# Mycoremediation of Heavy Metals and/or Metalloids in Soil

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### Abstract

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

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

### Keywords

Soil pollution · Heavy metals · Filamentous fungi · Mycoremediation

## 8.1 Introduction

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

macronutrients, plants also need certain micronutrients in order to develop and complete their life cycle.

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

It has been a regular practice in many regions of the world for more than 400 years to apply municipal, industrial, and related effluents to land (Reed et al. 1995). As per the estimation, it was found that wastewater irrigates 20 million hectares of arable land globally. In practice, farmers are more focused on growing their yields and profits than on the benefits or threats associated with the environment. Even while wastewater effluents typically have low metal concentrations, they may eventually cause a significant metal accumulation in the soil if used to irrigate land over an extended period. The legacy of widespread distribution of metal pollutants in soil has been left to many nations by the mining and processing of metal ores in conjunction with industries. When dumped directly into natural depressions such as on-site wetlands, heavy and larger particles known as tailings that get deposited at the bottom of the flotation cell during mining can accumulate in high quantities (DeVolder et al. 2003). The extensive smelting and mining of zinc and lead ore have been contaminating the land and threatening human and ecological health. Most of the lengthy, expensive restoration techniques employed for these sites may not restore soil productivity. The environmental risk that heavy metals in soil pose to people is correlated with bioavailability. Another significant source of
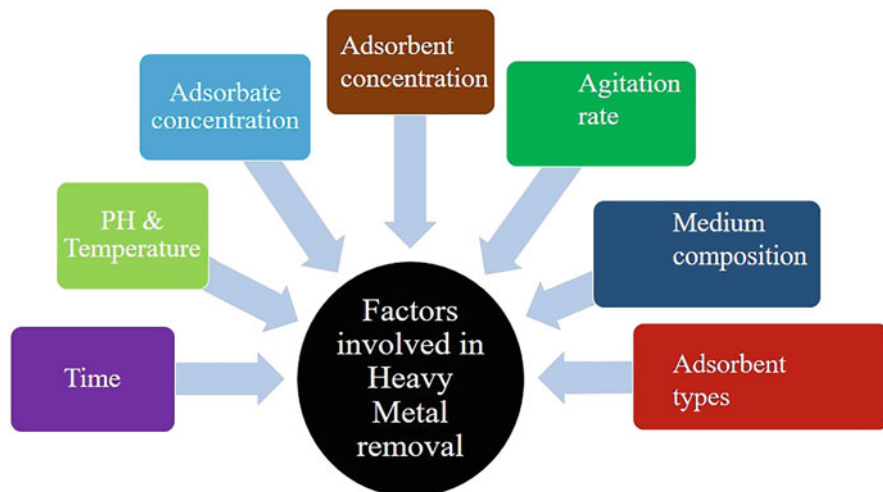
**Fig. 8.1** Factors involved in heavy metal/metalloid removal

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

## 8.2    Heavy Metals/Metalloids in Soil

All metals and metalloids having a density of more than $5 \text{ g cm}^3$ have been collectively referred to as "heavy metals" (Wuana and Okieimen 2011; Pendias and Pendias 2001). Generally, common transitional metals like zinc (Zn), copper (Cu), lead (Pb), cadmium (Cd), and mercury (Hg) are referred to as "heavy metals" in this context, whereas "metalloids" refer to a class of chemical elements that exhibit properties that fall somewhere between those of metals and nonmetals and naturally occur as poly-hydroxylated species. This category often includes the chemical elements arsenic (As), boron (B), silicon (Si), antimony (Sb), germanium (Ge), and tellurium (Te), as well as less frequent elements like astatine (At) and polonium (Po). These heavy metals and metalloids in the soil or water may substantially impact human and ecological health (Chan et al. 2016). Any metallic chemical element that has a high density and has the potential to be poisonous even at low

doses is referred to as a heavy (or trace) metal. Although heavy metals are easily absorbed and bioaccumulated in different plant sections, they are neither essential nor play a crucial function in cells' metabolic pathways (Nas and Ali 2018). Cobalt (Co), nickel (Ni), copper (Cu), vanadium (V), zinc (Zn), and chromium (Cr) are heavy elements that, at low concentrations, are not poisonous (Nas and Ali 2018).

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

Heavy metal and metalloid soil pollution is a problem that affects every nation on the planet. Since heavy metal contamination cannot biodegrade and builds up in the soil, hurting people, animals, and the ecosystem for a very long time, it has drawn more attention recently. Exposure to heavy metals and metalloids is linked to various health issues, including kidney problems, developmental and neurobehavioral difficulties, bone problems, blood pressure issues, and tumor growth. These issues become pertinent when there are appreciable concentrations of heavy metals in the soil. An estimated five million locations worldwide have soil that is polluted with heavy metals and metalloids. The primary source of this pollution is frequent anthropogenic activities. Developed nations like the USA, China, Australia, and EU members tend to have more heavy metal-contaminated areas than developing nations (Brito et al. 2020; Yu et al. 2020). The average global amounts of these pollutants in soil vary depending on the kind of soil, the environment around it, and

the distance from the source of contamination. Heavy metal/metalloid species continue to get attention worldwide due to the persistent nature of such damaging pollutants, which include static, durable, accumulative, and nonbiodegradable properties (Zhao et al. 2019). The soil near metal smelters has been contaminated by the heavy metal/metalloid species that metal smelting activities have discharged into the environment. The buildup of heavy metal/metalloid species poses a danger to the ecological environment, variety, functioning of soil microorganisms, food security, and human health. Soil microorganisms have a key role in defining the quality of the soil since they are the guardians of the ecosystem's structure and functioning (Hou et al. 2019). Although soil microorganisms can influence soil properties, the physicochemical properties of the soils can also have a large influence on them. According to research, microorganisms greatly enhance soil fertility, crop health, and nutrient circulation in the soil. It is commonly acknowledged that the toxic stress brought on by heavy metals and metalloids may significantly influence the number, variety, and ecological functions of the soil's microbial communities. For instance, heavy metal/metalloid pollutants have an impact on the ecological processes in soils that functional groups and a variety of functional genes sparked. As a result, the variety of microorganisms has diminished and the structure of soil microbial communities has changed even more. Numerous heavy metal/metalloid-tolerant bacteria may transform or eliminate heavy metals from polluted soil (Qiao et al. 2019). Bioremediation has been recognized as a promising green and sustainable method for cleaning up heavy metal pollution. Bioremediation has been recognized as a promising green and sustainable method for cleaning up heavy metal pollution. Furthermore, alterations in the chemical forms of heavy metal/metalloid species brought on by the physicochemical characteristics of soil may have a secondary effect on the makeup of microbial communities (Hu et al. 2021). Approximately 51 elements in the periodic table are considered heavy metals or metalloids. Because of their chemical properties and those of the soil, they are mobile and bioavailable in the soil. The interaction of soil components with metals and metalloids is influenced by the pH, the characteristics of the adsorbent surface, and the presence of cations and anions. Zinc (Zn), chromium (Cr), nickel (Ni), manganese (Mn), cadmium (Cd), lead (Pb), copper (Cu), and arsenic (As) are the most prevalent heavy metals and metalloids. The most hazardous substances are those with Cr, Cu, Zn, Cd, Pb, Hg, and As in them. As the underlying bedrock weathers, they are frequently discovered as ores (sulfides of Pb, Co, Fe, As, Pb, Zn, Ag, and Ni, and oxides of Se, Al, Mn, and Sb). Along with sulfides of arsenic, mercury, lead, and cadmium, chalcopyrite, $CuFeS_2$, and pyrite, $FeS_2$, are naturally occurring sulfides of copper and iron in the soil. In particular, ore mining and refining, using pesticides and fertilizers, and solid wastes all contribute to the environmental problem by raising the levels of heavy metals and metalloids. Heavy metals and metalloids are used in many industries, increasing market demand, and worldwide output. Many biological processes, including the nervous system, production of complex molecules, respiration systems, and control and functioning of enzymes, require trace amounts of copper, selenium, zinc, iron, vanadium, and manganese. Electronic gadgets, especially semiconductors, are made largely from

metals, including iron, zinc, tin, lead, copper, and tungsten (Koller and Saleh 2018). It is clear that certain elements, particularly chromium, copper, zinc, and lead, are employed in many industries and that there is a significant annual output worldwide, wherein the United States, China, Australia, Russia, Peru, and Mexico are the major producing nations (Raffa et al. 2021). Microbial bioremediation lowers the expense of the heavy metal pollution treatment process while also being effective, economical, and ecologically benign (Mishra 2017). The primary mechanisms for microbial removal of heavy metals are biosorption, which includes ion exchange, redox reactions, adsorption of chemicals, precipitation, and formation of a complex with organic ligands; secondly, biomineralization which includes bioleaching, which involves releasing heavy metal ions from insoluble ores through dissolution or complexation; and thirdly, bio-oxidation (González Henao and Ghneim-Herrera 2021).
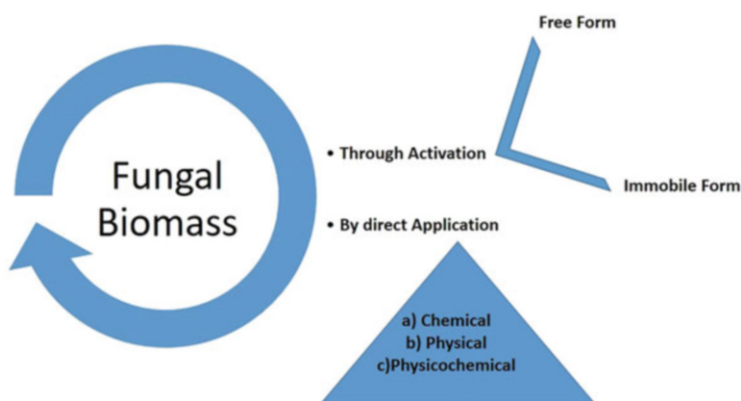
## 8.3  Mycoremediation of Soil

### 8.3.1  Important Fungal Species Involved in Bioremediation

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

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

**Table 8.1** Fungi used to remove metals and contaminants

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



**Fig. 8.2** Mycoremediation of heavy metals

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

Trichoderma fungi are well adapted to aid in eliminating lead from the environment. Hence, *Trichoderma asperellum* may be used in mycoremediation and may play a supporting function in soil phytoremediation (Bandurska et al. 2021). The study of the interaction between the cell surface of fungi and heavy metals is

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

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

### 8.3.2   Toxic Compounds Degraded by Fungi

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

Thiol is a substance utilized to signal cells and is thought crucial. Thiol synthesis has increased in the plant species *Aspergillus flavus*. Gamma-glutathione makes up one of the two tails of glutathione, and the other tail belongs to the thiol group. Here,

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

Through various enzymatic processes, fungi may change hazardous metals and metalloids into less toxic forms, changing the concentrations of heavy metals in the environment. Using mercuric reductase, fungi may detoxify organomercury compounds, and the resulting mercury, Hg(II), can then be further reduced to the more combustible elemental mercury, Hg(0). Similarly, it happens in the conversion of As(V) to As(III) by arsenate reductases, which are a few common detoxification processes that may be involved once As(V) enters the fungal cells via the phosphate transporters (Gonzalez-Chavez et al. 2011). It is shown that three contiguous genes control *Saccharomyces cerevisiae*'s resistance to arsenic, a transcriptional regulator (ACR1), an enzyme arsenate reductase (ACR2), and a plasma membrane arsenite efflux pump (ACR3). The methylation of inorganic arsenic to create volatile derivatives is another mechanism by which fungi are resistant to metals and metalloids. Metals and metalloids can be methylated by an enzymatic process in which the metal is transferred to the methyl group. The methylated metal compounds commonly differ from their parent compounds in terms of toxicity, solubility, and volatility. Metals that can be methylated include Pb, Hg, and Sn and metalloids like Se, As, and Te. Monomethylarsonic acid and dimethylarsenic acid can be converted to volatile trimethylarsine oxide by *Candida humicola*, *Gliocladium roseum*, and *Penicillium* sp. (Cullen and Reimer 1989). The heat-resistant *Neosartorya fischeri* was found to effectively volatilize (up to 23% of total As) (Hartmann et al. 2003). Reactive oxygen species (ROS) produced by heavy metals like copper, iron, chromium, cadmium, lead, and mercury can lead to oxidative stress, affect calcium homeostasis, and cause damage to DNA (Klaunig et al. 1998). ROS generation has the potential to make fungi poisonous and harm a variety of vital macromolecules, including lipids, proteins, and nucleic acids. Metal/metalloid tolerance in fungi has been linked to their capacity to remove ROS (Fujs et al. 2005). Due to their high thiolate sulfur content, small proteins (between 2 and 7 kDa), such as metallothioneins, can bind metal ions for storage and detoxification in both

eukaryotes and prokaryotes. In addition to glutathione (GSH), glutathione disulfide or oxidized glutathione (GSSG), non-protein sulfhydryl groups (NP-SH), and protein-bound sulfhydryl groups (PB-SH), it has been shown that cysteine-rich peptides, such as phytochelatins, and other thiol substances can bind metal ions and scavenge ROS. Additionally, the response of fungi to metal/metalloid exposure or their detoxification is significantly influenced by antioxidant enzymes. Numerous antioxidant enzymes have been found in fungi, and they may neutralize ROS and its byproducts or repair the harm they cause. The ability to shield cells against metal/metalloid-induced stress has been demonstrated for superoxide dismutase (SOD), glutathione peroxidase (POD), glutathione reductase (GR), glutathione S-transferases (GSTs), and catalase (CAT) (Shen et al. 2015). Jiang et al. (2015) demonstrated that the synthesis of NP-SH, GSH, PB-SH, and GSSG, as well as the induction of antioxidant enzymes, greatly altered *Oudemansiella radicata*'s responses to Cu exposure or Cu detoxification.

### 8.3.3   Enzyme Involved in the Biodegradation of Toxic Compounds

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

**Hydrolases (EC3)**: Hydrolase enzymes such as nitrilases, aminohydrolases, and organophosphorus hydrolases are among the most helpful in the bioremediation of numerous chemicals, including pesticides and herbicides and nitrile, polymers, and organophosphorus compounds. Some other hydrolase enzymes include lipases and cutinases (Ufarté et al. 2015). **Nitrilases (EC 3.5.5.1)** can hydrolyze the triple bonds present between the carbon and nitrogen (known as the nitrile group) in polymers, herbicides, and plastics in a stereo-, regio-, or chemoselective manner, resulting in the production of carboxylic acid and ammonia. Many species, such as *Streptomyces* sp., *Fusarium solani, Rhodococcus rhodochrous, Aspergillus niger*, and others, can express these enzymes (Martinkova et al. 2017). **Organophosphorus hydrolases (EC 3.1.8.2)** are organophosphate chemicals that were produced and utilized not just

as pesticides but also in warfare and the pharmaceutical industry. The enzyme known as organophosphorus hydrolase, which also goes by the name phosphotriesterase, is one of the enzymes that may be used for the bioremediation of organophosphorus chemicals. *Aspergillus niger* and *Penicillium lilacinum* are two examples of well-known fungus species that are responsible for the synthesis of this enzyme (Martinkova et al. 2017). **Ligninolytic peroxidases**: White-rot fungus (WRF) and other groups of fungi generate enzymes that break down lignin, and these enzymes have a wide range of uses in bioremediation. Because of the strong nonspecificity and high non-stereoselectivity of these enzymes, they are able to digest a wide variety of molecules that are resistant to degradation. These four varieties include things like laccase (LAC), lignin peroxidase (LiP), manganese peroxidase (MnP), and versatile peroxidase (VP) (Kaur et al. 2016).

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

well as to the detoxification of these substances (Raab et al. 2004). Antioxidant enzymes have been isolated thanks to the work done by fungi. These antioxidant enzymes have the potential to either get rid of reactive oxygen species (ROS) and their derivatives or repair the harm caused by these substances. It has been shown that the enzymes superoxide dismutase (SOD), catalase (CAT), glutathione peroxidase (POD), glutathione reductase (GR), and glutathione *S*-transferases (GSTs) are all capable of protecting cells from the damage that is caused by metals and metalloids (Shen et al. 2015). Jiang et al. (2015) discovered in their research that the production of NP-SH, PB-SH, GSH, and GSSG, as well as the activation of antioxidant enzymes (including SOD, POD, CAT, and GR), played a significant role in *Oudemansiella radicata*'s reactions to copper toxicity or copper detoxification. These enzymes were found to be involved in the production of NP-SH, PB-SH, GSH, and GS.

## 8.3.4 Bioaugmentation and Biostimulation

### 8.3.4.1 Bioaugmentation

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

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

**Selection of Microbes**
Bioaugmenting microorganisms played different roles in polluted site augmentation in the literature. Soil augmentation uses several microbial strains or consortia. Soil contaminants influence soil quality and soil microbial populations, which perform many vital tasks. Selecting the right microbial strains or consortiums is crucial for successful soil augmentation. Fast growth, easy culturing, high pollutant concentration resistance, and tolerance of a wide variety of environmental conditions are just a

few characteristics of microorganisms that must be considered when choosing a strain or microbial consortia. Soil contamination can also be remedied by harvesting beneficial microorganisms from other polluted areas that have been exposed to the same or comparable chemicals and then reintroducing them to the target area (Adams et al. 2020).

### 8.3.4.2 Biostimulation

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

### Mechanism of Stimulation

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

### Factors Affecting Stimulation

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

Biostimulation has the potential to remediate several contaminants, including polyester polyurethanes, sulfate, and petroleum hydrocarbons. Sulfate contamination of groundwater is harmful to ecosystems and human health. They are being

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

### 8.3.5   Agricultural Effluents and Their Mycoremediation

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

## 8.4   Factors Affecting Mycoremediation

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

**Table 8.2** List of some fungi used for the mycoremediation process

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

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

(continued)

**Table 8.2** (continued)

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

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

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

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

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

In developing fungus, heavy metal concentration initially increases the clearance rate, but it declines after reaching its optimal concentration. The first phenomena

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

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

## 8.5    Recent Advancements in Mycoremediation

Humans contaminate the environment by introducing heavy metals, radionuclides, hydrocarbons, and pollutants. The urban and industrial expansion has polluted surface and groundwater, harming persons and the ecosystem (Kour et al. 2021). Thus, the need for environmental ethics pollution-reduction methods is growing. Pesticides and herbicides protect crops from pests and weeds, enhancing productivity and yield. Agriculture has increased pesticide use. These poison ecosystems and are intransigent. Pesticides cause cancer, mutagenesis, immunosuppression, hormone imbalance, and other health problems (Gupta 2004). To use and abuse pesticides as a means of generating power, microorganisms have evolved various enzymes, activation mechanisms, and metabolic pathways (Goel et al. 2008; Kumar et al. 2021). Many different pollutants can be degraded by fungus via two different processes called mycodegradation and mycodeterioration. "Mycoremediation" describes the process of using fungus in nature to break down pollutants and garbage. Fungal species, including *Phanerochaete velutina, Coriolus versicolor,*
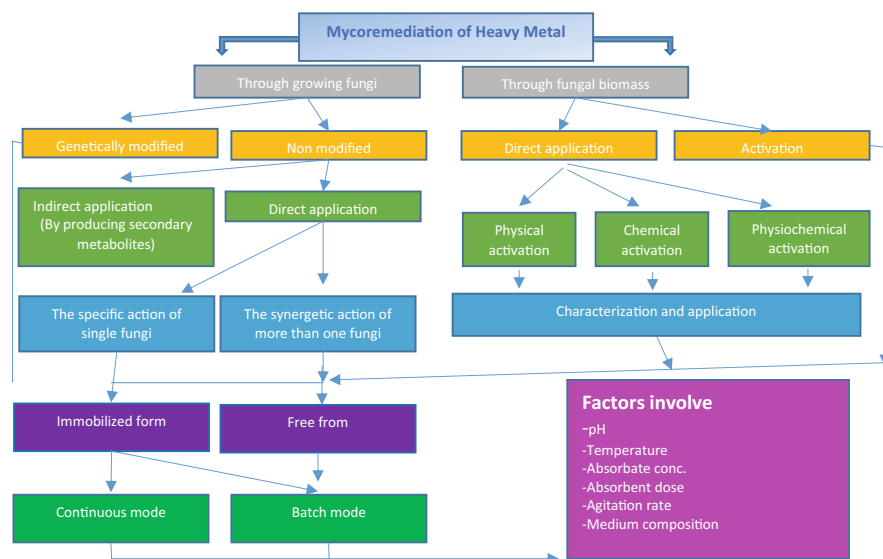
**Fig. 8.3** The overall process of mycoremediation of heavy metal

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

groundbreaking research, Wunch et al. (1999) documented for the first time the fungi's ability to degrade anthropogenic chemicals.

## 8.6 Conclusion and Future Prospectus

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

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

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

**Conflicts of Interest**   There are no conflicts of interest to be declared.

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