest that it is possible to remediate BPA through various routes. Proposed mechanism for BPA removal deals with adsorptive or absorptive mechanism and could be employed to remove BPA from wastewater or industrial effluent, the absorbed chemical will have same estrogenicity and toxicity. To achieve the aim of reduction in toxicity and hazardous effects of BPA, its conversion into less toxic compound is needed, and it can be achieved by biocatalysts.

12.5 BPA Bioremediation by Different Systems Using Laccase

There are so many fungi which are reported for the bioremediation of environmental pollutant BPA. Most of this reported fungus can remediate BPA by an enzyme known as laccase. More than 100 types of laccases from fungus are reported. Laccases are holoenzyme made up of glycoprotein (dimeric or tetrameric). This glycoprotein contains four copper atoms bound to three redox sites. Laccases are classified as oxidoreductases which are able to oxidize phenol and related substances using oxygen as electron acceptor. Laccase acts on a broad range of substrates like polyphenol, diphenol, substituted phenol, aromatic amines, and other inorganic compounds (Madhavi and Lele 2009). They are also known as "blue" oxidases or phenol oxidases (Gianfreda et al. 1999). Laccase acts on phenol by Cα oxidation, Cα-Cβ cleavage, and aryl alkyl cleavage. Oxidation by laccases generates free radical, which is unstable and undergoes nonenzymatic reaction such as deprotonation, hydration, or polymerization. Laccases can be visualized to function as a battery which stores electrons liberated after individual reaction and use them to reduce molecular oxygen. For the complete reduction of molecular oxygen to water, oxidation of reducing molecule or substrates is required (Thurston 1994).

Zeng and co-workers (2017) worked on white rot fungus *Trametes versicolor* and evaluated its potential for BPA removal. *Trametes versicolor* grown on mixed substrates named corn straw and wheat bran under solid state fermentation was able to produce highly active laccase. They compared BPA degradation by this fungus in two different conditions, degradation in solid state fermentation (SSF) and in vitro by just using purified laccase. Depending upon the results, it was concluded that SSF process had greater potential for BPA removal because of simultaneous laccase production and BPA degradation. In addition, 90% of the BPA estrogenic activity was removed in this process.

White rot fungi *Lentinus swartzii* and *Genoderma stipitatum* are able to produce laccase, and this laccase was employed for BPA as well as other environmental pollutant triclosan bioremediation. It was observed that after 6 h of laccase treatment, estrogenic activity of BPA was eliminated. From the mass spectrometry (MS) analysis, it was verified that laccase-oxidized products of BPA were having high molecular weight and formation of oligomers (dimers through pentamers) was seen, and they showed lower toxicity as compared to the parent compound (Arboleda et al. 2013).

In one of the reports regarding elimination of bisphenol A and nonylphenol (NP), laccases from *Coriolopsis polyzona* were used. In this experiment, submerged fermentation was carried out using poplar (*Populus* sp.) leaves. *Coriolopsis polyzona* produces laccase and manganese peroxidase. To ensure the presence of only laccase, catalase was added in reaction mixture, which will eliminate manganese peroxide activity by removal of hydrogen peroxide, and the only active enzyme in the system was laccase (Elisashvili et al. 2009). In this study, decrease in estrogenic activity was determined using Yeast Estrogenic Screen (YES) assay, and it was noted that estrogenic activity was considerably reduced after laccase treatment (Cabana et al. 2007).

In this study, the possible mechanism of BPA remediation was studied. After laccase treatment, full-scan Electrospray Ionization (ESI)(−) MS spectra of BPA solution was obtained, which showed the formation of high molecular weight compounds. It might be due to polymerization by laccase oxidation. The elimination of BPA by *C. polyzona* was because of polymerization and particularly dimer formation. According to ESI-MS spectra, this polymerization occurs by C-C bond formation, and it could be between phenol moieties of BPA. Similar results were obtained by Uchida et al. (2001), and they utilized *Thermopsis villosa* laccase for BPA bioremediation. The dimer produced after BPA oxidation was recognized as5,5-bis-[1-(4-hydroxy-phenyl)-1-methylethyl]-bisphenyl-2,2-diol.

Lignin-degrading basidiomycetes named *Stereum hirsutum* and *Heterobasidium insulare* were utilized to degrade bisphenol A. Both the strains of fungi were able to grow at 100 ppm concentration of BPA, and after completing mycelial growth, complete BPA degradation (99%) was achieved after 7–14 days at 30 °C. After BPA removal, samples were studied for their estrogenic activity using MCF-7 (Michigan Cancer Foundation-7), Caucasian women breast cancer cell line proliferation assay and (E-screen), and analysis of pS2 mRNA expression in MCF-7 cells. MCF-7 cell proliferates at 10^{-5} M BPA concentration, whereas cell proliferation was inhibited when treated with BPA along with *Stereum hirsutum* and *Heterobasidium insurable* in culture media. The pS2 mRNA is a potential marker for human breast cancer, and supernatant from BPA-treated culture media has shown decreased pS2 mRNA expression by 1.5-fold (Lee et al. 2005).

Apart from white rot fungus, filamentous fungi named *Aspergillus terreus* and *Aspergillus flavus* are also reported for the removal of environmental pollutant BPA. According to Fouda et al. (2015), these fungi are resistant to high concentration of BPA and can utilize it as a sole carbon source. In vivo mammalian cell line studies showed that *Aspergillus terreus* and *Aspergillus flavus* successfully degrade BPA and reduce its toxicity.

Reverse micellar-based systems have been successfully employed for bioremediation of BPA. Laccase from *Trametes versicolor* entrapped in the reversed micellar system effectively catalyzes the oxidation reaction of bisphenol A in isooctane: AOT-based system in the absence of a mediator. Laccase in the RM system exhibited a high and stable enzymatic activity, and better catalytic efficiency than laccase in aqueous media (Ingale et al. 2015). According to Michizoe et al. (2001), AOT-laccase reverse micelles system was able to remediate bisphenol A effectively into 4-isopropylphenol and 4-isopropenylphenol, whereas AOT-laccase complexes in water-saturated isooctane were not as effective as reverse micelles systems for BPA oxidation. Laccase obtained from mutant strain *Fusarium incarnatum* UC-14 was employed for BPA degradation in isooctane: AOT micellar system. This system found to eliminate up to 94% of 200 ppm BPA in 75 min at 50 °C and pH 6.0, laccase oxidizes BPA into 4,4-(2 hydroxy propane 1,2 diyl) diphenol, bis (4-hydroxylphenyl) butenal, and 2-(1-(4-hydroxyphenyl) vinyl) pent-2-enal detected by GC-MS analysis (Chhaya and Gupte 2013).

Bioremediation of BPA using laccase is highly effective for the reduction of its reproductive toxicology. Enzyme preparation containing laccase from *Ganoderma stipitatum* was employed for BPA remediation. Enzyme-treated samples were subjected to toxicity testing using micro-crustacean *Daphnia pulex*-based toxicity bioassay. Enzyme-treated BPA samples (after 48 h of enzyme treatment) showed no mortality toward *D. pulex* in any of tested dilution (Arboleda et al. 2013). BPA samples treated with laccase were also subjected to estrogenicity testing using Yeast Estrogenic Screen (YES) assay. It was reported that BPA estrogenic activity was reduced up to 70% and 50% after 3.5 h of laccase treatment from *Ganoderma stipitatum* and *Lentinus swartzii.* After 6 h of laccase treatment from both strains was able to reduce estrogenicityup to 90%. BPA oxidation using laccase generates phenoxy radicals, and these BPA oligomers lacks structural attributes necessary to bind with human estrogen receptor (Fang et al. 2001; Tsutsumi et al. 2001).

12.6 Conclusion

BPA bioremediation using laccase in aqueous systems has been extensively studied, but its remediation in nonaqueous system is relatively a new approach. For the intermediation of BPA laccase enzyme produced by white rot fungi extensively studied and reported. Among all the reported types for nonaqueous catalysis, reverse micellar catalysis is by far stand out as the most appropriate option. Laccase entrapped in reverse micelles is an efficient system for BPA removal, and formation of microemulsion-based organogel provides double immobilization of enzyme which minimizes problems like enzyme leaching. It is a stable environment for enzyme catalysis. Nonaqueous catalysis is an interesting dimension in recent times due to the unexpected yet fundamental behavior of biocatalysts in this system (Gupta and Roy 2004). This phenomenon has upper hand for some specific bioconversions; hence, there is much more to explore in this field.

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Chapter 13
Nanoparticle-Mediated Adsorption of Pollutants: A Way Forward to Mitigation of Environmental Pollution

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Microorganisms for Sustainability 26, https://doi.org/10.1007/978-981-15-7455-9_13

Abstract Environmental pollution is the major problem faced by the developing and developed countries of the world due to urbanization and industrialization. Pollution occurs in the environment when the earth nature does not know how to convert the material into some other form due to its complex and resistant nature. Causes of soil pollution are disposal of industrial wastes (contains heavy metals), residential wastes, transportation wastes (oil spills), and agricultural practices (fertilizer, pesticide application). Many pollutants such as Cd, Hg, Pb, As, nitrate, phosphate, and organic compounds like polychlorinated biphenyl (PCB) contaminate water and soil. On the other hand, the use of nanomaterials to remediation of environmental pollutants attained the rapid growth in the current century. Nanomaterials are having a large surface area and reactivity, which make them excellent adsorbents and catalysts. Due to the smaller size, nanoparticles can make it possible to access the areas for remediation of pollutants by major mechanisms like physical adsorption, chemical adsorption, chelation, fixation, filtration and oxidation, and reduction. Moreover, modification of nanosurface with various ligands or surfactants enables the nanomaterials to be a good adsorbent. Making use of these efficient adsorbents to remediate the pollution is outlined here with various examples and mechanisms.

Keywords Environmental pollution · Nanoparticles · Remediation · Metal oxides · Carbon nanotubes

13.1 Introduction

The issue of environmental pollution is very sober in the globe and is disturbing the soil and environment; environmental pollution is mainly caused by dumping of toxic chemicals, particulate matter in the air, water, and soil. This not only causes the destruction of biodiversity but also degradation of soil, plant, animal, and human health. Increasing pollution levels in the environment is making us to think of better technological discoveries to curb the ongoing pollution in the soil and environment immediately. The conventional chemical and physical techniques such as oxidation-reduction, ion exchange, adsorption, precipitation, membrane filtration, reverse osmosis, electrolytic removal, and flocculation are adopted for the removal of trace metals and other pollutants (Wang 1992; Marian et al. 2002). However, operational cost, quantity, and low efficiency of these conventional technologies bring the worrisome outputs. To overcome these, scientists used some other alternative materials to adsorb the metal pollutants such as clay mineral namely zeolite, montmorillonite, attapulgite, kaolinite, bentonite, and activated carbon (Sharma et al. 2009). But due to their unavailability and higher quantity required to replenish, the contaminated sites need a new alternative which could serve as efficient absorbents with small quantity. The nanotechnology brainchild of scientists offers great advantages over the conventional strategies to improve the existing environmental cleanup technologies. Moreover, application of nanomaterials has widened up the possibilities of usage of nanomaterials in the different scientific fields as the cleanup (remediation) of the environment and purification of contaminated water and the detection and prevention of contaminants in the soil environment.

13.2 Nanoparticles and the Environment

Nanotechnology is a science where materials at the nanoscale (10^{-9} m) govern the activity of reaction. Nanoparticles are group of atoms assembled with 10^{-9} m scale which is the dimension in between of ionic size (10^{-10} m) and of macroscopic bulk materials. The atoms present in the nanostructure are very small in size and are generally distributed near the surface of the nanomaterials. When compared to the bulk materials, the nano-sized materials articulate different atomic, electronic, magnetic, physical, and chemical properties and reactivity (Banfield and Zhang 2001). Size of the material ranges from micron (10^{-6} m) to nano (10^{-9} m) level which changes the properties such as surface area, surface area to volume ratio, and reactivity (Mamalis 2007), which results in the improvement of number of active sites for interaction, adsorption capacity, and catalytic reactivity transform to better adsorbing materials than other common materials. Nanoparticles are always existing in our environment through either natural sources or anthropogenic sources (Karthikeyan et al. 2019). Natural nanoparticles are generally inherited from weathering, transport, metal binding, and other global biogeochemical processes. Moreover, the presence and participation of natural nanoparticles influence the bioavailability of essential and metal elements to plants, animals, and humans, further, through its high buffering capacity which helps in stabilizing the environmental systems (Tipping 2002). Therefore, it is very important to have the quantity of synthesized nanoparticles at control and much lesser than the natural counterparts in an ecosystem. The organisms have to develop or build befitting defense mechanisms to overcome these manufactured nanoparticles because their structural and electro-chemical characteristics vary from those found in nature (Hartland et al. 2013). Various type of nanoparticles are distributed in nature (Fig. 13.1), and they are classified as follows:

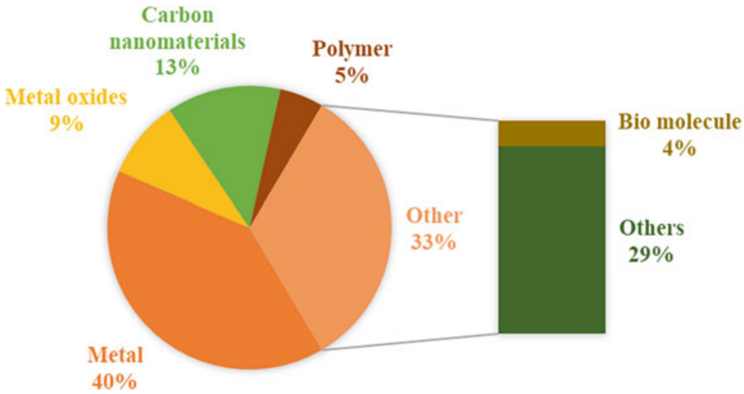

Fig. 13.1 Distribution and usage of different types of nanoparticles

13.2.1 Oxide Nanoparticles

Oxide nanoparticles have smaller size and more number of corner and edged surface sites will display distinctive physical and chemical properties. The structural characteristics namely lattice symmetry, low surface energy, the electronic properties of the oxide (Philip 2001), and band gap influenced conductivity and chemical reactivity (Rodriguez 2002) of the nanoparticle influences the activity and stability of the oxide nanoparticles. This structural phenomenon has been detected in many oxide nanoparticles such as TiO_2, Al_2O_3, Fe_2O_3, ZrO_2, MoO_3, CeO_2, and MoO_x (Ayyub et al. 1995; Samsonov et al. 2003; Song et al. 2001). A wide range of nanoparticles of metal oxides are naturally present in soil and also synthesized using metal targets including iron (Fe), aluminum (Al), titanium (Ti), zinc (Zn), nickel (Ni), copper (Cu), cobalt (Co), magnesium (Mg), cerium (Ce), yttrium (Y), gadolinium (Gd), etc. The physico-chemical properties of oxide nanoparticles is size dependent and has special significance in chemistry. Industrial applications of oxide nanoparticles are absorbents, sensors, ceramics, and catalysts. Size-defected or non-stoichiometry effects and structural or electronic quantum size are two important interrelated parameters that influence the size-dependent oxide chemistry. Metal oxides are mostly used as absorbent and catalysts which is based on their redox potential and acid–base properties; further, these qualities are warranted by their state of oxidation and coordination environment. Several metal oxides were tried by our scientists to reclaim the heavy metal contaminated water and soil, namely iron oxide (Raven et al. 1998), aluminum oxide, zirconium oxide (Hristovski et al. 2008a, 2008b), copper oxide (Taman et al. 2015), and manganese oxide (Lenoble et al. 2004).

13.2.1.1 Metal Nanoparticles (MNPs)

These metal nanoparticles could be chlorides, sulfides, oxides, hydroxides, and fluorides species of metals or pure metals (namely Ag, Pt, Ti, Zn, Fe, Au) with submicron scale. The main characteristic features of MNPs are large A/V ratio; large surface energies; "dangling bonds" in large numbers, transitional electronic structure; specific chemical properties, quantum confinement; store more electrons (e^-), short range ordering; and a large quantity of coordination sites in corners and edges. These MNPs are produced either chemical or physical methods. These particles mainly used in catalysis (Campelo et al. 2009), sensors, drug delivery, etc.

13.2.2 Carbon-Based Nanoparticles

The carbon-based nanomaterials (CBNs) are nanotubes (either single-walled and/or multi-walled), fullerenes, nano diamonds, and graphene obtained using graphite as starting material. Carbon-based nanomaterials possess huge mechanical strength, optical features, electrical, and thermal properties (Krüger 2010) (Fig. 13.2). Carbon nanotubes (CNT) and activated carbon and graphene are mostly used in biomedical applications such as smart drug delivery, labeling agents in biological applications, removal of metallic pollutants, and biomaterial reinforcements. In recent times, mostly these carbon nanomaterials are largely used in the removal of heavy metals and dye from contaminated waters with regard to its nontoxicity, more availability, high surface area and porosity, established structure, and excellent sorption capacities. Although major applications are more useful as absorbents, but still CNTs are proven to be cytotoxic because of more cellular uptake, agglomeration, and oxidative stress in organisms (Yang et al. 2012). The recent steady increase in CBN production volumes posing a major concern is their potential interactions with living organisms and incorporation into food chains with yet unknown consequences.

13.3 Synthesis of Metal Oxide, Metal and Carbon Nanomaterials

Efficiency of the nanoparticles varies with the size, crystallinity, and zeta potential. These characteristics are sustained by the way it has been produced or synthesized. It is clear that choosing appropriate method from available synthesis protocol is highly important. The physical and chemical methods are very useful for the production of monodispersed nanoparticles. These techniques are detrimental to the environment as they leave harmful, inflammable, and persistent toxic chemicals (Kowshik et al. 2002). Further these methods have the residues of these dangerous chemicals on the surface of end produces of nanoparticles could lead to undesirable consequence in

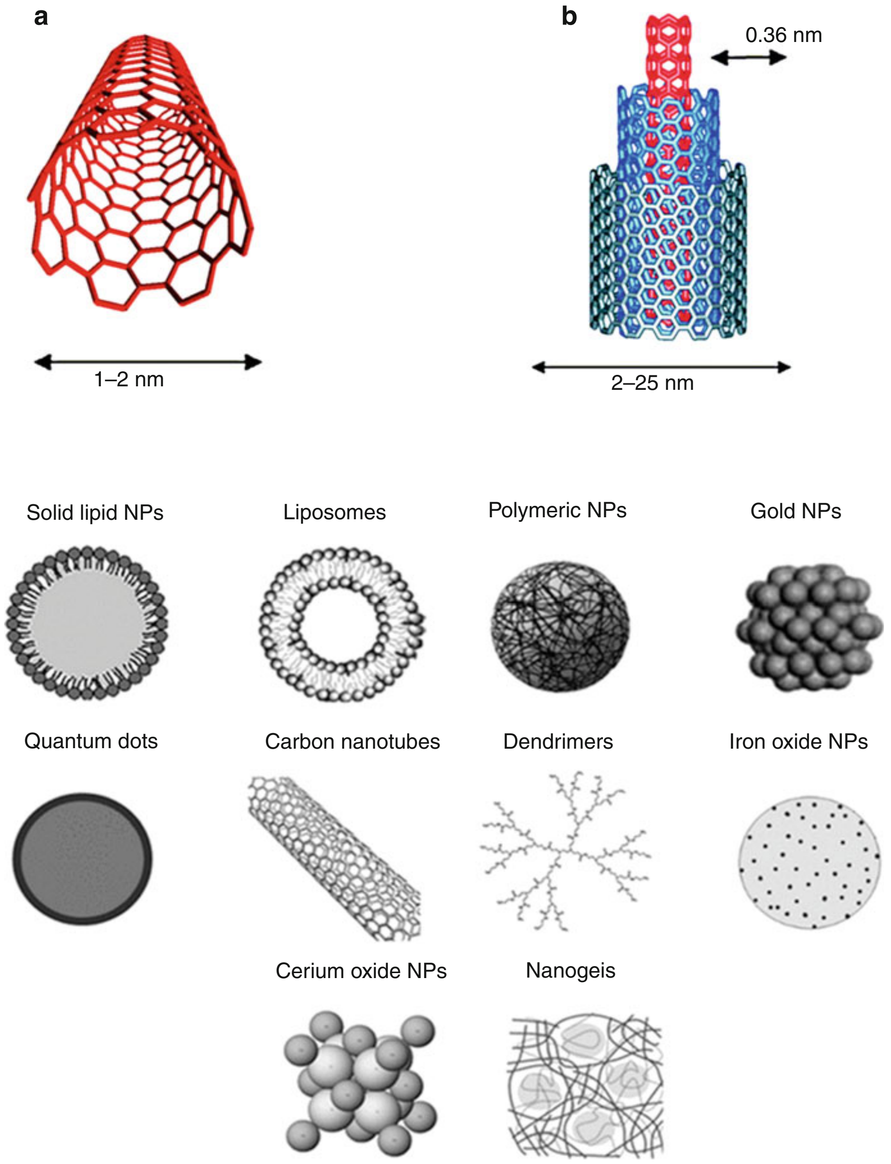

Fig. 13.2 Structures of carbon nanotubes (**a** and **b**) and different nanomaterials (Adapted from Rabbani et al. 2016)

the medical applications (Jain and Ag 2000). Henceforth, production of nanoparticles through highly eco-friendly, clean, biologically well-suited, and less toxicity methods has more advantage. Many protocols applying biological, chemical, and physical means, which cover bottom-up and top-bottom approaches, namely

Table 13.1 Synthesis of metal nanoparticles through sol-gel method

Nanoparticle	Diameter (Å)	Chemical source	Reference
Nano-Al_2O_3 powder	0.6, 3.0	Aluminum chloride hexa hydrate	Zeng et al. (1998)
Nano-Al_2O_3 particles	5.0	$Al[O–CH(CH_3)_2]_3$, C_6H_{12}	Pacheco and Rodriguez (2001)
Nano-Al_2O_3–SiO_2 particles	3.0	$Si(OC_2H_5)_4$, ammonium hydroxide, isopropanol, C_2H_5OH, $C_{12}H_{27}AlO_3$	Pacheco and Rodriguez (2001)
Maghemite	1.0	Ferric and ferrous chloride, ammonium hydroxide	Hu et al. (2005)
Nano-TiO_2	0.5	$C_8H_{15}F_6N_2P$	
Nano-NiO	0.4–2.2	$Ni(CH_3CO_2)_2·4H_2O$, $C_2H_2O_4$, C_2H_5OH	Thota and Kumar (2007)

ball milling, electro deposition, gas condensation, spark discharge generation, pyrolysis (spray and laser), thermal (photo, plasma, flame), sol-gel process, low-temperature mechano-chemical synthesis, mechanical alloying ion sputtering, green synthesis through microorganisms, and leaf extracts are the extensively followed techniques in the production of nanoparticles (Grieve et al. 2000; Trindade et al. 2001; Murray et al. 2005; Kammler et al. 2001). Among these methods, sol-gel of chemical method having more advantage over the other methods due to its high recovery, degree of control and desire size during the synthesis protocol (Kornak et al. 2005; Sarkar et al. 2007) (Table 13.1).

Although biological means of nanoparticle production are considered as safe, economically feasible, environmentally sustainable, and ecologically acceptable method, these green approaches utilize biological components, largely prokaryotes and eukaryotes. Biological systems have been given more attention and highly subjugated for production of nanoparticles because of environmental safety and could be an effective alternative options to chemical and physical means of nanomaterial production (Javed et al. 2011). Biological methods employ biological agents like plants, algae, fungi, actinomycetes, yeast, bacteria, and viruses for making nanoparticles (Gaidhani et al. 2013; Nagajyothi and Lee 2011). The biological processes of making nanoparticles are less energy dependent, mostly acceptable, ecologically sound, and green route. The most abundant organisms in our biosphere is bacteria. This biogenic approach greatly depends on ambient environmental conditions such as pH, temperature, and pressure that influence the bacterial growth and development as well as activities. The nanoparticles manufactured through biological methods tend to have larger specific surface area, greater catalytic properties, and improved enzyme activity (Seo et al. 2006). In spite of prevalence and practices of abundant chemical methods of nanoparticle fabrication, frequent problems are often encountered with stability, agglomeration, and crystal formation in long time exposures (Rajasree and Suman 2012) (Fig. 13.3).

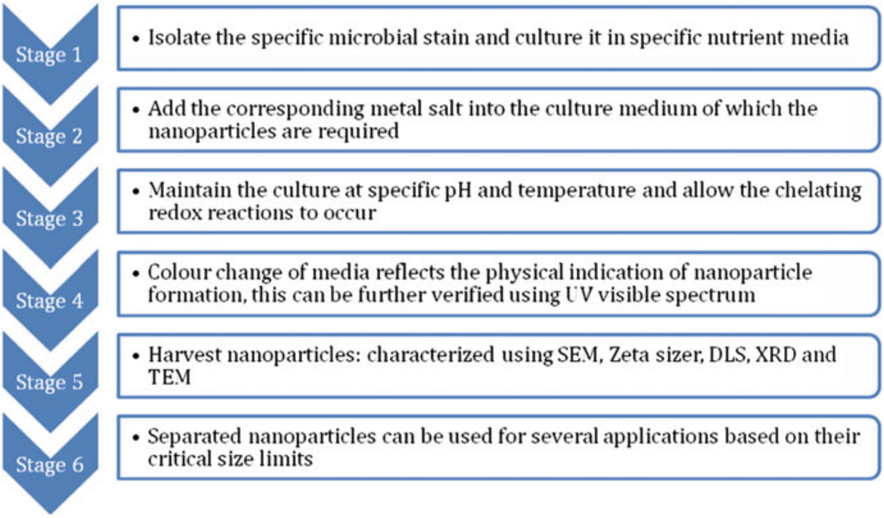

Fig. 13.3 Generalized flowchart for biosynthesis of nanoparticles using microorganisms

13.3.1 Mechanism Used by Bacteria

The most versatile location of biosynthesis of nanoparticles is biological cellular entities and their cell membrane (Mandal et al. 2006) that mediated through biological or biochemical enzymatic reactions following either intra- or extracellular route. The manufacturing of nanoparticles using biological agents is still a complex process, and actual definite mechanism is not arrived yet because biological agents adopted/employed different mechanisms with different metals. Also different bio-molecules are responsible for the synthesis of nanoparticles. According to Beveridge et al. (1997), the mechanisms of biosynthesis of nanoparticles could be oxidation and reduction reactions that alter the toxicity and solubility, efflux system, biological absorption and accumulation, extracellular complexion, or precipitation of metals and absence of specific metal transporters in the biological systems. The extracellular production of nanoparticles has more commercial as compared to intracellular process (Beveridge et al. 1997) (Table 13.2).

At ambient temperature and pressure, the metal pollution remediation (rate of reduction of metal ions) by biological methods is found to be much faster. Metals can be adsorbed and accumulated in microbial cells such like bacteria (Juibari et al. 2011), yeast (Huang et al. 1990), fungi (Castro-Longoria et al. 2011), and alga (Darnall et al. 1986). The bioremediation of metals takes place by means of the biochemical enzymatic activities; the enzymes secreted by microbes hydrolyze the metals, thereby reducing the metal contents in the given environment.

Adsorbents made up of nonmetals have displayed better efficiency as well as cost-effective when compared to that of adsorbent of usual materials (Rickerby and Morrison 2007; Brumfiel 2003; Theron et al. 2008). The following criteria are

Table 13.2 Bacterial species involved in intra- and extracellular synthesis of nanoparticles

Sl. no.	Name of bacteria	Type	Size (nm)	Reference
1.	*Rhodopseudomonas* sp.	Ag	6–10	Manisha et al. (2014)
2.	*Bacillus megaterium*	Ag, Cd, Pb,	10–20	Prakash et al. (2010)
3.	*P. aeruginosa SNT1*	Se	Spherical/ contour	ND
4.	*Pseudomonas fluorescens*	Au	50–70	Rajasree and Suman (2012)
5.	*Lactobacillus* sp.	Ag	2–20	Ranganath et al. (2012)
6.	*Streptomyces* sp. *HBUM171191*	Mn, Zn	10–20	Waghmare et al. (2011)
7.	*Bacillus cereus*	Ag	10–30	Prakash et al. (2011)
8.	*Aquaspirillum magnetotacticum*	Fe_3O_4	40–50	Mann et al. (1984)
9.	*Planomicrobium* sp.	TiO_2	8.89	Malarkodi et al. (2013)
10.	*Lactobacillus acidophilus, Lactobacillus casei, Klebsiella pneumonia*	Se	50–500 50–500 100–550	Sasidharan and Balakrishnaraja (2014)
11.	*Lactobacillus sporogens*	ZnO	145.7	Saifuddin et al. (2009)
12.	*Lactobacillus*	TiO_2	150	Azhar et al. (2011)
13.	*Pseudomonas aeruginosa*	Ag		Shivakrishna et al. (2013)
14.	*Magnetotactic bacterium*	Fe_3S_4, FeS_2	7.5	Mann et al. (1990)
15.	Sulfate-reducing bacteria	FeS	2	Watson et al. (1999)
16.	*Magnetospirillum magnetotacticum*	Fe_3O_4	47.1	Philipse and Maas (2002)
17.	*M. magnetotacticum (MS-1)*	Fe_3O_4	50	Lee et al. (2004)
18.	*Bacillus cereus*	Cds	30–100	Harikrishnan et al. (2014)
19.	*Actinobacter* sp.	Magnetite	10–40	Bharde et al. (2005)
20.	*Exiguobacterium mexicanum PR*	Ag	5–40	Padman et al. (2014)
21.	*Acinetobacter* sp. *SW 30*	Au	20 ± 10	Wadhwani et al. (2014)
22.	*Brevibacterium casei*	Co_3O_4	5–7	Kumar et al. (2008)
23.	*Pseudomonas aeruginosa*	Au	15–30	Husseiney et al. (2007)

important for acceptance of nanoparticles to consider them as adsorbents (a) should be nontoxic, (b) high sorption power even under low concentration (c) adsorb over the surface easily, (d) must be recyclable and (e) able to get adsorbent back by reversible process; however, the high adsorption power of nanoparticles is the main criteria for eliminating heavy metal ions from wastewater (Cloete 2010; Savage and

Diallo 2005). By means of various processes like sedimentation, centrifugation, filtration, magneto deposition, flocculation, and coagulation along with extraction, combustion, and acid treatment, the nanoparticles are separated from the water.

13.4 Remediation Mechanisms of Nanoparticles

Fundamental basis of nanotechnology is to explore and exploit the unique properties of nanomaterials which do not exist in the micro and macro particles present in the nature. Because of these unique properties, nanomaterial applications in many fields are increasing day-by-day to overcome the environmental pollution. The physical and the chemical changes in the aforesaid properties of nanoparticles with bio-organisms are interesting phenomenon, though many of them are little known, it can be further investigated for their applications in multi-fields of science. Various technologies such as filtration, chemical reactions, adsorption, absorption, and photo catalysis are involved to eliminate pollutants from various ecological media (e.g., soil, water, and air) (Fig. 13.4). High reactivity, huge surface area to volume ratio, and strong sorption of nanoparticles make them suitable for the treatment of wastewater. Nanoparticles of metal oxides are used for removing pollutants and purification of aqueous system. It was found that TiO_2 and Fe_2O_3 nanoparticles are extensively used for heavy metal removal with nearly 98% removal capacity from aqueous system. Ground water remediation especially using zero-valent nanometals is promising due to the availability and effectiveness of degrading or sequestering contaminants (Lowry 2007). The CNTs and nano-TiO_2 are mostly employed for the treatment of surface water including purification, disinfection, and desalination; and the targeted contaminants are metals, organic contaminants, and pathogens (Chong et al. 2010). Biogenic uraninite nanoparticles are very much useful in bioremediation of subsurface uranium contamination (John et al. 2008).

In this section, various physical, chemical, and biological means with which nanoparticles interact with other environmental materials, either living and nonliving, are depicted briefly as below:

13.4.1 Physical Mechanism

The physical means of adsorption of nanoparticles are mediated through van der Waals forces and H bonds and also high surface area to pore volume favors this mechanism (Arayne and Sultana 2006).

The adsorption is a process in which the adsorbate is accumulated on the adsorbent surface and generally occurs in the surface. Nature of the bonding depends on the details of the species involved, and classified into two categories as physical adsorption, i.e., physisorption (bonding between adsorbate and adsorbent by physical weak van der Waals forces), chemical adsorption, i.e., chemisorption (through

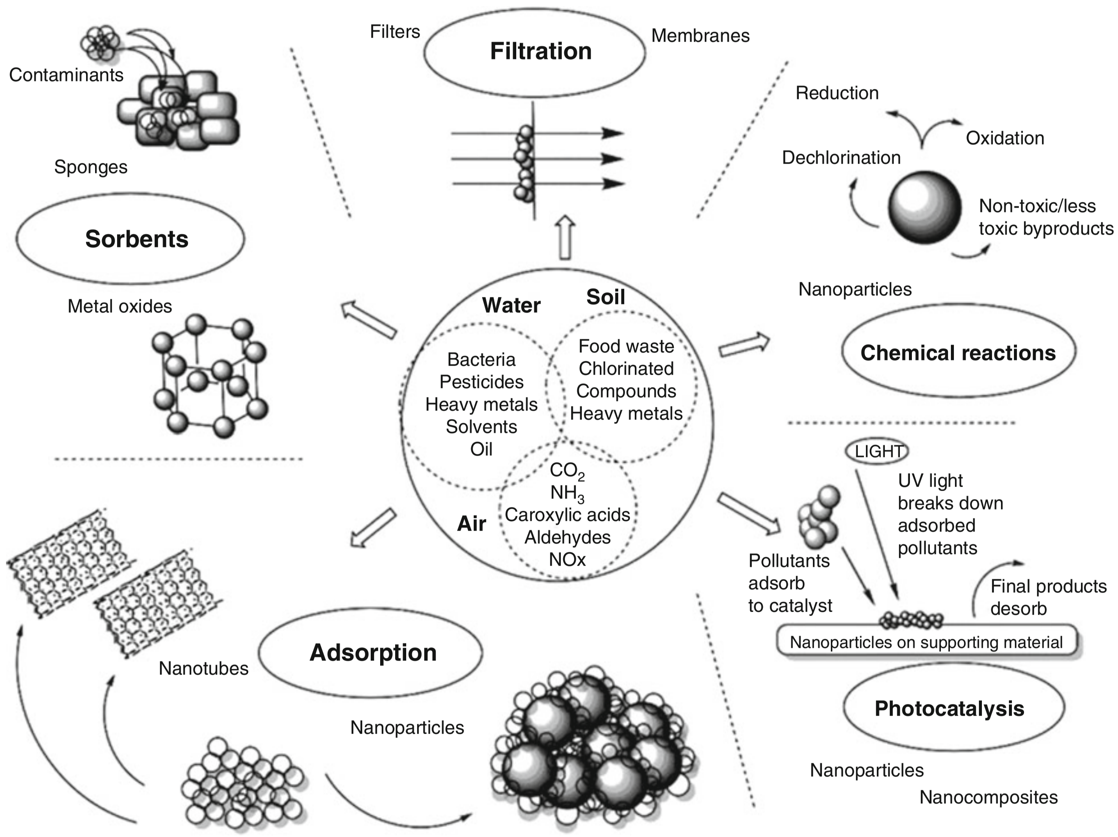

Fig. 13.4 Various approaches of environmental remediation involving nanomaterials (Adopted from Guerra et al. 2018)

covalent bonding between the adsorbate and absorbent or due to electrostatic attraction). Different types of nanomaterials have been introduced such as nanosorbents including CNTs, zeolites, and dendrimers for the removal of heavy metals from water/wastewater because of their unexceptional adsorption properties. Basic parameters like temperature and pH of the metal solution govern the adsorption properties and reactions of nanoparticles with metal. Upon increasing the temperature, the ability of the adsorbent material increases, and beyond pH 8.0 (alkaline range), the adsorbent materials began to lose their affinity toward the adsorbate and reduce its adsorption efficiency (Ragab et al. 2017). Targeted molecular delivery rate highly depends on the critical shear rate at which the release of adsorbed chemical out of polymer surface and controlling of this shear rate in desorption pattern could be useful in targeted molecular delivery system enabled through nanoparticle. Vo and Papavassiliou (2016) also studied the effect of shear rates and particle shape on physical adsorption of polymers on carbon nanoparticles were studied. Next to shear strength and rate of the nanoparticles, particle size also influenced the adsorption (either physical or chemical), for instances, size-driven adsorption of water on the 10 nm nano-hydroxyapatite was fivefold greater than that of adsorption on the 40 nm nano-hydroxyapatite which reveals the influence of size on the adsorption (Szałaj et al. 2019).

The equilibrium stage of adsorption could be calculated according to the following equation:

$$Q_e = V\,(C_o - C_e)/m,$$

where V is the solution volume (L); m is the mass of adsorbents (g); and C_0 and C_e are the initial and equilibrium adsorbate concentrations, respectively. The adsorption capacity also depends on the experimental conditions, nature, and type of adsorbent. Metal-infused composites of carbon nanotubes also been involved in the removal of heavy metals ions present in the environment. For instance, CNT composite infused with Fe and CeO_2 have been reported in the arsenic (As) removal from wastewater. Due to the presence of more adsorption sites in the composite carbon nanotubes governs and shows the fast adsorption kinetics and moreover reduction in short intra particle diffusion distance between the site and the particle also plays vital role here. As discussed earlier, pH level and ionic activity of environment govern the efficiency of the nanoparticle used for the removal, and the effectiveness of nanocrystalline TiO_2 on arsenic removal is very high at neutral pH = 7, which is shown to be more effective and active photo catalyst than commercially available TiO_2.

13.4.1.1 Photo-Fenton Reaction

Organic contaminants present in the environment go through various photo chemical reactions, and the contaminants are converted into hydrolysable products by photochemical reaction (Table 13.3). Photo-Fenton process is generation of free oxygen radicals from encompasses hydrogen peroxide (H_2O_2) with iron ions reaction to

Table 13.3 Mechanism involved in remediation

Mechanism	Novel properties governing the mechanism	Examples of nanomaterials
Adsorption	High specific surface area and assessable adsorption sites, selective and more adsorption sites, short intraparticle diffusion distance, tunable surface chemistry, easy reuse, and so forth	CNTs/nanoscale metal oxide and nanofibers
Disinfection	Strong antimicrobial activity, low toxicity and cost, high chemical stability ease of use, and so forth	Nano silver/titanium dioxide (Ag/TiO_2) and CNTs
Photocatalysis	Photocatalytic activity in solar spectrum, low human toxicity, high stability and selectivity, low cost, and so forth	Nano-TiO_2 and Fullerene derivatives
Membranes	Strong antimicrobial activity, hydrophilicity, low toxicity to humans, high mechanical and chemical stability, high permeability and selectivity, photocatalytic activity, etc.	Nano Ag/TiO_2/zeolites magnetite and CNTs

form active oxygen species that oxidize organic or inorganic compounds (Dogreula et al. 2009). The traditionally accepted Fenton mechanism is the oxidation of ferrous to ferric ions to decompose H_2O_2 into hydroxyl radicals and is represented as follows:

$$Fe^{2+} + H_2O_2\text{-----------}Fe3^{+} + OH^{-} \rightarrow 1$$

$$Fe^{3+} + H_2O_2 \quad \text{----------}Fe^{2+} + O_2H^{+}H^{+} \rightarrow 2$$

Effectiveness of Fenton reaction highly depends on the dosage of Fenton reagents including H_2O_2, optimal molar ratio of Fe^{2+}, and operational pH of the system (Aljuboury et al. 2014) (Fig. 13.5).

13.4.2 Chemical Mechanism

13.4.2.1 Complexation

Inner-sphere complexation through covalent bonding is the main process by which most of the trace metals bind with nanoparticles and generally complexation reactions initiated by surface functional groups such as hydroxyl, carboxylic groups present over the spheres. Examples of inner-sphere complexation existing between metal ions and common metal oxides, humic substances and other colloids, have been shown to be the predominant mechanism of adsorption (Bargar et al. 1997; Alcacio et al. 2001), and the reaction at the particle surface is as follows:

$$S - OH_{(aq)} + M^{z+}{}_{(aq)} \leftrightarrow S - OM_{(aq)} + H^{+}{}_{(aq)}$$

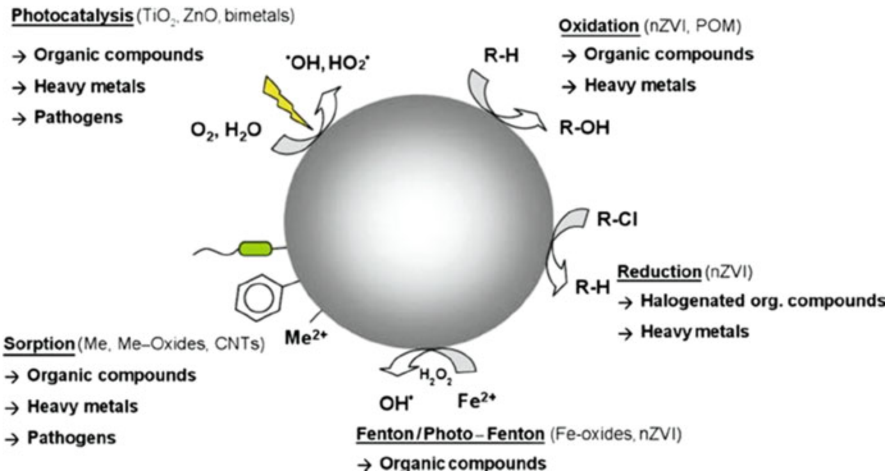

Fig. 13.5 Processes involved in the removal of contaminants from soil and environment (Adapted from Stanic and Nujic 2015)

Fig. 13.6 Schematic diagram of conversion of carboxyl into carboxylate and adsorption of metallic ions by nano-Fe_3O_4 (Adapted from Gangadhar et al. 2012)

When metal (M^{z+}) makes complexation with hydroxyl group (S-OH), members could deprotonate the hydroxyl thus, renders the affinity toward the metals. Metals in inner-sphere complexes are more strongly bound and less labile which restricts the metal bioavailability. Complexation is mainly oriented by the magnetic behavior of metal nanoparticles like Fe_3O_4, etc. Magnetic property of the magnetic nanoparticles (Fe_3O_4) is the major factor for complexation, and it can be further induced by modification of their external surface with the addition of additives (either polymer or mild acids like acrylic acid and crotonic acid) which makes them as good absorbents in the removal of contaminants. While the efficiency of the adsorbents of heavy metals is very less when pH of the resultant solution moving down to less than zero point charge of (3–4). Whereas generation of negative charges by the conversion of carboxyl sites into carboxylate anions in the alkaline medium may increases the adsorption gradually until pH $>$ pHzpc arises due to the increase in alkalinity (Fig. 13.6).

Also poly nanofibrous nanocompounds will act as efficient adsorbents due to its nature and presence of amino groups and act as active sites on the poly fibrous chains and possess bi-functional property to adsorb both cationic and anionic metallic contaminant compounds at favorable pH value of the solution (Gangadhar et al. 2012).

13.4.2.2 Oxidation–Reduction and Acid–Base Properties

Metal oxides are used as absorbents or catalysts because of their redox and acid–base properties, and these properties are highly interrelated (Reddy 2006). The surface modification by the addition of inorganic and organic molecules over the surface of the nanoparticles stabilizes and prevents the oxidation. Moreover, functional groups provide platform of active sites for the enhancement of removal efficiency (Zhang et al. 2013). Nanoparticles with a high surface area and porosity exhibit a higher photocatalytic activity by enhancing the photon absorption (Pelaez et al. 2012). This activity plays a crucial role by oxidizing or reducing the metal impurities present in the polluted environment and results in the increased removal rate for the particular metal ion concentration (Saien et al. 2014). Nanoparticle photocatalyst is activated when the irradiation energy is equal to or greater than the band gap present in the active site of the particle, and the generated charge over the particle either can produce heat or can be used to reduce or oxidize the species present at the surface of nanoparticle (Wang et al. 2015a, b). In general, these generated charge/valance would be nullified by metal so that the removal rate increases and detoxification of water takes place.

13.4.2.3 Immobilization of Contaminants

The stabilized nanoparticles possess the ability to adhere metal contaminants on their site and immobilized for the longer period. Stabilizers are natural polysaccharides and can make a dispersion nanoparticles by electrostatic stabilization (formation of electrical double layer and repulsion between solution and capped particles), steric stabilization (polymer coating induces the osmotic repulsive force), and (3) electrosteric stabilization. Stabilized nanoparticles are having higher affinity toward the metal contaminants. Especially, sulfur-containing iron compounds/minerals such as pyrite (FeS_2), greigite (Fe_3S_4) are known to offer strong affinity for Hg (K sp of HgS $= 2 \times 10^{-53}$). However, nonstabilized FeS particles tend to aggregate and thus are not deliverable into contaminated soil/sediment.

Many studies revealed that Hg^{2+} adsorption increased by the introduction of iron sulfide nanoparticles (FeS). Gong et al. (2012) found that the Hg(II) adsorption capacity increased by 20% as the molar ratio of FeS increased from 0 (nonstabilized) to 0.0006 (stabilized). Moreover, major removal mechanisms involved in Hg are complexation, precipitation (formation of cinnabar and metacinnabar), ion exchange and Cr(VI) removal by stabilized FeS (Wang et al. 2011). Next to sulfide

Table 13.4 Removal of metals with various nonstabilized and stabilized particles (Adapted from Liu et al. 2015)

Particles	Target material	Removal efficiency	References
Nonstabilized nZVI	Cr(VI)	52%	Wang et al. (2010)
Stabilized nZVI	Cr(VI)	94%	Wang et al. (2010)
Nonstabilized FeS	Hg(II)	1700 mg/g	Liu et al. (2008)
Stabilized FeS	Hg(II)	3499 mg/g	Gong et al. (2014)
Nonstabilized magnetite	As(V)	26.8 mg/g	Liang et al. (2012)
Stabilized magnetite	As(V)	62.1 mg/g	Liang et al. (2012)

compounds, phosphates are found to be effective for immobilization of Pb, Cd, and Cu in contaminated soil and water, governing the remediation of heavy metals. Specifically, iron phosphate nanoparticles are effective in heavy metal immobilization.

Stabilized vivianite nanoparticle with Fe^{2+} plus phosphate

$$3Fe^{2+} + 2PO_4{}^{3-} + 8H_2O \rightarrow Fe_3(PO_4)_2 \cdot 8H_2O$$

actively involves in in situ immobilization of Pb(II) in contaminated soils and Cu (II) in soils and Cu leachability reduced by 63–87% (Table 13.4).

13.5 Biological Mechanisms Involved in Adsorption/ Absorption of Nanoparticles

Nanoparticles (NPs) are currently been used for drug and gene delivery, bio-detection of pathogens and proteins alike, tissue engineering, tumor imaging and targeting. NP technology has found a unique niche in the field of biomedicine and biotechnology with its rapidly burgeoning repertoire of application. Due to this small size, NPs get gateway ticket into the cells and to translocate across the cells, tissues, and organs, thus are being used in biomedical research. Most of the NPs are polar molecules and cannot easily transgress cytoplasmic membrane (CM) and employs endocytotic pathways to enter the cells. Therapeutic efficacy (TE) is determined by the way NPs enter the cell. Hence, information on mechanisms involved in cellular uptake is crucial for assessing the fate of NPs and its toxicity (Albanese et al. 2012). Nanoparticles enter the cell via preferentially uptake pathway. NPs composed of poly(lactic-co-glycolic acid), D,L-polylactide and poly(ethylene glycol-co-lactide), and silica (SiO_2)-based nanomaterials enter the cell by clathrin-mediated endocytic pathway. Coumarin-based solid–lipid NPs enter the cells via non-energy-dependent pathway as the structure of these NPs are similar to the CM. All the lipid-based NPs utilize the clathrin-mediated endocytosis pathway. The herceptin-coated gold NPs enter the cell via receptor-mediated endocytosis by means of membrane $ErbB_2$ receptor (Jiang et al. 2008). Irrespective of function, most membranes have a bilayer of amphiphilic lipids with hydrophilic heads and hydrophobic tails (Edidin 2003; McMahon and Gallop 2005). This makes the bilayer a selective barrier for entry of small biomolecules, which enter cell by passive diffusion. Nevertheless, entry is controlled by other mechanisms also, viz. channel, receptor, or transporter (Sabolić et al. 1995). Nanoparticles and colloids regulate metal bioavailability by influencing metal speciation and other processes at the organism–environment interface. Nanoparticle metal complex decreases the freely available fraction of TMs to cross the cellular membrane of an organism (Slaveykova and Wilkinson 2005). Nanoparticles and colloids may also alter metal bioavailability by decreasing the mass transport toward the organism surface and lability of the associated metal. Under diffusion-limited conditions, the bioavailable metal is proportional to the diffusion coefficients of the complexes and their liability (Buffle et al. 2009). Microorganism can survive and grow in high concentration of toxic metals due to their chemical detoxification as well as due to their energy-dependent efflux from the cell by membrane protein that functions either as ATPase or as chemo-osmotic or proton anti-transporters.

Silver nanoparticles are used as water disinfectant to remove *E. coli*; TiO_2 nanoparticles involved in water disinfectant and soil remediation to decontaminate MS-2 phage, *E. coli*, hepatitis B virus, aromatic hydrocarbons, biological nitrogen, phenanthrene, and bimetallic nanoparticles (Pb, Cu, Fe, Ni, etc.) are adopted to remove chlorinated and brominated contaminants from water and soil (Bennett et al. 2010; Zan et al. 2007). Silica nanomaterials are applied in wastewater treatment to remove heavy metals and cationic dyes and also involved in adsorption of CO_2, H_2S, aldehydes, and ketones from gaseous systems (Wang et al. 2015a, b). Modified carbon-based nanomaterials and carbon nanotubes are applied in aqueous and gaseous systems to decontaminate fluoride, SO_x, H_2, NH_3, heavy metals, pesticides, pharmaceuticals, benzene, and metals (Yang et al. 2013). Polymer-based nanomaterials are employed in environmental remediation of volatile organic compounds, polynuclear aromatic hydrocarbons, metals, dyes, and microbes (Guerra et al. 2018; Khare et al. 2016).

Salient approach of nanomaterials as adsorbent-specific features of oxide and carbon-based nanomaterials: Oxide and carbon-based nano-adsorbents are most effectual and cost-effective for the rapid removal and recovery of metal ions from wastewater effluents due to their large surface area and optimal magnetic properties (Aillon et al. 2009; Zhang et al. 2013). They can be reused as adsorbent after magnetic separation for removing the noxious toxic contaminants (Chen and Mao 2007). Numerous studies demonstrate that bulk iron oxides have good efficiency for the removal of heavy metals from aqueous solutions. But due to their high surface area, nanoparticles have better efficiency than bulk particles of the same materials. Another benefit of nanoparticle adsorbents is that they are nontoxic and are not harmful for the environment. Several studies have been initiated and stated that nanoparticles have better efficiency in removing metallic pollutants or contaminants from aqueous/water/groundwater solutions. Among these metal oxides, iron oxide, aluminum oxide, and titanium oxide have more surface area and adsorption capacity over the others and are widely used for the removal of metallic pollutants from aqueous solutions and industrial effluents. Iron oxide and its different forms such as goethite, maghemite, hematite, and crystalline ferric oxide have a high surface area which can be used as an adsorbent for the removal of heavy metals (Hu et al. 2006; Deliyanni et al. 2006). It was reported that a maximum adsorption capacity of 0.21 mmol of Cu^{2+}/g was found at pH 6.0 by using iron oxide (Huang et al. 2006) and the removal of As(V) and As(III) (Dixit and Hering 2003). In addition to iron oxide nanoparticles, nanoparticles of its zero-valent form have also been reported for the removal of metallic pollutants such as Cd, Zn, Se, As, Cr, and Ag and also been reported for the removal of hydrocarbons and organic compounds. The remediation of Cr(VI) and Pb(II) was increased by 30 times when these particles are in the form of nanoscale zero-valent iron compared to normal iron powder (Ponder et al. 2001). Similarly, it also removes arsenic by 5–10 times more than the micron-sized materials (Rickerby and Morrison 2007). Another metal oxide, i.e., alumina powder, has also been frequently used by different researcher for the removal of metal ions because of its low cost, high surface area, and good thermal stability and removes the ions such as Pb, Cr, Cu, Cd, and Hg from the contaminated environments.

13.6 Interaction of Nanoparticles with Living Cell Membrane

Generally nanoparticles enter through cell membrane which is governed by various cytosis mechanisms, namely phagocytosis and pinocytosis, which are further divided into subtypes of endocytosis. Pinocytosis is broadly divided into four categories, namely clathrin-mediated endocytosis, caveolin-mediated endocytosis, clathrin/caveolae-independent endocytosis, and micropinocytosis. Endocytosis involves engulfment of nanoparticles by membrane invaginations, followed by budding and pinching off to form endocytic vesicles (Doherty and McMahon 2009; Kumari et al. 2010).

13.6.1 Phagocytosis

Macrophages, monocytes, dendritic cells, neutrophils, fibroblasts, epithelial, and endothelial cells have phagocytic activity. Opsonization (attachment of antibodies, proteins, etc., onto NP surface) initiates the phagocytosis of NP surface (Aderem and Underhill 1999; Swanson 2008). Opsonized NPs are distinguished through specific ligand receptor, which starts a signaling cascade leading to subsequent engulfing and internalization of NPs, forming “phagosome” (Hillaireau and Couvreur 2009). Generally, phagocytes uptake effective when large NPs in the range of 200–1500 nm size (Tabata and Ikada 1988). Shape of NPs has significant impact on the cellular uptake of NPs (Champion and Mitragotri 2009). For instance, PEGylated gold nanorods are easily engulfed by phagocytes than gold nanospheres in ovarian-tumor-bearing mice (Nel et al. 2009).

13.6.2 Clathrin-Mediated Endocytosis (CME)

Nutrients and plasma membrane components, viz. cholesterol is transported *by means of* low-density lipoproteins (LDLs) and iron through the transferrin carrier. There are two types of CME, the first is through receptor-specific CME and the second is through receptor-independent CME. Hydrophobic and electrostatic interactions play significant role in the uptake of NPs by receptor-independent CME. Plasma membrane rich in clathrin aids in uptake or NPs through CME (Brown and Petersen 1999). Internalization of the membrane around NPs is achieved by adaptor and accessory proteins at clathrin nucleation sites (Schmid et al. 2006). Accessory proteins, viz., Epsin, amphiphysin, SNX9, stabilize membrane curvature. BAR proteins are attached to dynamin which cuts the budding vesicle and discharge into the cytoplasm (Praefcke and McMahon 2004). But, particles entering the cell by CME are commonly engulfed by degradative lysosomes (Doherty and McMahon 2009; Ehrlich et al. 2004).

13.6.3 Caveolae-Dependent Endocytosis (CDE)

Several biological processes like cell signaling, transcytosis, regulation of lipids, and membrane tension are regulated by CDE. Caveolae are 50–80 nm in size and flask-shaped membrane invaginations (7). Caveolin 2 protein aids in structural stabilization (Pelkmans and Helenius 2002). NPs entering CDE pathway sometimes escape lysosomal degradation, and this entry route is misused by some pathogens such as viruses to escape degradation (Carver and Schnitzer 2003).

13.6.4 Clathrin/Caveolae-Independent Endocytosis

This mechanism is utilized by cells lacking both clathrin and caveolae. Folic acid is the main component internalized through this pathway (Doherty and McMahon 2009). Folate-modified NPs avoid entry into lysosomes and are mostly retained in endocytic compartments or discharged directly into the cytoplasm (Kelemen 2006).

13.6.5 *Macropinocytosis*

This procedure does not use lipid rafts or pit-forming proteins. Large membrane extensions (cytoskeleton rearrangement) intertwine back to the plasma membrane, forming a large vesicle. Regardless of the presence of specific receptors, nonspecific bulk fluid uptake is carried out by this mechanism. This mechanism is mainly used for uptake of larger NPs (Kuhn et al. 2014) (Fig. 13.7).

13.7 Microenvironment-Driven Cellular Entry of Nanoparticles

Physicochemical properties of NPs are changed in biological system fluids, viz. blood and cell cultures. In biological fluids, surface of NPs is altered by the adsorption of biomolecules like proteins, called “protein corona” (Walkey and Chan 2012). Unambiguously, the composition of the protein layer (type, amount, and conformation of proteins involved) decides the biological identity of nanoparticles. Biological identity of NPs depends on several factors, viz. size, shape, and surface chemistry of NPs, protein abundance, temperature, ionic strength, and osmolarity (Prabhakar et al. 2013). Microenvironment is the exterior area/portion surrounding the target cell. Different microenvironment factors like fibrosis, extracellular matrix, and pH (Maeda et al. 2000; Blanco et al. 2015) modify the properties of NPs and their associations with the cell membrane and their intracellular fate. For NPs targeting tumor cells, tumor microenvironment (TME) decides their entry into tumor cells. The interaction of various microenvironmental factors, for instance, vascular endothelial growth factor (VEGF), prostaglandins, and matrix metalloproteinases (MMPs), and pH decide the entry of NPs. Zwitter ionic NPs can easily cross the TME and enter the tumor cells at pH ~6.8 by freeing anionic part and getting surface positive (Yuan et al. 2012). The microenvironment of the gastrointestinal (GI) tract like extreme pH, digestive enzymes, and low permeability of intestinal epithelium influences the crossing over of NPs through intestinal epithelium by means of transcytosis (Zhu et al. 2016). Consequently, microenvironment of the target cells should be apt for higher performance of NPs (Shi et al. 2017; Blanco et al. 2015).

13.7.1 *Organic Contaminants*

Different types of nanomaterials like nano sorbents, viz. CNTs and zeolites, have exceptional adsorption properties and are utilized for expulsion of organic contaminants from water/wastewater as well. Carbon nanotubes with their exceptional water treatment capabilities are widely used in the waste removal industries. In addition,

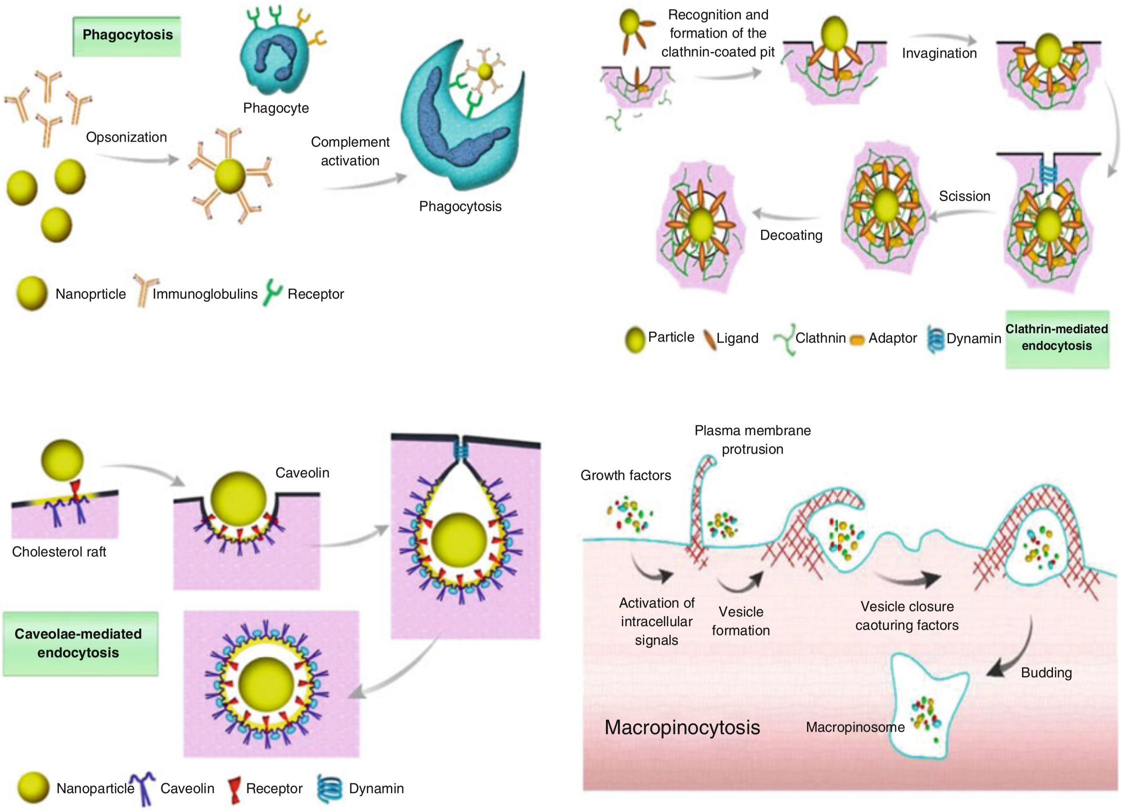

Fig. 13.7 Different mechanisms of endocytosis carried out by microorganisms (Behzadi et al. 2017)

metal oxide nanomaterials such as TiO_2 and CeO_2 have also been utilized in the degradation of organic pollutants (Nawrocki and Kasprzyk-Hordern 2010; Orge et al. 2011). Other than these, the latest research additionally demonstrated that carbon nanotubes may also prove to be the most effective tool in remediating contaminated water. In the course of the most recent couple of years, nano ZVI has been widely utilized in the degradation of organic contaminants like lindane, pentachlorophenol, and DDT in addition to nitrate, heavy metals like Cr(VI), As, and Pb(II). Zero-valent iron (ZVI) nanoparticles have relatively higher removal capacity than conventional iron particles for the removal and/or reduction of these organic/inorganic ions. The most important nano iron, i.e., nano ZVI (Fe^0) particles, is oxidized into +2 and +3 oxidation states, thereby reducing the organic contaminants present in the soil, water, and inorganic impurities.

Metallic iron (Fe^0) serves effectively as an electron donor:

$$Fe^0 \rightarrow Fe^{2+} + 2e^-$$

The standard reduction potential ($E°$) of nano zero-valent iron (Fe^{2+}/Fe) is -0.44 V, which is lower than many organic compounds like chlorinated hydrocarbons and metals such as Pb, Cd, Ni, and Cr, Therefore, these organic compounds and metals are subjected to reduction by nZVI nanoparticles. Likewise, photo catalysts like TiO_2 nanoparticles are used effectively for the treatment of water contaminated with organic pollutants like polychlorinated biphenyls (PCBs), benzenes, and chlorinated alkanes (Kabra et al. 2004). Nanocatalysts including semiconductor materials, zero-valence metal, and bimetallic nano particles are utilized for the degradation of organic contaminants (Zhao et al. 2011). The zero-valent iron is synthesized by reducing Fe^{2+} or Fe^{3+} by $NaBH_4$ under anoxic conditions and the reaction is as follows:

$$Fe(H_2O)_6{}^{3+} + 3\ BH_4{}^- + 3H_2O\text{-------}Fe^0 + 3B\ (OH)_3{}^+ + 10.5\ H_2$$

$$Fe^{2+} + BH^{4-} + 4H^2O\text{-------}Fe^0 + B\ (OH)_4{}^- + 2H_2$$

Soil natural organic matter (NOM) which constitutes various molecular humic and fulvic acids and hydrophilic organic compounds adds to the water contamination. A variety of carbon-based adsorbents have been utilized for the expulsion of organic contaminants, particularly nanoporous activated carbon fibers exhibited much higher organic sorption for organic compounds like xylene compounds; similarly, multi-walled CNTs exhibited higher adsorption capacities for trihalo methanes, chlorophenols, DDTs, etc. Besides, TiO_2 nanoparticles reported to remove the total dissolved organic matter in the water effectively. Metal doped TiO_2 like Si-TiO_2 and Fe(III)-TiO_2 were used to remove total organic matter and degradation of toluene dissolved in water. The use of nanofibrous composite system may use for removing of wide range of contaminants including bacteria/viruses, heavy metals and ions, and complex organic compounds by following set up to get

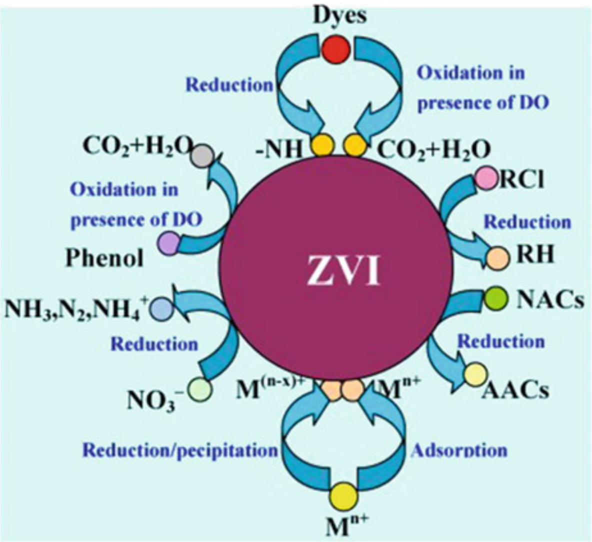

Fig. 13.8 Mechanism of ZVI on contaminants (Adapted from Fu et al. 2014)

safe water was proposed by Amin et al. (2014) (Fig. 13.9). In general, ZVI nanoparticles are most widely suitable for immobilization/remediation/arrest of toxic metals present in the soil environment induced by the reducing nature of ZVI particles (Fig. 13.8 and 13.9).

13.8 Nanoparticles for Soil Pathogen Diagnosis

Aside from environmental remediation, nanomaterials reported to diagnose the soil borne pathogens by multiplex dipstick immunoassay which can easily and rapidly identify potential serious plant soil pathogens, viz. *Fusarium* toxins, zearalenone, T-2 and HT-2 toxins, deoxynivalenol, and fumonisins in wheat, oats, and maize permitting experts to help farmers in the prevention of epidemics (Lattanzio et al. 2012). QDs are considered prospective tools for the identification of a specific biological marker in various fields with high thoroughness. They were utilized effectively in labeling cells, cell tracking, imaging, and DNA detection in vivo (Sharon et al. 2010). Nanomaterials with carbon were developed to influence electrochemical analysis electrode, so they can be used as a sensor (Sharon and Sharon 2008) to detect the residue of pesticide in plants. Despite the fact that there has been no patent documented so far exclusively for the diagnosis of plant disease

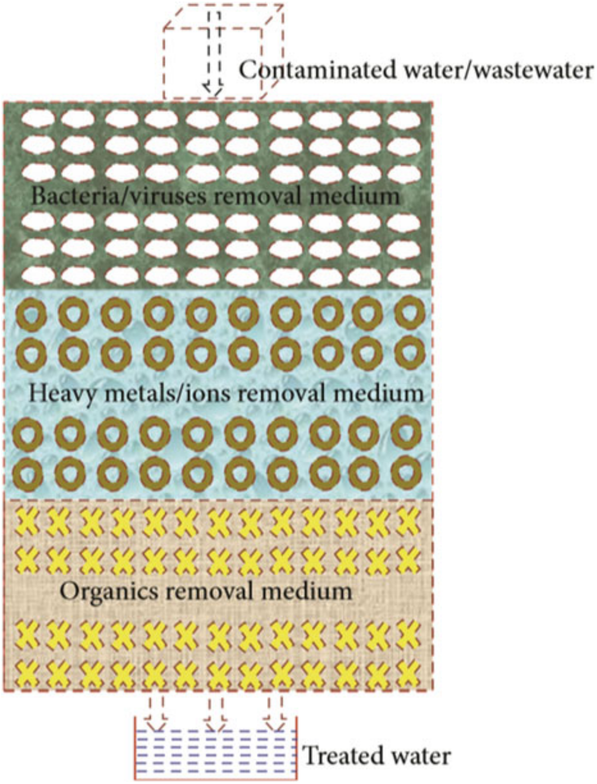

Fig. 13.9 Mechanism of nanocomposite for the removal of contaminants from wastewater (Adapted from Amin et al. 2014)

through nanotechnology techniques, these methods have improved the diagnosis of animal diseases and can be applicable to plant diseases as well.

13.8.1 Application of Nanoparticle in Soil Plant Pathogens and Its Risk Assessment

For example, colloidal iron nanoparticles have the capacity to perform as catalysts in redox reactions. In any case, nanomaterials may have side effects, and a risk assessment needs information regarding their distribution in the food chain and environment. Risk assessments are highly essential for understanding the behavior of nanoparticles to identify potential dangers associated with nanomaterial used for remediation. Side effects associated with the nanotechnology, particularly environmental risks associated with residual fate of nanomaterials and transport in the environment, are not yet completely investigated and comprehended since 2006–2015.

13.9 Disadvantages of Using Metal and Metal Oxide Nanoparticles for Remediation

Introducing new technology definitely has other side in addition to the positive facts and may have bio-efficacy issue, which needs to be studied widely and documented. The disadvantages of using nanoparticles as absorbents in the removal of metallic and organic contaminants are as follows.

13.9.1 Particles Instability

Nanomaterials can experience various transformations during the remediation process, because they are thermodynamically unstable and present in the region of high energy local minima. This causes deterioration of quality, poor corrosion resistance, and difficulty in structure maintenance.

13.9.2 Impurity

During nanoparticle synthesis, nitrides, oxides, and formation may aggravate from the impure environment. As nanoparticles are highly reactive, there is a possibility of impurity as well. In solution form, nanoparticles should be synthesized by means of encapsulation. So, it is very difficult to overcome impurity in nanoparticles.

13.9.3 Difficulty in Synthesis

While synthesizing nanoparticles, encapsulation has to be carried out, otherwise it is very difficult to maintain the nanoparticle size in solution form.

13.9.4 Biologically Harmful

Nanomaterials have been reported toxic and carcinogenic and may create irritation as they are transparent to the cell dermis. There is a need of detailed study on nanoparticle toxicity to ensure the safe usage of these wonder materials to remediate the environment.

13.10 Conclusion

Delivering a safer and secure environment to the future generation is the need of the hour and decade, due to demographic pressure on the nature by various activities like vehicular emission, climate change, shrink in agricultural land, contamination of environment, etc. Contamination of soil and water environment due to chemical and pesticide industries pose a great threat to the ecosystem. Compilation of literature on the nanoparticle has shown that unique properties of nanomaterials like small size and large surface area could be significantly used as adsorbent for waste site and water treatment through different processes such as physical and chemical adsorption, complexion, oxidation, and reduction. Surface-modified metal oxide and bimetallic nanoparticles are also used to enhance the photo catalytic activity and increased affinity of the contaminant toward the nanosites. Nanofibrous materials have extremely high surface-to-volume ratio and porosity and used to treat water and soil borne pathogens. Nanoparticles with less toxicity and minimum health risks may provide solutions to ensure safe water and soil, further ensuring the safer environment.

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Chapter 14
Nano-Bioremediation Application for Environment Contamination by Microorganism

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D. G. Panpatte, Y. K. Jhala (eds.), *Microbial Rejuvenation of Polluted Environment*,
Microorganisms for Sustainability 26, https://doi.org/10.1007/978-981-15-7455-9_14

Abstract Nano-bioremediation includes the utilization of nanomaterial in the treatment of polluted materials. Bioremediation has been practiced extensively as an accessible cost-effective method to regulate dangerous pollutants, such as heavy metals, in soil, and water. The biosynthesis of nanoparticles from microorganism is developing as nano-factories and conceivable software in environmental cleanup. The elimination of environmental contaminants (such as heavy metals, organic and inorganic pollutants) from polluted sites is called nano-bioremediation using nanoparticles/nanomaterial produced by bacteria with the aid of nanotechnologies. Three major strategies of bioremediation consist of use of microbes, flora, and enzymatic remediation. Nanoparticles can additionally be used for the remediation of soils, water contaminated with heavy metals, and natural and inorganic pollutants. For example, several complicated natural compounds, inclusive of long-chain hydrocarbons and organochlorines, are especially resistant to microbial and plant degradation. Nanoparticles can also be used in conjunction with phytoremediation in the enzyme-based bioremediation. A combined method regarding nanotechnology and biotechnology could overcome this limitation: nanoencapsulated enzymes would degrade complex organic compounds into simpler compounds, which would in turn be rapidly degraded by the joint activities of microbes and plants. Bacteria are capable of mobilizing and immobilizing metals, and in some situations, the microorganism which can minimize metal ions exhibits the capacity to precipitate metals at nanometer scale. Bacteria are used as a possible “biofactory” for the synthesis of nanoparticles such as gold, silver, platinum, palladium, titanium, titanium dioxide, magnetite, cadmium sulfide, and so on. The use of microorganism as a source of enzymes that can catalyze particular reactions to inorganic nanoparticles is a new rational biosynthesis method and use of enzymes, microbial enzymes, vitamins, polysaccharides, biodegradable polymers, microorganisms, and organic structures for synthesis of nanoparticles. Filtering successfully achieves the further purification of nanoparticles. The bacterial cells and S-layers have special metal binding capabilities which make them useful for technical applications in bioremediation and nanotechnology. Bacterial nanoparticles are useful in highly contaminated conditions for the detoxification and bioremediation of soil, water, and other habitats. Bioremediation by microorganisms typically requires the use of identified aerobic and anaerobic bacteria to remove pesticides and hydrocarbons. Rhizoremediation is a cheap and effective technique which is useful for remediating polluted soils through the combined action of plants and their symbiotic microbes in the rhizosphere. Capable microorganisms are designed to enhance their cell membrane transport or their enzymatic attributes to enable enhanced and wide-spectral pollutant degradation. Nanotechnology modification and adaptation will increase the efficiency and duration of the bioremediation in the future.

Keywords Bioremediation · Microorganism · Nanobiotechnology · Environment · Pollution

14.1 Introduction

In various organic species found in nature, many are blessed with the capacity to tolerate heavy metals. Science and technology developments make it easier for us to be worried about the potential of biological diversity to deplete pollutants called as bioremediation. This promises powerful novel technology for dealing with a wide range of pollutants. This science mediates phytoremediation (plants), rhizoremediation (plant and microbe interaction), and remediation by means of biosynthesis of nanoparticles (nanoparticles synthesized through microbes). Currently, maintaining ecosystem and biodiversity has become an increasingly important field of research, as well as a resource management goal. Maintaining habitats and biodiversity has become an increasingly important area of study, as well as a priority of resource management. Different synthetic chemicals are released daily which are environmentally hazardous and cause adverse effects to the ecosystem by entering the natural way of life like food chain. Soil and water are significant aspects of the biosphere that is polluted with anthropogenic substances. Contaminated with chlorinated chemicals, polycyclic aromatic hydrocarbon, heavy metals, and radionuclides is the most significant soil constituent (Acevedo et al. 2010; Ramzani et al. 2017). These contaminants sequestered between the ground surface and groundwater level in saturated and unsaturated layer of the soil underlying. Consequently, in addition to potential groundwater contamination, locations can also have a high concentration of organic pollutants in soil layers. They can cause detrimental effect on the flowers and fauna of affected habitats via uptake and accumulation in meal chains and, in some instances, pose extreme health troubles and or genetic defects in humans. Several methods have been applied to remediate these pollutants, such as incineration, thermal desorption, and drilling, but these process releases harmful by-products. Alternate of these approaches was used to convert pollutants into nontoxic compounds using naturally occurring microorganisms such as bacteria, fungi, actinomycetes, yeast, and plants.

Rhizoremediation, which is the well-developed bioremediation technique, involves the removal of specific pollutants from polluted sites through symbiotic interaction between host plants and microbes. The drawback of this process is that it is very sensitive to the level of toxicity and environmental conditions of the polluted sites, i.e., the conditions must be conducive to microbial activity and need to consider temperature, pH, etc. The downside of this method is that it is very sensitive to the toxicity level and environmental conditions of the contaminated sites, i.e., the situations need to be conducive to microbial pastime and must consider temperature, pH, etc. Phytoremediation is excavation of contaminants by the assistance of plants. This approach is soil specific, where some of the plants absorb the metals. With the recent development of nanotechnology, the combination of nanoparticles and biological processes has been effective in enhancing measurement precision, increasing the efficiency of bioremediation and expanding biochemical application in environmental science. Bioremediation-based nanoparticles have low environmental risk of genetic leakage and can provide additional functions and characteristics for the biochemical cycle.

14.2 A Brief Approach to Nanoparticle Biosynthesis Using Microorganisms

Nanoparticles synthesized using microorganism have emerged as a rapidly growing area of research in green nanotechnology around the globe, with various biological entities engaged in nanoparticle synthesis constantly forming an imputed alternative to traditional chemical and physical methods (Iravani and Publi 2014; Majlesi et al. 2018). Microorganisms and then plant extracts (Fig. 14.1) were used for synthesis in search for cheaper pathways for nano-product synthesis. Nanoparticle biosynthesis is a bottom-up approach where reduction/oxidation is the principal reaction that occurs. Microbial enzymes or plant phytochemicals with antioxidant or removal properties are typically responsible for reducing metal compounds in their nanoparticles.

14.3 Bioremediation Through Nanoparticles

14.3.1 Biosynthesis of Nanoparticles

Nanoparticles are synthesized by microbes, using “natural” approaches (Mishra et al. 2014). Green technology is the commonly accepted bioremediation process because of its nontoxic effect and its safe and environmentally friendly approach. In spite of the fact there are several strategies for the synthesis of nanoparticles like sol-gel method and chemical synthesis, however biological synthesis of nanoparticles is the

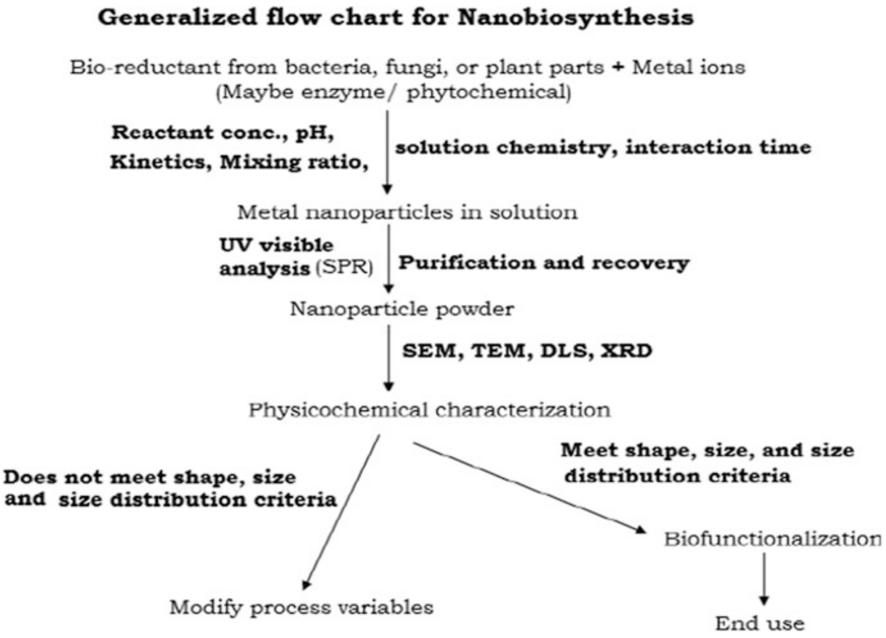

Fig. 14.1 Flowchart outlining nanoparticles biosynthesis (Yadav et al. 2017)

most desirable and eco-friendly approach (Mishra et al. 2014; Ramezani et al. 2019a, b). Nanoparticles synthesize living organisms, plants, and microbes through green nanotechnology approach. Due to their high tolerance and reproductive capacity, mainly microbes are used for commercial use and the rapid decontamination process. They are normally synthesized by the extracellular or intracellular metabolism of microorganisms from secondary metabolites. Synthesis of nanoparticles with special structure and dimension is a crucial part of nanobiotechnology. Such nanoparticles show useful variety along with changes in their shape and size (Ahmed et al. 2018; Ramezani et al. 2018).

Biosynthesis of nanoparticles is additionally a type of bottom-up strategy where the main response is reduction/oxidation. The microbial enzymes are responsible for transforming metal compound reduction properties into their respective nanoparticles (Prathna et al. 2010). The particles generated biologically have better catalytic reactivity and greater unique surface area (Riddin et al. 2010). Biosynthesized nanoparticle do not accumulate due to the presence of a specific microorganism secreted capping agent. Nanoparticle biosynthesis may be either intracellular or extracellular. Extracellular biosynthesis has increased a great deal of consideration due to low-cost prerequisite and no downstream processing necessities (Mishra et al. 2014). Upon addition of precursor molecule, the secondary metabolites and extracellular components present in cell-free extract conduct the redox reaction for particle biosynthesis (Fig. 14.2). The structure of the particles can also be varying by various biological and physical parameters. These particles can

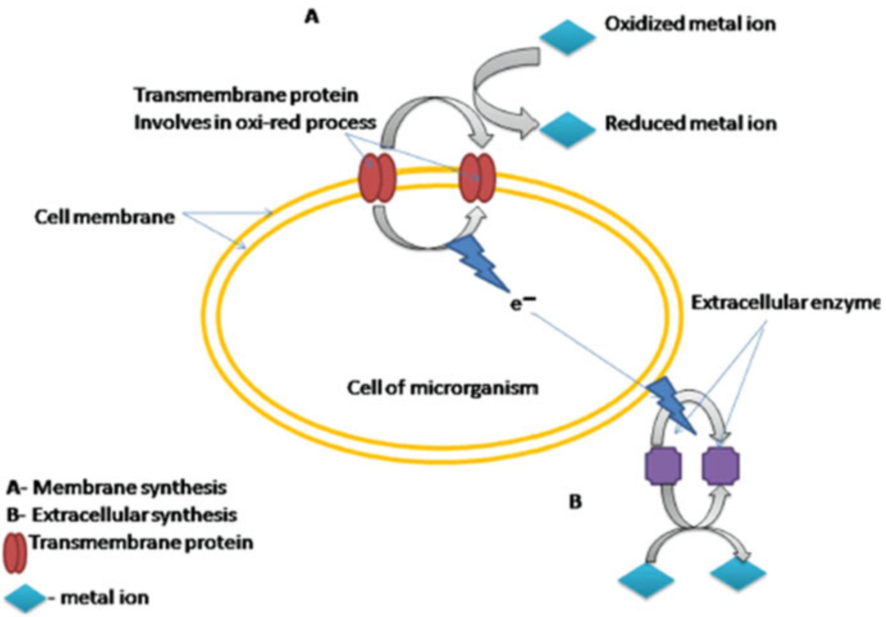

Fig. 14.2 Different processes of microbial biosynthesis of nanoparticles (Mishra et al. 2014)

additionally be characterized by means of UV-visible spectroscopy, zeta sizer, transmission electron microscopy, scanning electron microscope, Fourier infrared spectroscopy, and X-ray diffraction (Singh et al. 2014; Shrivastava et al. 2012).

14.3.2 Advantages of Nanoparticles

- Nanoparticles have the potential to absorb most of the quantity of pollution due to large surface area and high surface energy.
- It catalyzes the responses in quicker rate in contrast with bulk material, hence decreasing energy utilization during degradation or helping avoidance of contaminant release.
- The nanotized type of particles makes the pollutants available, thus encouraging remediation in situ rather than remediation in ex situ.
- The ability of nanoparticles to be coated with different ligands and the regulation of surface-area-to-volume ratio by adjusting the shape of the nanoparticles allow for high selectivity, sensitivity, and specificity sensor design (Mehndiratta et al. 2013).

14.4 Mechanisms for the Synthesis of Noble Metal Nanoparticles

Formulation of metal NPs can be related to the fact that in response to toxic conditions, metallophilic microbes produce genetic and proteomic reactions (Casals et al. 2012).

Heavy metal ions like Hg^{2+}, Ni^{2+}, CrO_4^{2+}, Ag^+, Co_2^+, Cu_2^+, Cd_2^+, Zn^{2+}, and Pb^{2+} may inhibit organism development. Microorganisms have evolved proteomic and genetic responses to alleviate the toxicity and to control the metal homeostasis (Sinha et al. 2014). Numerous metal resistance genes or gene clusters may reside in microorganisms that enable metals to be detoxified through a series of mechanisms such as efflux, complexation, or reduction of efflux precipitation. Thus metallophilic bacteria thrive in conditions containing heavy metal ions, such as efflux streams of metal processing plants, mine waste rock piles, and naturally mineralized areas (Reith et al. 2013). Another study discovered the active and passive mechanisms employed by *Shewanella oneidensis* for magnetite synthesis (Perez-Gonzalez et al. 2013).

When ferrihydrite was used as a last electron acceptor by bacteria, the PH around the cell increased that result in active Fe^{2+} particles. Later, via the passive process, localized concentrated ions of Fe^{2+} and Fe^{3+} at the cell wall increase the cell's supersaturation state.

The bacterial magnetite particle biomineralization (BacMP) is hypothesized to be a multi-step process. Cytoplasmic membrane invagination is the first step, and newly arranged vesicles serve as the BacMP membrane precursors. Vesicle formation in magnetotactic bacteria is believed to be an analysis mediated with GTPase in eukaryotes. Then, vesicles and cytoskeletal filaments are joined together in chains. The array of Fe^{2+} inside the vesicles by siderophores atoms (iron transporters) is the following stage of BacMP biomineralization. Oxidation-reduction regulates the internal iron firmly. Finally, BacMP-connected proteins initiate nucleation and also control magnetite crystal morphology. A variety of proteins attached to the BacMP membrane have a significant role to play in magnetite generation (Arakaki et al. 2008). The synthesis of cadmium sulfide NPs was also investigated by Sangha et al. (Sanghi and Verma 2009). They proposed that cysteine disulfide bonds are involved in the formation of NPs that assigned to breakage the SeH bond for the establishment of new bonds, which is a complex of Cd-thiolate ($Cd–S–CH_2COOH$) on the NP surface. The cadmium-thiolate complex carboxylic group (COOH) interact with the hydrogen bond rather than interacting with the amino protein group. The hydrogen bond is thus responsible for linking the amino group with a capped CdS. Beveridge et al. (1997) clarified the mechanisms under consideration for the biosynthesis of nanomaterials including toxicity and solubility changes, bioaccumulation, oxidation, reduction, biosorption, precipitation of efflux systems, and metal extracellular complexation. Cell wall affects greatly the intracellular synthesis of NPs. The electrostatically bound positively charged metallic ions against the negatively charged surface. As a result of the reduction, small diffused

NPs are obtained via the enzymes present in the cell wall (Jager et al. 2018). In the case of *Verticillium species*, Mukherjee et al. (2002) identified that the intracellular synthesis of NPs occurs through a step by step process. The mechanism mainly involves two stipulated steps, bioreduction and synthesis. A similar mechanism for the synthesis of NPs was found also in the fungus.

Nair and Pradeep (2002) have found that metal ions nucleate in the first place; hence, the formation of nanoclusters is the result of electrostatic interaction between the bacterial cell and metal clusters. Hence, the little nanoclusters get diffused through the bacterial cell divider. In the case of Actinomycete, the same process was observed (Sastry et al. 2003). NPs have been provided with extracellular bacterial synthesis by nitrate-reducing reduction of metal ions into nanocomposites (Ali et al. 2016; Jain et al. 2011).

14.5 Nanoparticle Approaches to Manage Pollution

Regulation of pollutants from the original source is a promising advance of controlling contamination. The contamination systems can be controlled by various ways:

- Reduction at the point of source, the controlling process is in situ, whereas degradation process is basically ex situ.
- The control mechanism is in situ at the point of source reduction while the degradation mechanism is essentially ex situ.
- Using less complicated products and disposable items.
- Prevent contaminant release at production sites and manipulate mechanism for combination into natural resources.
- Prevent the development of dangerous intermediates and by-products.
- Reduce energy utilization.

Biosynthesized gold nanoparticles are used successfully in bioremediation and in the production of biofuels. It was used for hydrogen production by oxidizing the carbon monoxide that can be used as a fuel cell. It is also used for the degradation of other organic contaminants including para-nitrophenol. In a recent analysis, paranitrophenol degredated to aminophenol in 30 min, using biosynthesized gold nanoparticles via *Trichoderma viride* as a heterogeneous catalyst (Mishra et al. 2014) (Fig. 14.3).

Nanotized zeolites is the process of catalysis and separation by oxidation of the hydrocarbons in the presence of visible light and excessive product yield. Nanoparticles of titanium dioxide have photocatalytic properties which display catalytic reactions in the presence of light (Shen et al. 2006). This also serves as an oxidizing agent in the presence of UV light and is therefore used in the prevention of emissions. The second approach to pollution control is the use of nanoparticles to eco-friendly nontoxic material. It helps in environmental sustainability. The carbon nanotubes in computers replace the cathode ray tubes, eliminating the use of heavy

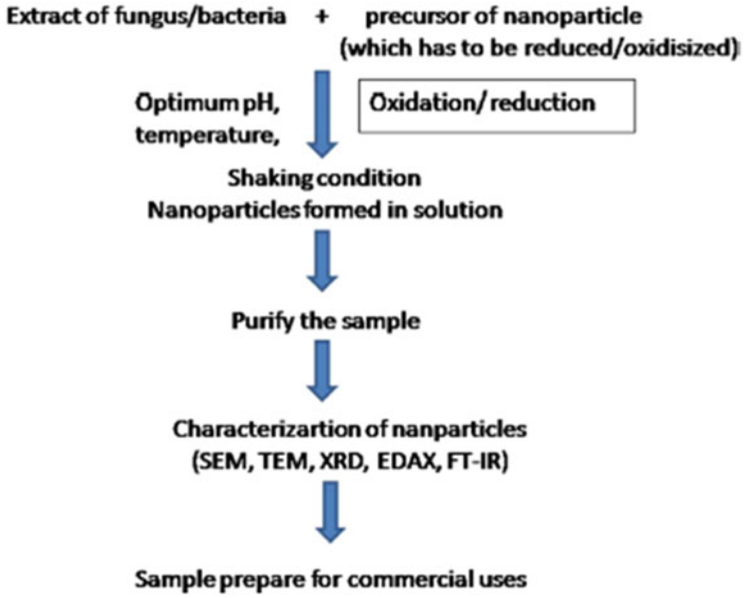

Fig. 14.3 Generalized chart for nanobiosynthesis (Mishra et al. 2014)

metals such as lead. A further example is the use of titanium dioxide and silicon in the formation of photovoltaic cells (Pizzini et al. 2005).

Mesoporous silica nanoparticle application (definite size of pores present in silica nanoparticles) improves the efficiency of adsorption, resulting in higher internal quantum performance.

14.6 Advantages of the Use of Biogenic Nanoparticles

Nanoparticles synthesized with biogenic agents such as bacteria, algae, and fungus are alternatives that are safer, superior, and effective in many ways than physical and chemical methods used. Biogenic nanoparticles are cheaper than nanoparticles synthesized utilizing physicochemical techniques as they employ biomolecules as reducing agents, thus getting rid of the requirement for high expensive chemical reductants consisting of sodium borohydride and hydrazine.

In spite of the fact that nanoparticles synthesized the use of chemical techniques that are giant in quantity, they require manufacturing of hazardous wastes that are damaging surroundings and human health, whereas biogenic mechanism does no longer produce such detrimental hazardous wastes. Furthermore, nanoparticles synthesized by using biogenic routes possess extra surface region that extensively complements adsorption ability for the elimination of environmental contaminants. Many of the biogenic nanoparticles incorporate lipid bilayer which presents stability and possesses higher physiological solubility, as a result of making them apt for numerous biomedical applications. In addition, the size and shape of nanoparticles may be controlled by adjusting the pH, the quality of the substrates, and the reaction time of touch (Li et al. 2010). Consequently, biogenic nanoparticles emerge as environmentally safe, cost-effective, less energy-intensive, and superior alternative to physicochemical methods for the production of nanoparticles in terms of quality, human health, and environmental effects.

14.7 Biological Synthesis of Nanoparticles

Nanoparticles can be synthesized by microbes by either intracellular or extracellular processes. In intracellular processes, positively charged metal ions get diffused into the negatively charged cell wall by electrostatic interactions. In intracellular strategies, positive charged metal ions are diffused by electrostatic interactions through the negatively charged cell wall. Additionally, endocytosis, carrier channels, and ion channels also promote the cytoplasmic influx of heavy metals. These toxic metals are then converted into nontoxic nanoparticles by the enzymatic machinery in the cell wall. Some of the extracellular processes are enzymes such as fungus synthesized nitrate reductase that converts metal ions into metal nanoparticles (Menon et al. 2017). Nanoparticle biosynthesis is generally related to characterization of nanoparticles via extraordinary techniques. Nanoparticle characterization offers a clear idea about their shape, size, surface area, chemical composition, and dispersity.

14.7.1 Bacterial Synthesis of Nanoparticles

Different species of bacteria have been shown to be capacity biofactories for the synthesis of nanoparticles including gold, silver, copper, iron, zinc, manganese, palladium, and many other nanoparticles designed. Bacteria can activate, immobilize, and precipitate metals, thereby facilitating the synthesis of nanoparticles. In a study published by Klaus et al. (1999), *Pseudomonas stutzeri* AG259, isolated from silver mines, was able to reduce silver ions, when put in a solution of silver nitrate, and the accumulated silver nanoparticle was discovered inside the preplasmic space of cell. He et al. (2007) suggested the formation of spherical gold nanoparticles of size ranging between 10 and 20 nm in an acidic environment through *Rhodopseudomonas capsulata*. Bacillus subtilis detected from rhizosphere soil has the ability to biosynthesis iron oxide nanoparticles (Sundaram et al. 2012).

14.7.2 Algae-Based Synthesis of Nanoparticles

Algae are photoautotrophic, oxygenic, and eukaryotic microorganisms that have the capacity to absorb carbon. There are numerous inherent benefits of using algae for the biosynthesis of metal nanoparticles, which encompass metal bioaccumulation potential, excessive tolerance, ease in coping with, and financial reasonability. In addition, large-scale secretion of extracellular algal enzymes enables the development of enzymes on an industrial scale (Thakkar et al. 2010). Marine brown algae secrete fucoidans (polysaccharides), known to have anticancer, anti-inflammatory, anti-viral, and anticoagulant effects, from their cell wall. Fucoidans have additionally been pronounced to display a key role in gold nanoparticle synthesis, for this reason offering a cleaner choice to conventional chemical-intensive techniques (Lirdprapamongkol et al. 2010). Brown algae cell walls are also rich in mucilaginous polysaccharides and carboxyl groups that have a key role in metal absorption and are also popularly used in nanoparticles biosynthesis (Khandel and Shahi 2016).

14.7.3 Synthesis of Nanoparticles Using Fungi

These are noticeably easy to treat and are a good source of extracellular enzymes, enabling nanoparticles synthesis. Synthesis of nanoparticles using fungus is economically feasible and creates large amounts of nanoparticles while when contrasted with microscopic organisms and green growth.

Besides, filamentous organism has high bioaccumulation capacity and high metal resistance, is ease in downstream handling, and is economically feasible. Fungi have been suggested to be able to intracellular synthesis of gold nanoparticles (AuNPs), wherein ultra-thin areas of fungal cells demonstrate the presence of gold nanoparticles in the vacuoles of cells (Menon et al. 2017). Intracellular synthesis of silver nanoparticles (AgNPs) was reported in Verticillium by Mukherjee et al. (2001). Exposure of fungal biomass to aqueous solution containing Ag + resulted in metal ions being reduced and AgNPs of size 25 ± 12 nm produced. TEM images further verified that the nanoparticles synthesized to Ag are morphologically spherical. Even few yeast strains were exploited for nanoparticles synthesis. In a study by Sen et al. (2011), two different strains of *Saccharomyces cerevisiae* have been exploited for the synthesis of gold nanoparticles. Two separate strains of *Saccharomyces cerevisiae* were exploited for the gold nanoparticle synthesis in a report by Sen et al. (2011). Reduction in situ from Au^{3+} to Au(0) was facilitated by providing small doses of γ-energy in the cytoplasm of the cell, and nanosized Au^{3+} was observed inside the nucleolus. Reductants derived from yeast for the synthesis of gold nanoparticles have been used as reagents. A smaller number of yeast species, however, have been identified as capable of synthesizing nanoparticles. Fungi are a large source of diverse extracellular enzymes that affect synthesis of nanoparticles. They were commonly used for the biosynthesis of nanoparticles, and for some of them, the mechanistic aspects regulating the formation of nanoparticles were also reported. Nanoparticles with well-defined dimensions can be obtained with fungi, in addition to monodispersity. Compared to bacteria, fungi may be used as a medium for generating larger quantities of nanoparticles. A reason is nanoparticles are produced by microbiological methods at a much slower rate than that observed when using plant extracts. In the biosynthesis of metal nanoparticles via a fungus, enzymes are produced which reduce a salt to its metal nanoparticles via the catalytic effect (Oksanen et al. 2000). This is one of the major disadvantages of microorganism-based biological synthesis of nanoparticles and needs to be addressed if it is to compete with other methods. For industrial applications, fungi should have certain properties like high production of different enzymes or metabolites, fast growth rates, easy handling in large-scale production, and low-cost production process specifications that offer advantages over other fungal methods (Vahabi et al. 2011). Fungi have an advantage over other biological systems because of wide range, simple methods of cultivation, reduced time, and improved cost-efficiency.

14.7.4 Bacteria in Nanoparticle Synthesis

Bacteria have an excellent potential to absorb heavy metal ions and are one of the best candidates for the synthesis of nanoparticles. For example, some bacterial species have developed the capacity to turn to explicit resistance systems to quell stresses like hazardous of metal particles or metals.

Some of them have been found to survive and expand even at high concentrations of metal ions (e.g., *Pseudomonas stutzeri* and *Pseudomonas aeruginosa*) (Haefeli et al. 1984; Bridges et al. 1979). Brock and Gustafson (1976) further reported that when growing on elemental sulfur as an energy source, *Thiobacillus ferrooxidans*, *T. thiooxidans*, and *Sulfolobus acidocaldarius* were able to reduce ferric ion to the ferrous state. *T. thiooxidans* had the option to reduce ferric iron aerobically at low pH medium vigorously. The ferrous iron framed was steady to autoxidation, and *T. thiooxidans* could not oxidize ferrous iron; however, the bioreduction of ferric iron utilizing *T. ferrooxidans* was not vigorous in view of the quick bacterial reoxidation of the ferrous iron within the presence of oxygen (Brock and Gustafson 1976).

14.7.5 Comparison of Production of Nanoparticles Using Plants, Fungi, and Bacteria

Due to the single-phase biosynthesis cycle, the absence of toxicants and the occurrence of natural capping agents, the synthesis of nanoparticles by plants is gaining

Fig. 14.4 Benefits of biogenic nanoparticles relative to chemically synthesized nanoparticles

importance nowadays (Gurunathan et al. 2009). Although fungi and bacteria need a comparatively longer incubation time to remove metal ions, phytochemicals that are water soluble do so in much less time. Hence, plants are better candidates for the synthesis of nanoparticles compared to bacteria and fungi. The effect of nanoparticles varies from plant to plant and depends on their mode of operation, size, and concentration (Manzer et al. 2015) (Fig. 14.4).

14.8 Nano-phytoremediation Applications

14.8.1 Challenges of Nanoparticles

Although nanoparticles have proven promising effects in treating contaminated sites, there are few issues related to their loss of reactivity with time, transportation, and their impact on microorganisms (Bhakyaraj et al. 2017; Li et al. 2010). Iron nanoparticles exhibit a loss in their reactivity degree after a sure period, exhibit a blocking impact in the soil via clogging the pores of soil and proscribing the passage of fluids, and confirmed that stabilizers, such as lactate, can be used to increase the mobility of iron nanoparticle in flip felicitating their higher transport in soil (Soni and Prakash 2012, 2014). Another significant issue with nanoparticles is their harmful impact on the development of the microbial networks. Various research under controlled conditions have been carried out on the impact of nanoparticles on microbes, and the effects are located to be conflicting (Soni and Prakash 2012). Some of the researches have proven inhibitory consequences on microorganisms like *Staphylococcus aureus* and *Escherichia coli* (Soni and Prakash 2014; Morrison et al. 2002). Few different experiments have demonstrated stimulating effects of nanoparticles on microorganisms such as bacteria and methanogens as donors of electrons (Zhang 2009; Naraginti and Sivakumar 2014). Soil microorganisms are extremely essential for the natural nutrient cycle in the environment, and they can also degrade the organic pollutants naturally or reduce and immobilize heavy metals. Therefore, a drastic reduction in the microbial population will lead to a weakening of the soil's contamination resistance (Prasad and Jha 2009; Mashrai et al. 2013).

Nano-iron's toxic effect can disrupt the cell membrane by producing reactive oxygen compounds which cause microbial cell death. Nano-iron compounds may also impede nutrient absorption in microbes through the cell membrane inhibiting their growth (Chong et al. 2010; Dastjerdi and Montazer 2010). Iron nanocompounds have shown no impact on fungal colonial growth (Thome et al. 2015; Tratnyek and Johnson 2006). It was studied that the toxic impact of nanoparticles can be minimized with the aid of coating them with some natural polymers. Studies have also shown that microorganisms often generate different enzymes and polysaccharides in order to avoid and counteract nanoparticles toxicity (Zhang et al. 2018; Zeng et al. 2015).

14.9 Phytoremediation

The different forms of phytoremediation mechanisms are as follows:

1. Phyto-degradation: Toxins are metabolized or bio-transformed within the plant tissues in this kind of phytoremediation.
2. Biodegradation of the rhizosphere: Natural exudates such as enzymes are released via the roots of plants. In doing so, nutrients are supplied in the soil around the roots (rhizosphere), while microorganisms improve the biological degradation of pollutants.
3. Phytostabilization: The plant produces chemical compounds for this purpose that can sequester, precipitate, or immobilize contaminants. This also is known as phytosequestration (Phillips 2017).
4. Phytovolatilization: Plants accumulate organic pollutants containing water and release them into the atmosphere during transpiration through their leaves.
5. Phytoaccumulation (or phytoextraction): Plant roots absorb mineral salts and water in addition to nutrients, and store/accumulate toxins in plant stems and leaves. Such plants are harvested because they are stored and no longer destroyed, while metals, especially precious ones, are extracted from the plants. That is known to be phytomining. Accumulated dangerous wastes are disposed of safely.

6. Rhizofiltration: This procedure is a hydroponic framework for treating water streams. To irrigate the plants, polluted groundwater is pumped to the surface. Therefore, this can be used for ex situ groundwater treatment. The absorbance of roots and accumulation of contaminants (phytoaccumulation), and upon saturation, plants are harvested and disposed of upon saturation.
7. Phytohydraulics (hydraulic control): Many trees develop their dense thick into groundwater and take in massive portions of water.

This is done by degrading, reducing, or eliminating water table contaminants such as pesticides, toxic herbicides, fertilizers, explosives, and radioactive compounds from the groundwater (Phillips 2017). There are many plant species that can recover and remove pollutants from soil, surface water, groundwater, and sediments. Examples of these plants include: *Pennisetum glaucum* (millet) (Nwadinigwe and Obi-Amadi 2014), poplar tree (*Populus deltoides*), sunflower (*Helianthus annuus*), Indian mustard (*Brassica juncea*), *Sorghum vulgare*, *Cynodon dactylon* (*Bermuda grass*), and water hyacinth (*Eichhornia crassipes*).

14.10 Nanoparticle as a Sensor

There are various methods of detecting pollutants, but under current conditions and time consuming operation, these techniques are unable to determine the exact composition and type of the pollutant. Nanotechnology nowadays plays an important role in the sensing of pollutants by improving sensors that are more specific and sensitive for environmental monitoring, either by targeting the binding between the contaminant and the recognition element or by optimizing the transduction and electronic interface to the sensing layer. Sensor may be used to identify pollutants that are linked to organic pollutants, inorganic contaminants, or biologics.

14.11 Inorganic Contaminant Remediation

Inorganic contamination caused by coal mines, factories, coal burning, urban incineration, electroplating, generating energy and electricity, and power transmission has led to heavy metal accumulation that preserves and amplifies the environment. Heavy metals, separated by magnetic force by nanoadsorbent iron nanoparticles. The soil mercury (Hg^{2+}) is a significant component, and an excess of $HgCl_2$ is found which is a significant reason for soil pollution. Several bacteria have been documented to demonstrate the ability to withstand high metal concentrations and reduce them into volatile elementary form. Chromium compounds are used in different industries (e.g., textile dying, tannery, metallurgy, metal electroplating, electronics, and wood preservation); thus, significant amounts of Cr have been released into the atmosphere due to inadequate disposal and leakage (Kimbrough and Wakakuwa 1992). Cr(VI) is the environmentally toxic type and mobile. Zero-valent Fe nanoparticle has a strong reduction ability, Fe0 nano has a core-shell structure with a Fe0 core encompassed by a shell of oxide/hydroxide which becomes thicker as iron oxidation progresses (Li et al. 2009; Zhang et al. 2007). Shell thickness will increase during oxidation. Mines are the center of many heavy metals that occur in mines.

The microbial variety, are additionally tolerant for metal like Cu, Al, Zn, Co, Hg. Often microbes are adsorbed and converted into nanoparticles that can be quickly collected and used for industrial purposes (Salvadori et al. 2014). Salvadori et al. (2013) isolated *Hypocrea lixii* from copper mines wastewater, the dead biomass of *H. lixii* acted as a strong copper ion biosorbent and converted it into copper nanoparticles. This dead biomass is a strong adsorbent, reducing agent and offers stabilization when the nanoparticles are taken up and synthesized. These microorganisms utilized in bioreduction and bioextraction of contaminants in wastewater and groundwater.

14.12 Organic Contaminant Remediation

Polycyclic aromatic hydrocarbons (PAHs) are highly toxic organic contaminants widely distributed in terrestrial and aquatic ecosystems, as products of the incomplete combustion of fossil fuels. Polycyclic aromatic hydrocarbons (PAHs) are extraordinarily toxic organic pollutants distributed widely in terrestrial and aquatic ecosystems as results of the deficient fossil fuel combustion. Manganese peroxidase (MnP) developed by a Chilean white rotting fungus, *Anthracophyllumdiscolor*, was immobilized on nanoclay obtained from volcanic soil and evaluated its ability to degrade polycyclic aromatic hydrocarbons (PAHs) compared to free enzymes (Acevedo et al. 2010). Lignin peroxidase (LiP), laccase (Lac), and manganese peroxidase (MnP) were found to have a crucial role in the degradation of PAHs among the enzymes secreted by white rot fungi (Steffen et al. 2002). White rot fungus immobilized MnP by using itself secreted on nanoclay to degrade PAHs in liquid solution. Nanoparticles also can be utilized as biocatalysts for reductive dechlorination. De Windt et al. (2005) reported palladium Pd(0) nanoparticles can be deposited on the cell wall and inside the cytoplasm of *Shewanella oneidensis* and charged with H* radicals by adding different substrates such as hydrogen, acetate, and formate as electron donors in a bioreductive assay containing Pd(II). De Windt et al. (2005) suggested palladium Pd(0) nanoparticles can be located on the cell wall and within the *Shewanella oneidensis* cytoplasm and charged with H* radicals with the aid of adding different substrates such as hydrogen, acetate, and formatting as electron donors in a Pd(II) bioreductive assay. At the point when these charged Pd (0)-deposited *S. oneidensis* cells come into contact with chlorinated compounds; the H+ radical on the Pd(0) can react catalytically with PCP leading to the removal of the chlorine molecule from the chlorinated compounds. In addition, nanoparticles can be used to immobilize microbial cells which can degrade or biorecover particular chemicals. Dissimilar to regular cell immobilization on micron-sized media or a fixed surface, magnetic nanoparticles (i.e., Fe_3O_4) were covered on the surface of *Pseudomonas delafieldii* using ammonium oleate. By applying an external magnetic field to these microbial cells, these magnetic nanoparticle-coated cells have been clustered on the reactor wall at a particular position, isolated from the bulk solution and recycled for the treatment of the same substrate. Such microbial cells have been applied to a bioreactor at a high concentration of biomass and have been shown to desulfurize organic sulfur from fossil fuel (i.e., dibenzothiophene) just as effectively as non-nanoparticulated cells (Shan et al. 2005). Dyes are heterocyclic organic compounds used in industries and research organizations, which eventually mixed with air and waste, creating a layer of water after mixing with water bodies, which impedes the total incidence of sunlight on photosynthetic plants and bodies, leading to photosynthesis depletion and decreased oxygen intake, which becomes a serious problem for water animal and plants. Methylene blue is an aromatic heterocyclic compound which, in the presence of solar/UV light, can be degraded by the photocatalyst titanium dioxide (Jang et al. 2001) and can also decompose pathogenic bacteria such as *Pseudomonas aeruginosa*, *Escherichia coli*, and ammonia gas at high light intensity.

14.13 Heavy Metal Detoxification

Toxic metal compounds can be very efficiently converted to nanoparticles by microorganisms during their detoxification cycle. Biosynthesis of As, Se, Te, and CdS nanoparticles which are major soil and water contaminants are discussed in the following paragraphs.

14.13.1 Arsenic Nanoparticles Biogenesis

Arsenic is a metalloid that is very toxic because it inhibits common enzyme reactions and affects almost all organ systems. Arsenic is strongly related with lung and skin cancers. The arsine gas causes the syndrome to be hemolytic. Several microorganisms have been removed from arsenic-rich environments that can detoxify toxic arsenic compounds; however, very few have been documented during this reduction phase to produce arsenic nanostructures. In one research, Lee et al. (2007) studied the development by the dissimilarly metal-reducing bacterium *Shewanella* sp. of a large extracellular network of filamentous, arsenic-sulfide (As-S) nanotubes (20–100 nm in diameter by ~30 μm in length).

The As-S nanotubes, shaped with the aid of the reduction of As(V) and $S_2O_3^{2-}$, have been at the beginning amorphous As_2S_3 but developed toward polycrystalline phases of chalcogenide minerals realgar (AsS) and duranu site (As4S) with increasing the incubation time. The As-S nanotubes carried on as metals and semiconductors regarding their electrical and photoconductive properties. In another research, it was discovered that Fe(III)-reducing microorganisms would couple the reduction of solid phase Fe(III) hydroxides with the oxidation of organic carbon under anaerobic conditions. Nutrients and trace metals such as arsenic related with Fe(III) hydroxides can be mobilized by a microbially mediated reduction of the surface. Mechanisms of arsenic mobilization were studied using a series of controlled microcosm experiments containing aggregated arsenic-bearing ferrihydrite nanoparticles and a microorganism, *Geobacter metallireducens*, reducing Fe(III). The phase distribution of iron and arsenic was calculated by filtration and by techniques of ultracentrifugation. Biotic activity led to changes in the surface potential of nanoparticles and the occlusion of nanoparticle aggregates was deflated. Arsenic activated over time was found to be correlated exclusively with the nanoparticles in the biotic trials. Because arsenic contamination of natural waters due to mobilization from mineral surfaces is an essential route of human arsenic exposure, improved understanding of biologically mediated mechanisms requiring arsenic partitioning between solid and solution phases to establish effective treatment and remediation strategies is needed.

14.13.2 Biogenesis of Selenium and Tellurium Nanoparticles

Selenium is an important trace element, particularly used in the enzyme glutathione peroxidase system, which protects intracellular structures from oxidative harm. Excessive consumption or exposure of selenium can cause significant toxicity. Selenium, like arsenic, inactivates the sulfydral groups of amino acids. The potential utilization of microorganisms to biotransform metals has resulted in another new aspect of exploring the biological mechanisms toward the production of zero-valent elements, bi/multi-elemental quantum dots, and nanoparticles containing metals. The biogenesis of selenium nanomaterials was confirmed by Oremland et al. (2004) and Baesman et al. (2007) who pronounced efficaciously reduction of two species of chalcogenide oxyanion, viz. selenite/nate and tellurite/rate, by two anaerobic bacteria, *Bacillus selenireducens* and *Sulfurospirillum barnesii*, to elemental selenium and tellurium. Extracellular granules formed in the case of selenium consisting of stable, uniform Se0 nanospheres (diameter ~ 300 nm) and having monoclinical crystalline structures. In the case of tellurium, *B. selenireducens* initially shaped as nanorods (~10 nm) that group together forming larger rosettes (~1000 nm) composed of numerous individual shards.

On the other hand, *S. barnesii* shapes extremely irregular shaped nanospheres (diameter $<$ 50 nm), which coalesce into large composite aggregates. Se0 nanospheres' microbial synthesis results in special, complex, and compact nanostructural arrangements of the Se atoms. Such structures are likely to represent a variety of dissimilatory reduction enzymes that are ingeniously specific in various microbes. Remarkably, the latest chemical synthesis methods described in the literature cannot attain these conditions.

14.13.3 Biogenesis of Nanoparticles in CdS

Chronic exposure to cadmium affects the kidneys mainly and the bones secondary. The well-known cadmium-related "Itai-itai" or ouch-ouch disease was first identified in post-menopausal Japanese women who have been exposed to excessive levels of cadmium throughout their lives (Watanabe et al. 2000). Symptoms and signs of "itai-itai" disease can also occur in extreme osteoporosis and osteomalacia with serious renal failure concurrently, normochromic anemia, and low blood pressure (Alfvén et al. 2002), with an average urinary cadmium level of 20–30 μg/g creatinine in urine (Ezaki et al. 2003). Only some microorganisms were pronounced to synthesize cadmium nanoparticles. Among the first reviews of intracellular semiconductor nanoparticle synthesis, Sweeney et al. showed that, when cadmium chloride ($CdCl_2$) and sodium sulfide (Na_2S) were incubated with *Escherichia coli*, semiconductor nanocrystals of cadmium sulfide (CdS) are formed spontaneously. They showed that physiological parameters markedly affected the formation of nanocrystals. The transition into stationary process actually increased the yield by 20-fold.

Cunningham and Lundie were reported that *Clostridium thermoaceticum* precipitates CdS at the cell surface as well as in the medium when exposed to $CdCl_2$ in the presence of cysteine hydrochloride as a source of sulfide in the growth medium. Cunningham and Lundie found that, in the presence of cysteine hydrochloride as a source of sulfide in the growth medium, *Clostridium thermoaceticum* precipitates CdS both at the cell surface and in the medium when exposed to $CdCl_2$. Cadmium sulfide nanoparticles of an average size of 8.01 ± 0.25 nm can be formed by *Rhodopseudomonas palustris*, a photosynthetic bacteria. The cadmium sulfate solution incubated with *R. palustris* biomass changed to a yellow color from 48 h onward, indicating the formation of cadmium sulfide nanoparticles. The solution of cadmium sulfate incubated with *R. palustris* biomass modified from 48 h on to a yellow color, confirming the formation of cadmium sulfide nanoparticles.

The cadmium sulfide face-centered cubic (fcc) crystalline structure was confirmed by the pattern of electron diffraction. In addition, the cysteine desulfhydrase producing S2− in *R. palustris* was found to be in cytoplasm, and the content of cysteine desulfhydrase depending on the development phase of the cells was responsible for the arrangement of CdS nanocrystal, protein secreted by means of *R. palustris* stabilized the cadmium sulfide nanoparticles. Alternatively *R. Palustris* was able to transfer CdS nanoparticles from cells in an efficient manner (Bai et al. 2009). The yeasts *Schizosaccharomyces pombe* and *Candida glabrata* had been effectively cultured at cadmium levels of up to 100 mg^{-1} in a fed-batch process. Within 24 h, the *S. pombe* incorporated 20 mg Cd g^{-1} dry biomass. *Candida glabrata* had produced dry biomass of 8 mg Cd g^{-1} in 24 h. During and at the end of growth, the higher Cd uptake from *S. pombe* cells correlate with the elevated glucose concentrations.

Cell analysis with energy-filtering transmission electron microscopy-element specific imaging (EFTEM-ESI) showed that cadmium is not precipitated outside of the cells or at the cell wall but distributed uniformly inside the cell plasma. Cd is immobilized by an action system for intracellular detoxification. Chromatography of the size exclusion showed that Cd is related to a protein fraction between 25 and 67 kDa which corresponds to the theoretical molecular weight of 35 kDa CdS nanoparticles covered with phytochelatins.

14.13.4 Pt Nanoparticles

Platinum as a metal is not very dangerous, but platinum salts can cause several health effects, such as DNA alterations, cancer, allergic reactions of the skin and the mucous membrane, damage to organs such as intestines, kidneys, and bone marrow, and hearing damage.

Platinum as a metal is not very toxic; however, platinum salts can make many health impact, for example, alterations in DNA, cancer, skin, and mucous membrane allergic reactions, damage to organs including intestines, kidneys, and bone marrow, and damage to hearing. A risk of platinum is that it can potentiate the toxicity of certain harmful substances, such as selenium, in the human body. It was used to shape platinum nanoparticles using green chemistry approach metal ion-reducing bacterium *Shewanella algae*. Resting cells of *S. algae* were able to convert aqueous $PtCl_6^{2-}$ ions into elemental platinum at room temperature and neutral pH within 60 min, in the presence of lactate as an electron donor. Approximately 5 nm of biogenic platinum nanoparticles were developed and found to be in the periplasm, a suitable cell surface position for fast recovery of biogenic nanoparticles (Konishi et al. 2007a, b). To research the enzymatic mechanism for the complete bioreduction of platinum(IV) into platinum (0 nanoparticles), a consortium of sulfate-reducing bacteria was used. It was reported that two separate hydrogenase enzymes were described. First, using an oxygen-sensitive novel cytoplasmic hydrogenase, the platinum(IV) was reduced to platinum(II) through a two-electron bioreduction. Second, the platinum(II) ion was reduced to platinum (0) nanoparticles by a further two-electron bioreduction involving an oxygen-tolerant/periplasmic hydrogenase barrier. No exogenous electron donors were required because in situ metabolite oxidation (Riddin et al. 2009).

14.13.5 Other Metallic Nanoparticles, for Example, Gold and Silver

Gold and silver pure metal (elemental) is non-dangerous and non-irritating when ingested. Soluble compounds (gold salts) including gold chloride are harmful to the liver and kidneys. Popular gold cyanide salts such as potassium gold cyanide, utilized in gold electroplating, are harmful both by means of advantage of their cyanide and gold content. Due to its emerging applications in a variety of areas such as bioimaging, biosensors, biolabels, and biomedicines, the syntheses of gold nanoparticles have been the subject of intense interest in recent years.

Various microorganisms (*Pseudomonas stutzeri*, *Morganella* sp., *MKY3*, *Phoma* sp., *Verticillium*, *Lactobacillus*, *Fusarium oxysporum*, *Sargassum wightii*) have been reported to biosynthesize gold and silver nanoparticles by means of NADPH-dependent reductase enzymes that reduce metal salts to nanoparticles via the enzymatic metal reduction cycle of electron shuttles (Kaushik et al. 2010).

14.13.6 Palladium and Platinum NPs

Desulfovibrio desulfuricans as a sulfate-reducing bacterium (Yong et al. 2002a, b; Lloyd et al. 1998), and the bacterium-reducing metal ion, *Shewanella oneidensis*, were able to reduce soluble palladium(II) to insoluble palladium(0) with shape, lactate, pyruvate, or H_2 as the electron donor (de Windt et al. 2005). Konishi et al. (2007a, b) showed that *S. algae* resting cells were able to deposit NPs of platinum by reducing $PtCl_6^{2-}$ ions at pH 7 and 25 °C within 60 minutes. The periplasmic space contained biogenic platinum NPs of around 5 nm. For this situation, cell suspension changed the color from light yellow to black within 10 min. The black presence provided a convenient visible signature for the formation of metallic platinum NPs in microbes. The observed decrease in concentration of aqueous platinum was likely caused by the rapid reduction of $PtCl_6^{2-}$ ions into insoluble platinum. However, in the absence of lactate, the $PtCl_6^{2-}$ ions could not be decreased by *Shawella algae* cells. The $PtCl_6^{2-}$ ions have not been chemically reduced by lactate.

Yong et al. (2002a, b) also confirmed that *D. desulfuricans*, a sulfate-reducing bacterium, was only able to adsorb 12% of platinum(IV) ions from a 2 mM platinum chloride solution to the bacterial cells. In another analysis, Gram-negative cyanobacterium, *P. boryanum* UTEX 485, extracellularly formed Pt(II)-organic and metallic platinum NPs with a size range of 30 nm to 0.3 μm at 25–100 C for up to 28 days and 180 zwischen for 1 day with specific morphologies of circular, bead-like chains and dendritic chains (Lengke et al. 2006).

14.13.7 Selenium and Tellurium NPs

Selenium has photooptical and semiconducting characteristics which apply to photocopiers and microelectronic circuit devices. *Stenotrophomonas maltophilia* SELTE02 confirmed promising transformation of selenite (SeO_3^{2-}) to elemental selenium (Se0) collecting selenium granules either in the cellular cytoplasm or within the extracellular space. Additionally, *Enterobacter cloacae SLD1a-1, Rhodospirillum rubrum*, and *Desulfovibrio desulfuricans* have additionally been determined to bioreduce selenite to selenium both within and outside the cell with different morphologies such as circular, fibrillary, and granular form or with small atomic aggregates. *E. coli* also deposited elemental selenium in both periplasmic and cytoplasmic spaces and *P. stutzeri* also reduced selenite to elemental selenium aerobically (Narayanan and Sakthivel 2010). Hunter and Manter (2008) reported that *Tetrathiobacter kashmirensis* bioreduced selenite to the elemental red selenium under aerobic conditions. This bioreduction was assumed to be responsible for a 90-kDa protein present in the cell-free extract. Moreover, Yadav et al. (2008) confirmed that *P. aeruginosa* SNT1 biosynthesized nanostructured selenium through biotransforming selenium oxyan ions to spherical amorphous allotropic elemental crimson selenium each intracellularly and extracellularly. Furthermore, *Sulfurospirillum barnesii*, *Bacillus selenitireducens*, and *Selenihalanaerobacter shriftii* synthesized with monoclinic crystalline structures extracellularly stable uniform nanospheres (almost 300 nm) of elemental selenium Se0 (Oremland et al. 2004). Microbial synthesis of nanospheres of elemental selenium (Se0) makes unique, complex, compact nanostructured arrangements of the Se atoms. These structures resulted from the dissimilar reductions in the various microbes which were slightly different. In another research, the bacterial isolate *Pseudomonas aeruginosa* strain JS-11 was used to synthesize stable, mainly monodispersed, and spherical selenium NPs (with an average size of 21 nm). The bacteria showed significant selenite tolerance (SeO_3^{2-}) at a concentration of up to 100 mM, with an EC50 value of 140 mM.

The supernatant culture contained the capability of reducing soluble and colorless SeO_3^{2-} to insoluble red elemental selenium (Se0) at a temperature of 37°C. It was proposed that the metabolite phenazine-1-carboxylic acid released by strain JS-11 was responsible for biomimetic reduction of SeO_3^{2-} to Se0 nanospheres in culture supernatant along with known redox agents such as NADH and NADH-based reductases.

The authors clarified that the red-colored Se0 nanospheres that serve as a biosensor for nanotoxicity assessment, considering the inhibition of SeO_3^{2-} the bioreduction process in supernatant bacterial cell culture treated NPs as an endpoint of toxicity. In different words, the formation of red Se0 from SeO_3^{2-} could serve as a molecular marker, while essential bioreduction stage inhibition was considered an end point of toxicity for qualitative and quantitative toxicity assessment (Dwivedi et al. 2013). Extracellular reduction of palladium to PdNPs by Geobacter Sulfur reducing has been identified as a sustainable method for extracting catalysts from precious metals (Yates et al. 2013). Another recent study mentioned the selective electrocatalysis of molecular oxidation of biofuels using palladium nanoparticles based on *Shewanella oneidensis* MR-1 (Wu et al. 2018).

14.14 Removal of Heavy Metals from Environment

Heavy metals cause severe health issues for humans and other animals, because of their teratogenic and carcinogenic effects. It will consequently become vital to discover a route which gets rid of heavy metals from surroundings in a sustainable way. In industrial wastewaters from mining and metallurgical processing industries, heavy metals such as arsenic and copper are common occurrences. In a recent review, it has been reported that iron nanoparticles synthesized from natural consortium can adsorb arsenic, copper, zinc, and chromium from wastewater (Castro et al. 2018). Magnetite (Fe_3O_4), vivianite ($Fe_3\ (PO_4)_2{\bullet}8H_2O$), and siderite ($FeCO_3$) were biogenic precipitates obtained from crops. These biogenic adsorbents display greater adsorption ability and greater affinity for arsenate compared to chromate. Copper and zinc had been additionally adsorbed with organic nanoparticular elements. Groundwater and surface waters which contain high levels of arsenic, Fe(II), and Mn(II) adversely had an effect on the aquatic ecosystem and human health (Davolos and Pietrangeli 2013). In the synthesis of biogenic Fe–Mn oxides (BFMO), manganese(II)-oxidizing bacterium, *Pseudomonas* sp. QJX-1, separated from soil of manganese mines was used. Those oxides have been found to be able to oxidize and adsorb arsenic. The mechanism proposed includes an initial precipitation of BFMO on the surface of which Fe(II) was chemically oxidized to FeOOH and Mn(II) was biologically oxidized to form MnO_2, which together co-precipitated to adsorb and oxidize As as Fe–Mn oxide (Fig. 14.5). FeOOH has higher adsorption potential with lower oxidation potential complemented by BMO which has higher oxidation efficiency. In consonance, FeOOH and BMO generate BFMO, which promotes the adsorption and oxidation of As(III) and As(V) in an acceptable way. Around the same time, BMO is additionally successful at oxidizing Fe(II) to FeOOH, which

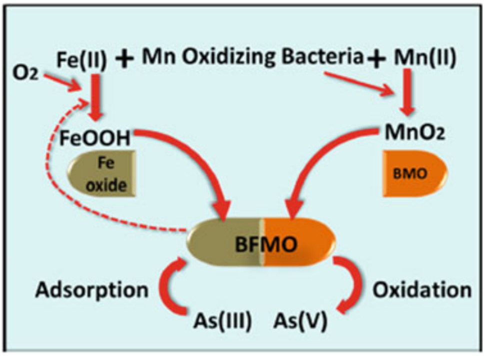

Fig. 14.5 Proposed mechanism of adsorption and oxidation of As(III) through BFMO

in effect additionally adsorbs remaining As(III) and As(V) (Bai et al. 2016), thereby remediating three pollutants.

14.14.1 As(III or V), Fe(II), and Mn(II) in Groundwater

Also, sulfate-reducing bacteria (SRB) may be used for treating chromium-containing wastewater (VI). These bacteria also promote sulfate and chemical oxygen demand (COD) of wastewater by using the organic compounds as their carbon source. Sorption studies carried out under engineered conditions on simulated wastewater resulted in a reduction of 81.9% COD, 89.2% Cr(VI), and 95.3% sulfate from synthetic wastewater (Verma et al. 2010).

Saunders et al. (2018) have documented using SRB to bioremediate the groundwater polluted with arsenic. Biogenic iron sulfides are also capable of extracting zinc ions from mine drainage water, indicating that this strategy may also remediate actual wastewater (Jencarova and Luptakova 2012). Hence, it can be inferred that SRB can be utilized as an environment friendly bioadsorbent for the elimination of sulfate and heavy metals from wastewater and groundwater. Synthesized biogenic manganese oxide (BMO) from *Pseudomonas putida* MnB1 was used to eliminate the heavy metals present in the area. In comparison to chemical synthesized manganese oxide (birnessite), BMO has proven to be an outstanding heavy metal adsorbent. The amorphous nature, high surface area, and small dimension of BMO make it a good adsorbent. BMO's adsorption capacity for zinc, lead, and cadmium was 7–8 times higher than that of birnessite, and heavy metal adsorption efficiency improved as pH and temperature were expanded from 3 to 6 and 15 to 30 °C, respectively. The increase in adsorption efficiency at higher temperatures also indicated an endothermic existence of the adsorption (Zhou et al. 2015).

The pollution of heavy metals from soil is a source of great concern. The combustion of fossil fuels and their atmospheric transport result in a three- to tenfold increase in soil mercury (Hg) concentration (Xu et al. 2014). Several remediation methods such as soil washing (Dermont et al. 2008), stabilization or solidification (Mulligan et al. 2001), thermal treatment (Busto et al. 2011), and biological methods (Permina et al. 2006) have been employed to deal with mercury contaminated soil.

Wang et al. (2017a, b) have recently reported bioremediation of Hg-contaminated soil by biogenic selenium nanoparticles synthesized from *Citrobacter freundii* Y9 (isolated from a bioreactor for anaerobic sulfate reduction). Nonreactive HgSe, which is less toxic and chemically inert, was reportedly formed in the presence of elementary mercury and elemental selenium. Additionally, under both aerobic and anaerobic conditions, nano-selenium(0) can absorb Hg(0) in soil. Hence, the use of nano-selenium for mercury immobilization is an effective way of remediating these polluted soils.

14.15 Conclusion and Future Prospects

Environmental pollution has become a big concern in an ever-growing area of growth. Nanotechnology has emerged to counter pollution as a powerful tool for cleaning the environment. Nanotechnology has the ability to revolutionize current technologies used in various industries, including reducing emissions. Nanotechnology can provide effective solutions to many pollution-related problems such as heavy metal contamination, chemical pollutant adverse effects, and oil emissions. Nanotechnology may have environmentally friendly alternatives, without damaging the natural environment. Several plants, fungi, and bacteria have been identified with greater effectiveness in collecting very large amounts of metals and are known as "super accumulators." These plants, fungi, and bacteria can be useful in bioremediating heavy metal. Nanomaterials in various shapes may be used to remove other contaminants from the atmosphere. In extracting certain heavy metals from contaminated areas, nanoparticles obtained from these plants, fungi, and bacteria have had actual application. Nanoparticles from plants, fungi, and bacteria in highly contaminated conditions are useful for detoxifying and bioremediating soil, water, and other habitats. Nanomaterials can serve as a sensor to detect contaminants, monitor pollutant release, and have potential for in situ and ex situ remediation. Gold and silver nanoparticles very well act as a heterogeneous catalyst to remove contaminants like para nitro phenol. In spite of the fact that field is rapidly growing, the precise mechanism of biosynthesis and bioremediation via nanoparticles remains unknown which needs to be explored. Soil microflora can be utilized for the synthesis of nanoparticles and may also be used as a bioremediator. Nanoparticles can also restrict pesticide use by biosynthesizing nanoparticles with native microbes which are emerging as a new technology for humanity to protect their crops. With the rapid development of eco-friendly microbial synthesis procedures, the emerging field of green nanotechnology needs to bloom to make the world greener and cleaner. NMs not only directly catalyze waste degradation and toxic materials, which are harmful to microorganisms, but also help increase the performance of microorganisms in waste degradation and toxic materials. It also shows that phytoremediation can be used in extracting heavy toxic metal from polluted soil. Therefore, based on the above topic, it can be said that it also has tremendous applications in bioremediation, like its applications in numerous other fields of research. Nanotechnology modification and adaptation will extend the quality and length of the bioremediation in the future. The breath of anticipated opportunities, cross-disciplinary complexity, breakthrough potential, historical track record, and the effect of nanotechnology's potential advantages leads to recognition of this field as increasingly significant.

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Chapter 15
Biosorption and Bioaccumulation of Pollutants for Environmental Remediation

Parteek Prasher, Harish Mudila, and Mousmee Sharma

Contents

Abstract Indiscriminate and incessant utilization of the available resources by anthropogenic activities principally pertaining to industry, agrochemicals, and metalliferous mining result in umpteen detrimental impacts on the ecosystem due to an unprecedented release of organic and inorganic contaminants. After undergoing immobilization, transportation, degradation, and bioaccumulation in the environmental compartments: air, soil, and water as well as in the ecological components: autotrophs and heterotrophs, these pollutants eventually integrate into food chain and food webs. The detrimental consequences of bioaccumulation of the pollution-causing agents in the ecosystem led to a large-scale adoption of the remedial efforts for mitigating the environmental contamination. However, the conventional efforts in the form of coagulation, flocculation, chemical precipitation, adsorption, ion exchange, electrochemical technologies, incineration, pyrolysis, membrane separation, implemented for the mobilization, immobilization, sequestration, or degradation of the target pollutants proved futile and uneconomical compared to the

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bioremediation-based processes that ensure a sustainable environmental remediation.

Keywords Biosorption · Bioaccumulation · Environmental remediation

15.1 Introduction

Industrial development and agricultural advancement resulted in levitating consumer demands, hence bringing a major paradigm shift in the policy-framing and decision-making processes (Briggs 2003). The ensuing consequences appearing in all the four domains of earth: biosphere, atmosphere, hydrosphere, and lithosphere as heavy metal and radionuclide contamination, xenobiotic toxication, unimpeded waste disposal, mounting landfills, chemical bio-magnification, SPM (suspended particulate matter) escalation, and inexorable marine dumping necessitate an imperative and immediate remediation (Verhaar et al. 1992). Biosorption and bioaccumulation approaches present prolific solutions for the contemporary environmental bioremediation paradigm compared to the conventional physicochemical methods. The microorganisms participating in bioremediation mainly assist in the elimination of life-threatening heavy metals with densities 5 g/cm^3 from the ecosystem that otherwise cannot be degraded by physical, biological, or chemical methods (Wu et al. 2016). The detoxification of heavy metals by microbes involves their preliminary transit inside the microbial cell by chemiosmosis (Volesky 2001). Further, the intruding heavy metals reportedly replace the metallic co-factors of the microbial enzymes or deactivate the enzymatic activity; essentially, by covalently binding to the thiol groups present on the active site residues of the target enzyme (Fomina and Gadd 2014). On the contrary, the microbial strains that display a remarkable heavy metal antagonism present a superior candidature to bioremediation. In addition to evolved metabolic pathways for maintaining homeostasis, the microorganism possess exclusive characteristics that utilize the toxic compounds as an energy source for various cellular processes (Volesky and Holan 1995). Similarly, the microbes also transform soluble and insoluble forms of xenobiotics, such as pesticides and heavy metals, to the less toxic environmentally benevolent forms. This chapter highlights the various microorganism-borne environmental bioremediation strategies for an eco-sustainable development.

15.2 Heavy Metals in the Environment

The heavy metals comprise metals and metalloids such as arsenic (As), lead (Pb), cadmium (Cd), nickel (Ni), mercury (Hg), chromium (Cr), cobalt (Co), zinc (Zn), and selenium (Se) and their salts with hydroxide (OH^-), sulfate (SO_4^{2-}), sulfide (S^{2-}), oxide (O^{2-}), phosphate (PO_4^{3-}), and $[SiO_4^{-X}]_n$ anions (Masindi and Muedi 2018). These possess a relatively higher density compared to water and are capable of instigating toxicity at a low level of exposure with a trace amount of higher than 10 ppm (Tiller 1989). The principal sources of heavy metals in the environment involve several geogenic and anthropogenic factors (Rhind 2009) that also include agricultural (Evans et al. 2019), industrial (Wang and Yang 2016), and pharmaceutical waste (Bielen et al. 2017). Besides, the domestic effluents (Gu and Yim 2016), as well as point sources such as mining, metal processing foundries and smelters, metal-based industrial processes, natural processes such as weathering, and volcanic eruptions (Armon and Starosvetsky 2015). Certain other factors such as metal evaporation from water resources to soil and ground water (Saxena et al. 2016), in addition to metallic corrosion (Costa and Vilarrasa 2013), and sediment resuspension also act as key pollution factors. Besides, the soil erosion of metallic ions and leaching of heavy metals (Fang et al. 2016) and atmospheric deposition (Fenn et al. 2015) also contribute to environmental contamination by heavy metal accumulation (Gonzales et al. 2016). An optimum concentration of essential heavy metals serves as micronutrients that assist in regulating several biochemical, metabolic, and physiological functions in autotrophs and heterotrophs (Page and Feller 2015). However, their biomagnification at various trophic levels (Ali and Khan 2019) in food chain and successive accumulation in food webs (Siric et al. 2016) results in severe environmental contamination due to an enhanced ecological toxicity (Qiu 2015) and development of carcinogenic conditions in higher trophic levels (Khan et al. 2015). The physiological toxicity of heavy metals comprises several mechanistic facets, characteristic for the metal in question (Jaishankar et al. 2014). However, the principal modes of mechanism involve exchange and coordination interactions with the biomolecules, such as enzymes, proteins, and vital organelles to form stable biotoxic compounds, thereby distorting their structures and restraining them from performing the optimum functions (Jan et al. 2015). Table 15.1 lists the sources, potential toxicity, and mechanism of environmental and physiological distress of some heavy metals.

15.3 Organic Pollutants in the Environment

The persistent organic pollutants (POPs) principally include synthetic chemicals that contribute to notable environment hazards (Jones and Voogt 1999) due to their persistence and potential for long-range transport in the environmental domains (Kelly et al. 2007) and, notably, an enhanced ability to incorporate into various

Table 15.1 Effect of heavy metals on the environmental health

Metal	Source	Occurrence	Threats	References
Essential				
Arsenic (As)	*Natural:* Volcanic eruptions, soil erosion, arsenopyrite *Anthropogenic:* Smelting and agriculture operations	*Inorganic forms:* Trivalent arsenite and the pentavalent arsenate *Organic forms:* Monomethylarsonic acid (MMA), dimethylarsinic acid (DMA), and trimethylarsine oxide	Arsenicosis, hyperkeratosis, leucomelanosis, hypohidrosis, adiaphoresis	Mandal (2017), Chung et al. (2014)
Cadmium (Cd)	*Natural:* Sedimentary rocks, marine phosphates *Anthropogenic:* Production of alloys, pigments, and batteries	*Inorganic forms:* Cadmium sulfide, cadmium carbonate, cadmium oxide, cadmium sulfide (mineral greenockite) *Organic forms:* Cadmium thiocarbamate	Itai-Itai disease, emphysema, pulmonary adenocarcinoma, prostatic proliferative lesions	Mudila et al. (2018), Hayat et al. (2019), Saini and Dhania (2020)
Chromium (Cr)	*Natural:* Occurs as Cr^{3+} (ferrochromite) *Anthropogenic:* Occur mainly as Cr^{6+}	*Inorganic forms:* Chromium chloride *Organic forms:* Chromium picolinate, chromium nicotinate	Chronic pharyngitis and rhinitis, pulmonary sensitization, tracheobronchitis	Rowbotham et al. (2000), Cohen et al. (1993)
Lead (Pb)	*Natural:* Rocks, sediments and minerals *Anthropogenic:* Lead batteries, photovoltaics, ammunitions	*Inorganic forms:* Galena (PbS), cerussite ($PbCO_3$), and anglesite ($PbSO_4$) *Organic forms:* Alkyl lead	Plumbism, encephalopathy, peripheral neuropathy	Flora et al. (2012), Valciukas et al. (1981), Gloag (1981), Needleman (2004)
Mercury (Hg)	*Natural:* Forest fires, volcanic eruptions *Anthropogenic:* Paper industry	*Inorganic forms:* Mercuric sulfide, mercuric/mercurous chloride *Organic forms:* Methyl mercury	Minamata disease, acrodynia, muscle atrophy	Teixeira et al. (2018), Bernhoft (2011)
Nonessential				
Nickel (Ni)	*Natural:* Weathering of rocks and soils, volcanic emissions, forest fires *Anthropogenic:* Burning of coal and heavy fuel oil,	*Inorganic forms:* Forms binary compounds with halogens, chalcogenides, and pnictides. Nickel ions can act as a cation in salts with many acids,	Dermatitis, neurological disorders, renal failure	Ashton (1972), Moore and Ramamoorthy (1984), Brix et al. (2016)

(continued)

Table 15.1 (continued)

Metal	Source	Occurrence	Threats	References
	mining, and refining processes, waste incineration	including common oxoacids *Organic forms:* Alkoxy compounds: nickel tert-butoxide $Ni[OC(CH_3)_3]_2$ Aryloxy compounds: $Ni(OAr)XL_2$ and $Ni(OAr)_2L_2$ ($L = N, P$)		
Copper (Cu)	*Natural:* Volcanic eruptions, windblown dust, and forest fires *Anthropogenic:* Mining activities, electrical manufacturing, pesticides and fungicides, leather processing, automotive brake pads	*Inorganic forms:* Oxides: malachite, azurite; sulfide: chalcopyrite, chalcocite, bornite *Organic forms:* Mainly as chelates	Kayser–Fleischer ring in cornea	Brewer (2010), Flemming and Trevors (1989)
Zinc (Zn)	*Natural:* Weathering, leaching, forest fires *Anthropogenic:* Mining activities, steel processing, waste incineration, electroplating, smelting	*Inorganic forms:* Sphalerite, smithsonite, hemimorphite, and wurtzite *Organic forms:* Mainly as organometallic compounds, enzyme cofactors	Malabsorption syndrome, peripheral neuropathy, sideroblastic anemia	Fiske (1994), Plum et al. (2010)
Cobalt (Co)	*Natural:* Weathering of rocks, seawater spray, forest fires *Anthropogenic:* Mine drainage, smelting, metallurgical, and chemical processes	*Inorganic forms:* Occurs as oxides, halides, and coordination compounds. Oxidation states range from −3 to +5. Main ores are cobaltite, erythrite, glaucodot and skutterudite *Organic forms:* Occur mainly as organometallics	Pernicious anemia, necrosis of leaves in tomato, alcoholic cardiomyopathy	Donaldson and Beyersmann (2005), Leyssens et al. (2017)
Selenium (Se)	*Natural:* Weathering of rocks and soil *Anthropogenic:* Waste materials	*Inorganic forms:* selenide, selenate, and selenite *Organic forms:* Selenomethionine,	Kashin–Beck disease	Lemly (2002), Staicu et al. (2017), Tan et al. (2016)

(continued)

Table 15.1 (continued)

Metal	Source	Occurrence	Threats	References
	from certain mining, agricultural, petrochemical, and industrial manufacturing operations	selenocysteine, and methylselenocysteine		

ecosystems by biomagnification and successive bioaccumulation leading to severe health effects (Beyer et al. 2000). The regularly encountered POPs include hazardous industrial chemicals such as polychlorinated biphenyls (PCBs) (Dai et al. 2016) especially polychlorinated dibenzo-p-dioxins (PCDD) (Weber et al. 2008) and dibenzofurans (PCDF) (Zhang et al. 2009), organochlorine pesticides, such as DDT (Jayaraj et al. 2016), as well as unintentional by-products of the industrial, agricultural, and domestic processes (Aktar et al. 2009). Notably, the POPs after biomagnifying in various food chains (Ren et al. 2017) eventually bioaccumulate in the higher organisms that exhibit the highest concentration of these POPs (Deribe et al. 2011). However, even lower percentage of POPs progress to cancerous conditions (Ljunggren et al. 2014), reproductive disorders (Vested et al. 2014), immune system malfunctioning (Stehlik and Dorfleutner 2007), neurodegenerative disorders (Saravi and Dehpour 2016), endocrine disorders, and genotoxicity (Chen et al. 2019a, b). Several countries banned the direct/indirect utilization of POPs by substituting with biodegradable substances (Lubick 2010); however, the technologically underdeveloped nations still rely on potentially hazardous organic materials for agricultural practices and to control the diseases such as malaria (Wei et al. 2007). Moreover, the distinct eating habits in the potentially vulnerable areas also elucidate the POP toxicity in masses (Fair et al. 2018). After traveling through various ecological food chains, the POPs bioaccumulate in complex food webs by accumulating chiefly in the animal body fat (Lee et al. 2017). Their percentage increases on traveling from the various trophic levels in the ecosystem, finally leading to their biomagnification (Goerke et al. 2004). Due to this phenomenon, the population in the areas with very high ingestion of fish, shellfish, or fat-rich wild foods face persistent risk of exposure of bioaccumulated POPs that eventually result in several health disorders (Juan and Frank 2012) (Table 15.2).

15.3.1 Bioaccumulation

In addition to radically transforming the ecological concentration of several substances, the anthropogenic activities increase the concentration of hazardous substances in the environment including their bioaccumulation from suspended particles, from sediments, from water bodies and through food chains (Chojnacka 2010). The rate of bioaccumulation in an organism depends upon an array of

Table 15.2 Effect of organic pollutants on the environmental health

POPs	Hazards	Source	References
DDT	Egg shell thinning in birds, endocrine disruption, carcinogenicity	Insecticides	Longnecker et al. (1997)
HCBs	Porphyria cutanea tarda, ulceration	Fungicides, pesticides, fireworks	Reed et al. (2007)
PCBs	Neurotoxicity, malfunctioning endocrine system	Heavy electricals, paint additives	Brauner et al. (2016)
Dioxins/ furans	Wasting syndrome, immunological effects	Waste incineration, herbicides, medical waste	Bommanna (2015)
Heptachlor	Neurodegeneration, immunological disorders	Insecticide, antimalarial	Chuang and Chuang (1998)
Mirex	Estrogen-related malfunctioning in females such as ovulation, pregnancy, and endometrial growth	Fire retardants and insecticides	Zitko (2003)
Aldrin/ dieldrin	Neurotoxicity, convulsions, anemia	Termite control insecticides	Wurster (1971)
Chlordane	Non-Hodgkin lymphoma	Insecticides in agriculture	Wu et al. (2014)
Endrin	Mutagenicity, neurotransmitter blocking, meningoencephaloceles	Rodenticide	Taiwo (2019)

biochemical and environmental factors in addition to the direct accessibility of the pollutant (Ael et al. 2012). Eventually, the ability of the participating organism to alter, store, or excrete the pollutant decides its ultimate fate in the ecosystem (Coat et al. 2011). The hazardous chemical pollutants bioaccumulate in the ecosystem (Walker 1990) by fixing their concentration in the tissues of organisms, hence preventing the physical, chemical, or biochemical degradation of the pollutant by restricting its direct exposure to the environment (Zhou et al. 2008). The bioaccumulated materials directly influence an individual's health and become a part of the food chain. Principally, the bioaccumulation of toxins starts within the primary producers such as phytoplanktons that are typically present at the bottom of a food web (Bandowe et al. 2014). As the rate of absorption from the effected water is faster than the rate of their metabolism, these toxins gradually start building up in the tissues of these microscopic photosynthetic organisms (Trapp 2009). Ultimately, the biomagnified substance becomes precarious to the heterotrophs present at the higher trophic levels (Torres and Johnson 2009). Notably, the magnification of bioaccumulators in the keystone species of ecosystem potentially raises the vulnerability of many species (Peterson and Schulte 2016). Occurrence such as oil spills releases polycyclic aromatic hydrocarbons (PAHs) that cause cancer in humans that feed on fish, shellfish, and mollusks bioaccumulated with PAHs (Almeda et al. 2013). Similarly, the nondegradable heavy metals upon bioaccumulation in the host organism lead to several detrimental effects by reacting with biomolecules such as enzymes, deoxyribonucleic acid, ribonucleic acid, and cellular proteins

(Engwa et al. 2019). Organisms such as shellfish that do not possess bioaccumulation-regulating mechanisms act as indicators of heavy metal accumulation (Streit 1998). Besides, the microorganisms possess several critical mechanisms for developing metal resistance that include intracellular chelation by metallothione in proteins and glutathione-derived peptides called phytochelatins (Kneer et al. 1992; Presta and Stillman 1997). Low molecular weight proteins, metallothioneins, rich in -SH groups validate the process of bioaccumulation by restraining from participation in the metabolic reactions because of their binding in biologically inactive form. Interestingly, the nonessential metals and ions bind with the thiol-containing groups and oxygen sites much more efficiently compared to the essential metals (Hughes and Poole 1989). Notably, for the fungi growing in the presence of heavy metals, the amino acids cysteine and glutathione display a superior production and rapidly transform into phytochelatins (Mendoza-Cozatl et al. 2005).

15.3.2 Biosorption

Biosorption involves the mitigation and exclusion of hazardous substances from the ecosystem predominantly by microbial systems such as bacteria, fungi, and microalgae (Volesky and Holan 1995). A typical biosorption phenomenon also includes precipitation and bioprecipitation, bioleaching (Fang et al. 2011), and surface complexation, apart from adsorption and absorption that result in stable interactions between adsorbate and the functional groups such as -SH, -COOH, -OH, -NH_2 present on the microbial adsorbents (Veglio and Beolchini 2007). Numerous investigations on a variety of microbes, plants, and animal biomass have ensured the identification of highly efficient and cost-effective biosorbents useful for elemental sequestration, pollution mitigation, and recycling (Gavrilescu 2004). The microbial biomass widely investigated for biosorption include cyanobacteria, archaebacteria, microalgae, seaweeds, filamentous fungi, unicellular yeasts, and lichens (Mattuschka and Straube 1993). Living matter such as microbes adopt diverse mechanisms such as chelation to bind to the metal ions through coordinate bonds in addition to the other physical interactions, thereby constructing a film on the surface of biosorbent (Fuks et al. 2006). The van der Waals interactions leading to physisorption or covalent bonding resulting in chemisorption also play significant role in facilitating biosorption (Kumar et al. 2008). The microbe-metal binding if metabolism dependent may involve energy from ATP for immobilizing the metal ions to the active functional head group ligands present on the microbial cell wall (Kotrba 2011). On the contrary, the metabolism-independent biosorption predominantly occurs in dead biomass. However, the living biological mass hold larger precedence over the dead mass for biosorption of heavy metals (Kratochvil and Volesky 1998) because living cells possess a higher ability for unremitting metal uptake and self-replenishment (Velasquez and Dussan 2009). Ultimately, the metal inside the microbial cell undergoes accumulation, detoxification, or efflux depending on the nature of biosorbent (Choudhary et al. 2017). However, the saturation of active metal binding sites of the biosorbent and the reversible sorption of metals on biomass pose challenges to the biosorption process (Arora and Vanza 2017); still, biosorption is a highly advantageous process due to an economical microbial biomass production for effectively sequestering multiple heavy metals at the same time in large volumes of wastewater (Atlas 1991). The biomass provides a hazard-free alternative for mitigating heavy metal pollution by substituting the use of hazardous chemicals and providing superior results over a wide range of conditions including temperature, pH, and presence of other metal ions (Sadowsky 2000).

15.3.2.1 Bacterial Biosorption

The bacterial cell wall presents first site of encounter with the pollution causing metal ions and organic dyes, where the adsorbate settles within the three-dimensional cell wall structure (Kuppusamy and Yun 2008). The negatively charged functional head groups profusely present on the bacterial cell wall as peptidoglycans (poly-N-acetylglucosamine and N-acetylmuramic acid) (Lebeau et al. 2011) play critical role in biosorption by interacting with positively charged organic dyes via electrostatic interactions, hydrogen bonding, or forming the chelate complexes with metal ions (Ansari et al. 2011). The thick peptidoglycans coating on Gram-positive bacteria possess polyalcohols, known as teichoic acid and teichuronic acid that covalently link to the lipids to form lipoteichoic acids (Gutnick and Bach 2000). The characteristic peptidoglycan envelope provides an overall negative charge to the Gram-positive bacterial cell wall that effectively interacts with the positively charged adsorbates (Gourdon et al. 2000). Contrarily, the cell wall of Gram-negative bacteria contains meager peptidoglycan, however; it is rich in phospholipids and lipopolysaccharides, giving an overall negative charge to the cell wall (Aryal and Kyriakides 2015). Likewise, the exopolysaccharides released by certain bacteria as a part of self-defense strategy in response to extreme conditions of pH, temperature, and starvation, efficiently sequester positively charged metal ions because of their anionic buildup (Philippis et al. 2011). Besides, the extracellular polymeric substances containing a complex blend of high molecular weight microbial biopolymeric (Shuhong et al. 2014) secretory byproducts in addition to proteins, polysaccharides, uronic acids, humic substances, and lipids also play vital role in biosorption (Zhao et al. 2014).

15.3.2.2 Algal Biosorption

The algae-based biosorbents mainly include seaweeds, micro/macroalgae conferred with numerous functional groups and biomacromolecules. The algal polysaccharide components such as xylans, alginic acid (Hamdy 2000), mannans, chitosan (Schiewer and Volesky 2000), glucans (Paredes et al. 2011), chitin (Benguella and Benaissa 2002), melanins (Gadd et al. 1990), hyaluronic acid (Crusberg and Mark 2000) that form a major part of algal biomass offer functional sites for facilitating the heavy metal complexation (Garcia et al. 2008). The -OH group present in algal polysaccharides develop a negative charge only at higher pH and display secondary metal binding properties at $pH > 10$ (Andrade et al. 2010; Ashkenazy et al. 2000; Naja and Volesky 2011). Interestingly, the algal chitosan and its cross-linked derivatives also contribute for the removal of harmful organic dyes from the aqueous solutions (Yang et al. 2010). The carboxylic functionalities present on the alginate polymer (Fourest and Volesky 1997; Byramoglu and Arica 2009) represent the copiously found group in the algae biomass sequester the majority of heavy metals of interest including Cd^{2+}, Fe^{2+}, Co^{2+}, Pb^{2+}, Cu^{2+}, Ni^{2+}at a pH near the characteristic dissociation constant of carboxylic acids present on the algal biomass (pK_0 near 5). Similarly, sulfonic group of fucoidan represents another abundantly present acidic functional group that facilitate metal biosorption generally at low pH (Mata et al. 2008).

15.3.2.3 Fungal Biosorption

Various macro fungi (Chew and Ting 2015; Wales and Sagar 1990; Chen and Ting 2017) possess ability to grow in diverse environments including the polluted soils, and water bodies adsorb heavy metals in their fruiting bodies, mycelia, and sporocarps (Sargin et al. 2015; Serrano-Gomez and Olguin 2015). The cell wall of fungi display commendable metal biding properties (Gadd and Rome 1988; Luef et al. 1991; Gadd 1994) due to the components such as chitins, mannans, glucans, as well as lipids (Yan and Viraraghavan 2008), polysaccharides (Salehizadeh and Shojasadati 2003), pigments such as melanin (Fogarty and Tobin 1996). Notably, the functional groups such as carboxyl, phosphate, uranic acids, proteins, nitrogen-containing ligands, chitin, or chitosan participate in metal binding (Congeevaram et al. 2007). Interestingly, the applications of physical and chemical treatment of fungal cells by autoclaving, dimethyl sulfoxide, surfactants, orthophosphoric acid, glutaraldehyde, and formaldehyde improve their biosorption potency (Kumari and Abraham 2007) (Tables 15.3, 15.4 and 15.5).

15.4 Conclusion

Bioaccumulation and biosorption approaches serve as highly effective green alternatives for bioremediation of the environmental pollutants. However, these strategies deliver partial results with certain organic pollutants that undergo partial degradation. Similarly, the nonbiodegradable heavy metals and radionuclides are occasionally bio-transformed to potentially toxic, less mobile forms. In addition, the culturing of the biosorbent microbe requires highly specific conditions for an optimum growth that may not be compatible with the conditions present at the contamination site. Lastly, bioremediation delivers optimum results after lengthy pilot procedures, compared to the conventional incineration and landfill strategies.

Table 15.3 Recent reports on biosorption of nonessential heavy metals by bacteria (2018–2019)

Bacteria	Strain	Heavy metal ion	Biosorption capacity (mg/g) *OR* % biosorption	Functional groups involved	Optimum conditions	References
Bacillus badius	AK	Cd^{2+}	131.58	Dead bacterial biomass	40 °C, pH 7	Vishan et al. (2019)
Bacillus subtilis	MC3B-22, MC3B-10	Cd^{2+}	251.91	Extracellular polymeric substances (EPS)	28 °C, pH 7	Camacho-Chab et al. (2018)
Raoultella sp.	X13	Cd^{2+}	50.30 (live cells) and 25.13 (dead cells)	$-OH$, $-NH$, $-CH_3$, $-C{=}O$, $C{-}N$, $-SO_3$, $-PO_4{}^{3-}$, $-SO_4{}^{-2}$ functional groups	28 °C, pH 7.2	Xu et al. (2019a, b)
Shewanella putrefaciens	CICC 22940	Cd^{2+}	88.54%	$-OH$, $-CONH-$, $C{=}O$, $-PO_4{}^{3-}$ functional groups	25 °C, pH 6	Yuan et al. (2019)
Pediococcus pentosaceus	FB145, FB181	Cd^{2+}	50.35–52.65	$-C{=}O$, $-CH$, and $-OCH_3$ groups	37 °C, pH 7.2	Le and Yang (2019)
Lactobacillus casei and *Lactobacillus acidophilus*	BL23, ATCC4356	Hg^{2+} CH_3Hg	42–94%	Internalization in the bacteria	30–37 °C, pH 7.2	Jadan-Piedra and Crespo (2019)
Rhodovulum sulfidophilum and *Afifella marina*	SRW1–5, SSS2–1, SSW15–1	Hg^{2+}	50.30 (live cells) and 25.13 (dead cells)	EPS containing $-OH$, $-C{=}O$, $-C_6H_5$, $-PO_4{}^{3-}$, $-OH$, $-SO_3H$, $-PO_4{}^{3-}$	25–35 °C, pH 7	Mukkata et al. (2019)
Pseudarthrobacter oxydans, *Pseudomonas frederiksbergensis*	MM20, SS18	Hg^{2+}	25% and 90%	Olefinic, $-OH$, $-NO_2$, $-COOH$, and $-CONH_2$ functional groups	15 °C, pH 8.3	Balan et al. (2018)
Bacillus thuringiensis	MC28	Hg^{2+}	99.94–99.98%	Extracellular polymeric substances (EPS)	35 °C, pH 8	Asare et al. (2018)
Bacillus sp.	DC-B2	Hg^{2+}	91.6%	Enzymatic reduction	25 °C, pH 7	Chen et al. (2019a, b)

(continued)

Table 15.3 (continued)

Bacteria	Strain	Heavy metal ion	Biosorption capacity (mg/g) *OR* % biosorption	Functional groups involved	Optimum conditions	References
Staphylococcus hominis	AMB-2	Pb^{2+}	66%	Exopolysaccharides	25 °C, pH 7.5	Rahman et al. (2019)
Bacillus licheniformis	BRE07	Pb^{2+}	113.84	–OH groups	30 °C, pH 6	Wen et al. (2018)
Arthrobacter sp.	GQ-9	Pb^{2+}	56.60	Cell wall exopolysaccharides	28 °C, pH 5.5	Wang et al. (2018a, b)
Paenibacillus peoriae	TS-7	Pb^{2+}	277.54	Exopolysaccharides	32 °C, pH 6.8	Fella-Temzi et al. (2018)
Lysinibacillus fusiformis	KMNTT-10	Pb^{2+}	79.4–96%	Dead bacterial biomass	27 °C, pH 6	Mathivanan et al. (2018)
Exiguobacterium profundum and *Ochrobactrum ciceri*	PT2 and SW1	As^{5+}	Not specified	Extracellular polymeric substances (EPS)	37 °C, pH 7	Saba et al. (2019)
Acidithiobacillus ferrooxidans	DLC-5	As^{3+}	Not specified	–OH and –NH groups	Not specified	Xu et al. (2019a, b)
Bacillus arsenicus	MTCC 4380	As^{3+} and As^{5+}	88.99	–OH, –CO and –CONH groups	Not specified	Podder and Majumder (2018)
Rhodococcus sp.	NA	As^{3+}	48.34	Extracellular polymeric substances (EPS)	28 °C, pH 7.2	Kumari et al. (2019)
Bacillus thuringiensis strain	WS3	As^{3+}	90%	Dead bacterial biomass	37 °C, pH 7	Altowayti et al. (2019)
Halomonas sp.	DK4	Cr^{6+}	81%	–OH, –COOH, $–PO_4^{3-}$, $–CONH_2$	32 °C, pH 7.4	Kalola and Desai (2019)
Sinorhizobium sp.	SAR1	Cr^{6+} to Cr^{3+}	285.71	Extracellular polymeric substances (EPS)	Not specified	Jobby et al. (2019)

Kocuria sp.	ASB107	Cr^{6+}	82.4	Dead bacterial biomass	32 °C, pH 4–4.5	Nesheli et al. (2018)
Synechocystis sp.	PCC7806	Cr^{3+}	75.4	Tryptophan-like substances, amino acid substances, and fulvic acid-like substances	Not specified	Li et al. (2019)
Staphylococcus sciuri	A-HS1	Cr^{6+}	86–93%	$–NH_2$, –COOH, $–SO_3H^-$, –OH	40 °C, pH 8	Elahi and Rehman (2018)
Microbacterium testaceum	B-HS2	Cr^{6+}	96%	$–NH_2$, –COOH, $–SO_3H^-$, –OH	37 °C, pH 7	Elahi et al. (2019)

Table 15.4 Biosorption of nonessential heavy metals by algae (2018–2019)

Algae type	Species	Heavy metal ion	Biosorption capacity (mg/g) OR % biosorption	Functional groups involved	Optimum conditions	References
Microalgae	*Chlorella vulgaris*	Cd^{2+}	97.43	Not specified	28 °C, pH 6	Kumar et al. (2018)
Macroalgae	*Nannochloropsis oculata*	Cd^{2+}	232.55	–OH, COO–, –CH and $–PO_4{}^{3-}$ groups	20–50 °C, pH (2–5)	Kaparapu and Prasad (2018)
Microalgae	*Cladophora rupestris*	Cd^{2+}	56%	Negatively charged algae cell wall	25 °C, pH 7	Zhang et al. (2019)
Microalgae	*Parachlorella* sp.	Cd^{2+}	96.20	–OH and –NH groups	35 °C, pH 7	Dirbaz and Roosta (2018)
Microalgae	*Spirulina platensis*	Cd^{2+}	82.3	Amino groups	25 °C, pH 8	Shao and Ebaid (2018)
Microalgae	*Scenedesmus obtusus*	Hg^{2+}	95	Phosphoryl functional group	28 °C, pH (4–7)	Huang et al. (2019)
Macroalgae	*Cladophora* sp.	Hg^{2+}	172.5	–OH, –NH, Si–O–, and –C=O– functional groups	16 °C, pH 5	Mokone et al. (2018)
Macroalgae	*Fucus spiralis*	Pb^{2+}	132	Polyphenols, fucoidan, and alginate	20 °C, pH 4.5	Filote and Volf (2019)
Microalgae	*Acutodesmus obliquus*	Pb^{2+}	Not specified	Auxins and cytokinins	Not specified	Piotrowska-Niczyporuk et al. (2018)
Macroalgae	*Sargassum Tenerrimum*	Pb^{2+}	6.65	Dead algae powder	28 °C, pH 5.2	Bai and Venkateshwarlu (2018)
Macroalgae	*Gelidium amansii*	Pb^{2+}	100%	Dead algae biomass	45 °C, pH 4.5	El-Naggar and Hamouda (2018)
Microalgae	*Chlorophyceae*, *Cyanophyceae*, and *Bacillariophyceae*	Pb^{2+}	Not specified	Dead algae biomass	pH 7.2	Abdelkareem et al. (2019)

Macroalgae	*Chara braunii*	As^{5+}	55.8	Calcified algae biomass	20 °C, pH 5	Amirnia et al. (2019)
Microalgae	*Microcystis aeruginosa*	As^{5+}	22.7	Dead algae biomass	pH 10	Wang et al. (2018a, b)
Macroalgae	*Sargassum glaucescens*	As^{3+} and As^{5+}	116.6 and 207.3	Dead algae biomass	pH 5.9	Tabaraki and Heidarizadi (2018)
Microalgae	*Chlorella coloniales*	As^{3+}	96.5	Dead algae biomass	pH 6	Jaafari and Yaghmaeian (2019)
Macroalgae	*Turbinaria vulgaris*	As^{3+}	92.12%	Dead algae biomass	20–40 °C, pH 3–5	Boddu et al. (2019)
Microalgae	*Scenedesmus* sp.	Cr^{6+}	92.89	Waste algae biomass	30 °C, pH 1	Pradhan et al. (2019)
Microalgae	*Pseudopediastrum boryanum*	Cr^{3+}	70%	Dead algae biomass	22 °C, pH 7	Sutkowy and Klosowski (2018)
Macroalgae	*Cladophora glomerata*	Cr^{3+}	107.5	Dead algae biomass	38 °C, pH 3–5	Godlewska et al. (2018)
Microalgae	*Spirulina platensis*	Cr^{6+}	81.2	Waste algae biomass	60 °C, pH 1	Nithya et al. (2019)
Macroalgae	*Cladophora* sp.	Cr^{6+}	142.85	Dead algae biomass	20–40 °C, pH 2	Rangabhashiyam and Balasubramanian (2018)

Table 15.5 Biosorption of nonessential heavy metals by fungi (2018–2019)

Fungi	Strain	Heavy metal ion	Biosorption capacity (mg/g) *OR* % biosorption	Functional groups involved	Optimum conditions	References
Neopestalotiopsis clavispora	ASU1	Cd^{2+}	185.3	Extracellular polymeric substances (EPS)	32 °C, pH 7.5	Hassan et al. (2018)
Fusarium solani	Not specified	Cd^{2+}	92.4%	Dried fungal biomass	28 °C, pH 6	Kumar et al. (2019)
Phanerochaete chrysosporium	Wild type	Cd^{2+}	71.43	Dried fungal biomass	20–40 °C, pH 4–8	Noormohamadi et al. (2019)
Pleurotus ostreatus	Not specified	Cd^{2+}	85%	Dried and dead fungal biomass	pH 5	Kocaoba and Arisoy (2018)
Saccharomyces cerevisiae	Wild type	Hg^{2+}	88.9%	Fungal biomass	25–35 °C, pH 4–6	Hadiani et al. (2018)
Flammulina velutipes, Auricularia polytricha, Pleurotus eryngii, and *Pleurotus ostreatus*	Wild type	Hg^{2+}	69.35	Fungal spores	35 °C, pH 6	Li et al. (2018)
Aspergillus niger	Wild type	Hg^{2+}	27.2	Fungal spores	30 °C, pH 4–6	Cui et al. (2018)
Pleurotus eryngii	Not specified	Pb^{2+}	92.22	Fungal biomass	pH 7	Amin et al. (2018)
Aspergillus penicillioides	F12	Pb^{2+}, Cd^{2+}	90%	$–NH_2$, COO–, –SH, –PO_4^{3-} and –OH	30 °C, pH 8	Paria et al. (2018)
Aspergillus niger	PTN31	Pb^{2+}	66.8	Extracellular Polymeric Substances (EPS)	30 °C, pH 5	Dang et al. (2018)
Simplicillium chinense	QD10	Pb^{2+}, Cd^{2+}	57.8 and 88.5	Rhizosphere-fungi interaction	Not specified	Jin and Deng (2019)

Aspergillus oryzae	TLWK-09	As^{5+}	54.12	Fungal mycelia	28 °C, pH 7	Liang et al. (2019)
Penicillium chrysogenum	F1	As^{3+}	81.23%	Fungal-ferrihydrite composite	35 °C, pH 6	Peng et al. (2018)
Laccaria bicolor	Wild type	As^{3+}, Cd^{2+}	40%	Enzymatic	pH 4	Khullar and Reddy (2018)
Trichoderma sp.	MG	As^{3+}, Pb^{2+}	68% and 59%	Carbonates	pH 9	Govarthanan et al. (2019)
Saccharomyces cerevisiae	Not specified	Cr^{6+}	99.66%	Extracellular polymeric substances (EPS)	pH 6.5	Rossi et al. (2018)
Aspergillus flavus	Wild type	Cr^{3+}	81%	Fungal biomass	pH 4.5	Ghosh et al. (2018)
Aspergillus niger	Mutant	Cr^{6+}	97.1%	Fungal spores	40 °C, pH 2	Ren et al. (2018)
Aspergillus niger, Aspergillus fumigatus, and Penicillium rubens	M1DGR, M3Ai, M2Aii	Cr^{3+}	79%	Fungal biomass	30 °C, pH 5.5–6.2	Khan et al. (2019)

Nevertheless, a comprehensive environmental bioremediation program guarantees superior results compared to the contemporary remediation approaches.

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