

MICROBIAL BIOREMEDIATION OF METALLOID-CONTAMINATED ENVIRONMENTS: A SHORT REVIEW ON REMOVAL BY MICROORGANISMS

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Abstract

The permanence, bioavailability, and toxicity of metal ions make heavy metal contamination a serious environmental problem. Even though chemical and physical remediation methods have been around for a while, they frequently have drawbacks. The application of living organisms for environmental cleanup, or bioremediation, has drawn more attention. Microorganism-based biotechnological methods have previously demonstrated notable progress and are still being developed; different microbial strains can efficiently eliminate heavy metals. The main traits of heavy metals and how they interact with microbes are examined in this research. It describes the fundamentals and varieties of bioremediation techniques, including successful pilot-scale bioreactor investigations, and highlights the mechanisms underlying microbial resistance. Due to their innate resistance mechanisms and natural adaptation to pollution, special attention is paid to native bacteria that have been isolated from contamination. Additional benefits of using bacterial biofilms or consortia include increased resilience and the capacity to utilize several metabolic pathways, which allows for the remediation of multiple heavy metals at once. It also explores how emerging technologies like metagenomics, genetic engineering, and nanotechnology hold promise for enhancing bioremediation

procedures. To sum up, bioremediation is a very viable and sustainable way to deal with heavy metal pollution and improve the health of the ecosystem.

Keywords: *Bioremediation, contaminated, heavymetal, microorganisms.*

Introduction

Industrialization has significantly contributed to environmental pollution, introducing various hazardous waste systems. Microorganisms show an important role in determining the fate of these contaminants by influencing their characteristics, transformation, distribution, transportation, and mineralization. They show efficacy in cleaning up a variety of environmental pollutions, like heavy metals (HMs) and organic chemicals. While organic pollutants can be easily broken down and removed from the environment through microbial metabolism, because they are not biodegradable, heavy metals continue to exist. Rather, microbial activity can change heavy metals into forms that are more mobile, bioavailable, or less poisonous. Furthermore, metals can be more easily removed from contaminated settings because microorganisms can adsorb and concentrate them within their cells. This makes the microorganism a critical tool in addressing pollution and offers significant practical applications. 22 heavy metals have some biological significance out of 53 heavy metals present. Because of their poor solubility, elements such as cerium (Ce), tin (Sn), zirconium (Zr), thorium (Th), and gallium (Ga) have little biological impact (Fashola MO et al., 2016). Biochemical, physiological, and metabolic activities depend on trace metals like molybdenum (Mo), manganese (Mn), and iron (Fe) functioning as enzyme cofactors, micronutrients, and osmotic regulators. Even though they are hazardous, metals like vanadium (V), nickel (Ni), copper (Cu), chromium (Cr), cobalt (Co), wolfram (W), and zinc (Zn) are nonetheless important trace elements. Others, like mercury (Hg), uranium (U), lead (Pb), arsenic (As), cadmium (Cd), silver (Ag), cadmium (Cd), and antimony (Sb), are mostly hazardous and offer little advantages. Lead (Pb), As, Cd, Cr, Cu, mercury (Hg), and Zn are common pollutants in contaminated areas (Isakovski MK

et al., 2020). Because of pedogenetic weathering processes, heavy metals are present as insoluble forms at trace levels in the environment naturally. But because of the disruptions caused by human activity to these natural geochemical cycles, metal buildup has accelerated to levels higher than background values. Heavy metal-containing wastes are released directly into the environment by industrial processes such as mining, surface finishing, energy production, metallurgy, and electroplating. Additionally, trace levels of hazardous metals like Cd and Pb are frequently present in soils along with metals like Mn, Cu, Co, Fe, Ni, Zn, and Mo that are introduced by fertilizers. Animal wastes used as fertilizers in agriculture frequently include elevated levels of Zn and Cu from growth promoters in pig and poultry farming, and historically, pesticides containing Cu, Hg, Mn, Pb, or Zn were commonly utilized (Volarić A et al. 2018). This chapter aims to discuss heavy metals present in various forms in the environment. Further describe the general as well as microbial mechanism used to remove the heavy metal-polluted water.

Heavy metals present in the environment

Although heavy metals (HMs) naturally arise in the environment and are essential for various biological processes, their accumulation in living organisms can be harmful. Common environmental contaminants include As, Cd, Hg, Ni, Cr, Pb, and Cu (Harischandra et al., 2019). Cd enters the atmosphere through both human and natural activities, with exposure occurring via contaminated food, air, or water. It accumulates in soils and sediments due to industrial waste, absorption, and surface runoff but provides no benefits to plant growth or metabolism while posing severe health risks (Hayat et al., 2018).

Mercury is one of the most toxic HMs present in the biosphere, with its levels rising due to human activities. When it interacts with aquatic sediments, it forms methylmercury, a highly toxic compound that contaminates the food chain through fish and seafood, leading to neurological disorders in humans upon ingestion (Gworek et al., 2020). Similarly, lead, though naturally occurring in trace amounts, is increasingly released into the environment due to mining, manufacturing, and

fossil fuel combustion. Excessive lead exposure, particularly in children, causes severe health complications when ingested through lead-contaminated dust or other sources (Loh et al., 2016).

Manganese (Mn), which exists in multiple oxidation states, is abundant in nature. The combustion of gasoline additives such as methylcyclopentadienyl manganese tricarbonyl (MMT) results in the emission of manganese oxides. While Mn is crucial for physiological functions, excessive exposure leads to toxicity (O'Neal and Zheng, 2015). Cr is primarily found in the environment as Cr (III) and Cr (VI), with the latter being highly toxic.

Industrial activities can convert Cr (VI) to the less harmful Cr (III). Cr industrial use contributes significantly to environmental contamination, with ferrochrome industries being a major source (Coetzee et al., 2020). Co is widely distributed in nature, found in plants, soil, rocks, and water, and used in alloys. However, tiny amounts of Co are generally harmless. Excessive exposure can be deadly and extremely poisonous. Ni is a naturally abundant element; both natural and man-made sources release it into the atmosphere. Prolonged nickel exposure can result in allergies, respiratory issues, and diseases like lung cancer and cardiovascular problems (Genchi et al., 2020; Lu et al., 2005). Cu is a vital micronutrient that plays a key role in essential plant functions like chlorophyll production, protein metabolism, and photosynthesis. However, Cu deficiency disrupts metabolic functions, excessive exposure leads to toxicity.

Zinc is an essential metal that is needed as a cofactor in many enzyme activities. Depending on exposure amounts and techniques, its toxicity varies. Mining and smelting are primary sources of zinc emissions, negatively impacting ecosystems and living organisms. A poisonous substance called antimony is released into the atmosphere by both man-made and natural activities, such as volcanic eruptions. Workers in industrial areas face antimony exposure, leading to respiratory issues, cardiotoxicity, and even carcinogenic effects. Thorium is discharged into the environment through natural water systems and industrial processes. Because it is

more poisonous than the majority of heavy metals, exposure to it can cause serious health issues (Figure1).



Figure1: Diagrammatic description of environmental heavy metals.

Microbial mechanism for removal of HM polluted water

Microorganisms use numerous tactics to remediate HM-contaminated soils and play an important role in metal oxidation, as demonstrated by *Thiobacillus ferrooxidans*, which promotes the oxidation of metal sulfides, resulting in the release of heavy metals. Through sulfur oxidation, microbes facilitate the conversion of sulfide ores into metal ions via biological leaching. Additionally, some microbes contribute to metal reduction, thereby lowering their toxicity. For example, the removal efficiency of HM-nFeS for Cr(VI) was 12–20% lower than that of DM-nFeS due to variations in their reduction capabilities. The following section delves deeper into the specific microbial pathways involved in heavy metal remediation.

Bioleaching

Bioleaching is a key microbial mechanism for remediating polluted soils. Chemolithotrophs and acidophiles facilitate the oxidation of Fe(II) to Fe(III) and the reduction of sulfur (S) to sulfuric acid (H_2SO_4), aiding in the dissolution of metal oxides and sulfides, which subsequently releases heavy

metals. Microbes act as reducing agents in bioleaching and can also recover and extract heavy metals. Research has indicated that recovery rates are high, such as 98.7% Cd recovery using *Annona squamosa*-based absorbents, 100% Cu recovery with *Pseudomonas putida*, and over 90% Cu and Pb recovery with *Enterobacter*. Acidophiles and chemolithotrophs contribute by producing acids and oxidizing sulfur compounds, making bioleaching eco-friendly, energy-efficient, and effective at low temperatures (Adetunji et al., 2023).

Bioaccumulation and Biosorption

Bioaccumulation and biosorption are essential microbial strategies for remediating contaminated soils. In biosorption, microorganisms utilize their cellular structures to adsorb and sequester heavy metal ions on binding sites located on their cell walls. Various microbes, including *Bacillus subtilis*, *Rhizopus arrhizus*, *Magnetospirillum gryphiswaldense*, and microalgae, generate biosorbents that facilitate heavy metal removal. Bacteria, in particular, are highly effective because of the large surface-to-volume ratio and also the existence of diverse chemisorption sites. Dead bacterial cells, like *Bacillus sphaericus*, often show even higher biosorption capacity compared to living cells. Bioaccumulation, however, involves actively transporting ions of heavy metals across the cell membrane into intracellular regions via ionic channels and carrier-mediated transport. Microbes have been shown to bioaccumulate metals such as Ni, Pb, Hg, Cr, and Cd. For instance, *Microbacterium* sp. reduced Cr (VI) uptake by 88%, and *Microbacterium liquefaciens* eliminated 90–95% of Cr. These microbes may use heavy metals in the iron metabolism or detoxify them through enzyme production, making them effective in heavy metal remediation. (Naskar et al., 2020).

Biotransformation

Biotransformation enables microorganisms to convert toxic metal ions into less harmful forms. Bacteria employ various mechanisms, such as oxidation, reduction, isomerization, hydrolysis, demethylation, and methylation to adapt to environmental changes. For instance, *Micrococcus* and

Acinetobacter oxidize the toxic arsenic species As(III) convert into a less soluble and non-harmful form, while Bacillus species capable of tolerating Cr(VI) reduce it to the less toxic Cr(III). Additionally, processes like biofilm formation and biological chelation aid microbes in mitigating heavy metal toxicity, making biotransformation a crucial strategy for effective remediation (Adetunji et al., 2023).

Biovolatilization

Bio-volatilization is a microbial method in which toxic heavy metals are enzymatically transformed into volatile, less harmful compounds, thereby reducing their presence in soil and water. This mechanism relies on enzymatic reduction and methylation, involving enzymes such as arsenic methyltransferase, mercury reductase, and antimony methyltransferase to convert metals like arsenic (As), mercury (Hg), and antimony (Sb). For example, bacterial methyltransferases modify arsenate As(V) into volatile methylated forms that are released into the atmosphere. Similarly, enzymes like mercurial lyase and MerA in bacteria and archaea facilitate mercury volatilization. Additionally, fungi such as Scopulariopsis brevicaulis efficiently convert As(V) and Hg(II) into less toxic forms (Boriová et al., 2014).

Biomining

In biomining, microorganisms play an important role in mineral formation, aiding in the immobilization of heavy metals. Certain bacteria, such as Sporosarcina ginsengisoli, facilitate the production of calcite, aragonite, and vaterite, while Bacillus subtilis promotes lead (Pb) mineralization by releasing phosphates. Fungi like Penicillium chrysogenum also contribute by mineralizing lead (Pb) and chromium (Cr). Additionally, Pseudomonas putida aids in the precipitation of cadmium (Cd) by forming carbonate and phosphate minerals. Microbes generate extracellular polymeric substances (EPS) and organic acids, while siderophores bind to metals, forming stable complexes that limit metal uptake by plants and immobilize them in the soil, thereby reducing their toxicity (He et al., 2019).

General mechanism of heavy metal removal

Various processes have been proposed to address metalloid pollution across different environments, like chemical, physical, and biological approaches. Although all these techniques aim to detoxify and remediate pollutants, bioremediation stands out as an effective option for minimizing the toxic effects of metalloids while enabling their recovery for industrial applications. In recent years, this approach has gained significant attention due to its affordability, eco-friendliness, and ease of implementation. Additionally, bioremediation requires no specialized technical equipment or skills and usually doesn't generate harmful byproducts or extra garbage. Among the microorganisms involved, bacteria play a key role in bioremediation because of their small size, high population density, rapid growth, adaptability to diverse environments, and ease of cultivation and management. Key factors influencing the efficiency of bioremediation include soil type, organometallic ions, nutrient availability, the nature and concentration of pollutants, moisture levels, redox potential (Eh), microbial community dynamics, solubility, pH, temperature, and electron acceptors. Bioremediation techniques can be broadly classified into in-situ and ex-situ methods. Mycoremediation, which involves using fungi, represents an effective strategy for removing metalloids (Zhang et al., 2020). Another approach, known as phytoremediation, utilizes algae, microalgae, or pollutant hyperaccumulator plants to remediate contaminated areas. A related method, phytobacterial remediation, combines plants with endophytic bacteria, offering an additional biological approach for addressing pollution in affected regions. Bioremediation utilizes living organisms to decrease the bioavailability of pollutants in the environment and minimize their toxic effects. Metals and metalloids can be removed from contaminated sites through various mechanisms, including bioleaching, bioaccumulation, biotransformation, biomineralization, biosorption, and microbial involvement in chemisorptions (Talukdar et al., 2020). Conversely, bioaccumulation is an active, energy-dependent, and often irreversible process where ions are transported into the cell and retained intracellularly through specific proteins and channels. Recent interest has shifted toward

biotransformation, a process driven by oxidation-reduction reactions. The oxidation states of metalloids, which can be changed by electron gain or loss, have an impact on their toxicity (Sher et al., 2019). Figure 2 shows an overview of the main mechanisms underlying the resistance of bacteria to metals. Their potential in bioremediation applications is being investigated more and more (Table 1).

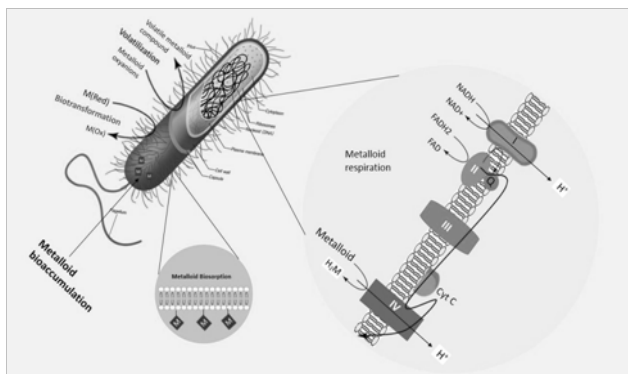


Figure 2: General mechanism of heavy metal removal

Table1: Examples of micro organis msstudied and strategically treated for Heavy metal bioremediation methods

Sl. No.	Speciesname	Heavy metals	Ref.
1	Rhizobium	Zn, Pb, As, Cu, Cd, Hg, and Se	(Pajueloetal., 2008)
2	Rhodococcus,	Cr,Cd,and Pb	(Goswamietal.,2017)
3	Ochrobactrum pseudinter medium	Cr	(Tandonet al., 2020)
4	Rhodococcus	Dye	(Nazarietal., 2022)
5	Lactobacill us plantarum	Cr	(Ameenetal., 2020)
6	Pseudomona saeruginosa	Zn andCr	(Awasthietal., 2015)

Conclusion

Even while research on the bioremediation of metalloids has advanced significantly, little is known about the mechanisms and the particular needs of the microbes. Advanced techniques such as proteomics and metabolomics offer promising avenues for uncovering the detailed processes involved in bioremediation. Additionally, specialized software could be developed to predict the optimal combination of electron shuttles, enzymes, cofactors, nutrients, microbial strains, and physicochemical conditions needed for effective ex-situ bioremediation of contaminated sites. The connection between nitrogen and sulfur cycles and metalloid decontamination, as well as the role of microbes engaged in these cycles in bioremediation, is an intriguing area that warrants further investigation. Furthermore, proteomic and transcriptomic analyses could provide valuable insights into the synergistic interactions among microbes that diminish metalloids, ultimately mitigating their poisonous effects. These approaches could pave the way for more efficient and targeted bioremediation strategies.

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