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Potential of plants and microorganisms for bioremediation technologies for mine rehabilitation

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Abstract
The mining industry is one of the priority sources of environmental pollution by potentially toxic metals. The impact on the environment remains significant even after the end of mining activities. Numerous studies report the environmental impact of abandoned mines. Therefore, cleaning of mine territories from the pollution is of priority importance. Phytoremediation and microbial remediation are some of the methods. The study of plants for their possible use in phytoremediation is of great interest. Such works are of great importance in developing modern phytoremediation technologies, as they allow us to find new hyperaccumulators for possible mine reclamation.
Microorganisms possessing resistance to heavy metals, such as fungi and bacteria, as well as unicellular algae, may be used to clean up tailings contaminated with potentially toxic metals. The microbiological method of tailings treatment is based on the ability of microorganisms to transform and decompose chemical compounds.
Microbial remediation and phytoremediation are attracting more and more attention due to their relatively low cost and environmental friendliness. A large number of studies related to the investigation of mine plants and microorganisms and their utilization for mine cleanup demonstrate the promise of using bioremediation. Further development of bioremediation technologies will be associated with wider implementation of the research findings in practice and the possible use of biotechnology in bioremediation.
The successful practical application of mine bioremediation requires a complex interdisciplinary approach associated with biological, ecological, biotechnological, and geographic-geological areas.

Keywords
mine; phytoremediation; microbiological remediation; pollution ; potentially toxic metals; mine rehabilitation

Introduction

Mining plays an important role not only for other industries but also for the economy as a whole. (Karn et al., 2021). Mining production is increasing worldwide. However, the mining industry is one of the primary sources of environmental pollution caused by heavy metals. The impact on the environment remains significant even after the end of mining activities. There is a large number of abandoned mines around the world. This is the particular case for lead-zinc mines, the vast majority of which have been abandoned for decades (Gutiérrez et al. ,2016).

Tailings may contain high levels of toxic metals such as lead, copper, cobalt, nickel, cadmium, manganese, molybdenum, iron, and others. In addition, tailings contain high levels of cyanide and rhodanide, which are also harmful to the environment. The content of potentially toxic metals could be very significant. Thus, Courtney (Courtney, 2013) reported that Pb concentrations are up to 10000 mg/kg and Zn concentrations are up to 20000 mg/kg in tailings storage facilities. On the other hand, Wang et al. (2016) reported Fe concentrations of 144 mg/kg and 83000 mg/kg. Rzymski et al. (2017) evaluated the chemical composition of water discharged from copper mine wastes. These authors collected samples from copper mine tailings, and the results showed that the total copper concentration ranged from 259.3 mg/L to 2.77 mg/L and from 0.02 mg/L to 0.002 mg/L for Mo, among many other heavy metals.

The release of copper from the waste rocks of an abandoned mine in Brazil amounted to 7.2 tons over 30 years (Perlatti et al., 2021). Although mining in the Cartagena-La Union (SE Spain) mining district ceased in 1992, various studies have shown that large quantities of toxic metals continue to be transported into nearby ecosystems (Conesa and Schulin, 2010).

In abandoned lead-zinc mine tailings in China, Pb, Zn, Cd, and As are critical heavy metals in soils near tailings that require more attention (Han et al., 2023). Even former post-mining mounds - the ancient remains of temporary mining operations - are more heavily contaminated with potentially toxic metals than their surroundings (Podgórska and Jóźwiak, 2024).

Abiotic factors may influence the dispersion of potentially toxic metals from mines. For example, climatic influences such as intense rainfall greatly influence the dispersion of metals in semi-arid areas since soils are generally poorly covered by vegetation (Navarro et al., 2008). In the territory of a gold-silver mine, Cd, Cu, Pb, and Zn are dispersed due to the movement of debris under the influence of wind and water (Jung, 2001).

Thus, the problem of heavy metal pollution may not be limited to the mine areas but may be of a more significant nature. Therefore, cleaning of mine territories from the pollution is of priority importance. Phytoremediation and microbial remediation are some of the methods. In recent years, there has been great interest in mine rehabilitation and bioremediation research, especially phytoremediation.

The aim of the article was to consider the potential of plants and microorganisms for bioremediation technologies in mine rehabilitation.

The originality of this review is the consideration of using the potential of plants both plants and microorganisms in mine rehabilitation

Phytoremediation

2.1. Characteristics of reviews on mine phytoremediation and related topics

There are a variety of interesting reviews on phytoremediation. Here are examples of some of them: some reviews are related to specific regions, for instance, the exploitation of mines in the Mediterranean basin (Boi et al., 2023), and other reviews discuss phytoremediation of abandoned mines in Korea (Lee et al. 2023).

A certain number of reviews specialize in a particular topic. For example, a review on the recultivation of iron ore mine tailings using organic additives in combination with phytoremediation (Sarathchandra et al. 2023). A review related to phytoremediation of environments impacted by the acid drainage of mines (Thomas, Sheridan, and Holm, 2022). A review related to rhizosphere management to improve plant growth and phytoremediation of copper mine tailings (Pérez et al., 2021). Phytoremediation by Biochar of heavy metal-contaminated mine tailings is also discussed (Das et al., , 2021).

The effects of chromite contamination on plants and the environment, as well as phytoremediation of Cr-contaminated soils, were evaluated by Ghosh and Maiti (2021). The differences in reclamation, reclamation, and phytoremediation, as well as the importance of geochemical processes in the remediation of sulfide mine tailings, were assessed by Xie and van Zyl (2020).

One review notes the gaps in achieving geochemical stability of tailing ponds (Punia, 2019). The ecological potential of plants for phytoremediation and eco-remediation of fly ash and mining waste sediments is considered (Gajić et al., 2018).

There are few reviews with a broader focus. One of these reviews comprehensively discusses the background and application of phytoremediation (Wang et al., 2017).

This review is broadly focused and will not only deal with phytoremediation but also with the microbial remediation of mines.

2.2. Phytoremediation technologies

Phytoextraction, phytostabilization, phytovolatilization, and rhizofiltration can be distinguished in phytoremediation (Sharma et al., 2023).

Phytoextraction and phytostabilization are of particular interest.

Phytoextraction has great potential as a method for cleaning up soils contaminated with metals. (Seth et al., 2012). This phytoremediation method has great promise for the cleanup of mine soils.

Strategies for the use of phytoextraction are different. These strategies may be related to the type of plant species used: natural hyperaccumulators, fast-growing plant species with high biomass production, and genetically modified plants (Suman et al., 2018). Another strategy is to increase the bioavailability of potentially toxic metals. The efficiency of phytoextraction can be improved by chemical, microbial, soil, and genetic approaches related to bio-availability, uptake, and sequestration of potentially toxic metals (Asgari Lajayer et al., 2019). A number of studies on the use of phytoextraction for the remediation of mine soils have been conducted. The high potential for uptake of antimony from contaminated soil by wild plants grown at three antimony mines has been demonstrated (Zhang et al., 2021). Potential phytoextraction from mine waste was evaluated using two species that are endemic to New Caledonia (Losfeld et al., 2015). The effectiveness of phytoextraction of plants that accumulate potentially toxic metals and the effect of chemical chelators on the removal of cadmium, lead, zinc, and copper (Cu) from rice fields that had been continuously irrigated with mining wastewater from mines during a 55-year period was shown (Tai et al., 2018). Studies related to the investigation of mine flora and its accumulating abilities in relation to potentially toxic metals have great potential for developing phytoextraction technologies.

Phytostabilization is of great importance in reducing the bioavailability of heavy metals.

Phytostabilization of mine tailings is a technology for soil remediation but requires further research related to the study of new plant species to be used in phytostabilization and chemistry of mine tailings in ongoing field trials (Mendez and Maier, 2008).

Rhizofiltration refers to using plants to remove pollutants, mainly used for water purification (Yadav et al. , 2011). This technology may hold promise for mine water treatment (Tapia et al., 2024).

The study of mine plants for their possible use in phytoremediation is of great interest. The results of different studies show the great potential of native species for their possible use in phytoremediation (Chang et al., 2018). Such works are of great importance in the development of modern phytoremediation technologies, as they allow us to find new hyperaccumulators for possible mine reclamation.

3. Microbiological remediation

The microbiological method of tailings treatment is based on the ability of microorganisms to transform and decompose almost all chemical compounds. These processes are diverse and depend on the physical and chemical conditions of the environment, the nature of the pollutant, the composition of microbial communities, etc. Microbial remediation is characterized by a simple process, eco-friendly, and low energy consumption, which makes it competitive with chemical and physical methods resulting in high reagent consumption, energy consumption, and environmental pollution (Pathak, Dastidar and Sreekrishnan, 2008, 2009; Dusengemungu et al., 2020; Liapun and Motola, 2023). Comparing biological and chemical leaching, for example, the biological method has been shown to be advantageous. Bacteria that oxidize iron and sulfur actively contributed to eliminating Cu, Ni, Zn, and Mn from tailings (Aromaa et al., 2013). Other authors investigated the possibility of vanadium removal using three species of microorganisms. It was shown that bacteria - *Acidithiobacillus thiooxidans* and *Pseudomonas putida* are able to remove more than 90% of vanadium. However, the maximum vanadium removal was observed in the case of the use of ascomycete *Aspergillus niger* and was about 94% (Mirazimi, Abbasalipour, and Rashchi, 2015). The use of a mixed bacterial culture consisting of *Acidithiobacillus ferrooxidans* and *Sulfobacillus thermosulfidooxidans* resulted in the leaching of zinc from lead-zinc sulfide tailings. Interestingly, the results of the bioleaching residue toxicity assessment showed that the use of *Acidithiobacillus ferrooxidans* culture resulted in a significant 20-fold reduction in the potential environmental risk index of the tailings, turning them into non-hazardous waste (Liao et al., 2021). Studies by other authors have also shown that biological leaching reduces Zn and Pb contamination by 96.36% and 95.84%, respectively. Toxicity and environmental risk analysis showed that the biological leaching process significantly reduces the environmental risk caused by metals present in tailings (Ye et al., 2021). Some authors, by detecting the presence of *Acidithiobacillus ferrooxidans*, already point out their presumed involvement in oxidative processes in mines, as in the case of the Shanouch nickel deposit (Khaynasova and Pashkevich, 2019).

Thus, microorganisms possessing resistance to heavy metals, such as fungi and bacteria, as well as unicellular algae, may be used to clean up tailings contaminated with heavy metals.

3.1. Specific features of the interaction between microorganisms and metals

The interaction between microorganisms and metals is a complex set of different processes in nature that involve various ones.

3.1.1. Biosorption

Biosorption (passive absorption) can be carried out by dead biomass or living bacterial cells by surface complexation on the cell wall and other outer layers (Raklami et al., 2022). Eukaryotic photosynthetic microorganisms, microalgae, are actively used for this purification method. Since 1990, the use of microalgae for bioremediation of metal-contaminated areas has been described. Shanab et al. (2012) reported a high percentage of bioabsorption of mercury, cadmium, and lead by Pseudochlorococcus - up to 97%, 86%, and 70%, respectively. Zhou et al. (2012) found that Chlorella pyrenoidosa and Senedesmus obliquus completely removed zinc and copper from aqueous solutions. Gani et al.(Gani et al., 2017) showed the efficiency of bioremediation of several heavy metals (Zn, Fe, Cd, and Mn) from domestic and food wastewater using Botryococcus sp. In the study of Palma et al. (Palma et al., 2017), the bioremediation potential of Chlorella-like microalgae consortia for the removal of heavy metals (Ni 24.8%, Co 10.5%, Mn 24.8%, and Sr 26.4%) from nickel processing industries was investigated. A number of works clearly indicate the bioadsorption capacity of various algae, primarily Chlorella vulgaris and Scenedesmus spinosus. These algae have shown not only high resistance to metals from mine water, such as Cu and Mo but also their intensive elimination. In the case of Chlorella vulgaris, removal of Mo up to 64.7% and Cu up to 99.9% was observed.

Gram-positive bacteria, in particular, have a high biosorption capacity among other bacteria as they have a thick peptidoglycan cell wall (van Hullebusch, Zandvoort, and Lens, 2003; Ahluwalia and Goyal, 2007). Such bacteria include Bacillus sp. (Ren et al., 2015; Shameer, 2016), which can be considered as a broad-spectrum adsorbent. Bacillus sp has been successfully applied for the removal of metals such as Cu(II), Pb(II), Cr, Zn, and Cd (Wang et al., 2006). Several works have shown the major role of surface polysaccharides of Bacillus in metal adsorption (Shameer, 2016). It should be noted that Bacillus can also perform bioremediation at low temperatures (Ren et al., 2015). Micrococcus luteus is also a good biosorbent of Cu Pb, although it is inferior to *Bacillus* sp. *Sporosarcina* sp. is used in this study (Zhao et al., 2016) to remove Cr (VI) in marine sediments. Other Gram-positive bacteria, such as Cellulosimicrobium, Aeribacillus are also used as heavy metal adsorbents.

However, gram-negative bacteria such as Acinetobacter sp, Stenotrophomonas sp., Methylobacterium sp., and Pseudomonas sp. also exhibit sorption properties. It has been shown that adsorption occurs due to carboxyl and hydroxyl groups in the cell walls of Pseudomonas aeriginosa (An et al., 2020).

To optimize the efficiency of biomining, the influence of a number of factors, such as pH, temperature, initial concentration of contaminants, or the amount of biosorbent, is evaluated. The binding mechanism depends on the chemical nature of each pollutant and the initial amount of biomass. However, other factors must be taken into account, such as the possible toxicity of contaminants to bacterial cells if living cells are used in this process.

3.1.2. Bioaccumulation

Bioaccumulation (active absorption) is a process in which potentially toxic metal ions pass through the cell membrane into the cytoplasm and bind there to proteins or accumulate in vacuoles. Bioaccumulation occurs in two stages: the adsorption of metal ions on the surface of cells, known as the biosorption method, and the active transport of metals within cells. Zolgharnein et al. (Zolgharnei et al., 2010) demonstrated the uptake of metal ions, copper, zinc, cadmium, and lead by the bacterium Pseudomonas aeruginosa. Pseudomonas putida accumulated cadmium both intracellularly and in the periplasm, indicating the presence of metal binding and/or efflux systems in cells that mediate resistance to metal toxicity (Manara et al., 2012). The accumulation of metal ions in the cytoplasm and periplasm was also reported for E. coli (Nnaji et al., 2023).

Microorganisms have evolved various mechanisms of metal resistance, such as intracellular chelation by metallothionein proteins and glutathione-derived peptides called phytochelatins (Kneer et al., 1992; Presta and Stillman, 1997) and metal accumulation in vacuoles (Volesky, 1994; Raspanti et al., 2009). The bioaccumulation process is supported by synthesizing low molecular weight proteins such as metallothionein, which are rich in thiol (cysteine) groups. They bind potentially toxic metals into non-biologically active forms, eliminating them from the metabolism. The amino acid cysteine is a precursor of known heavy metal chelators such as metallothioneins, glutathioneones, and phytochelatins (Cobbett and Goldsbrough, 2002; Clemens, 2006).

3.1.3. Biomineralization of metal ions

Biomineralization of metal ions is the formation of minerals due to the activity of microorganisms (Tayang and Songachan, 2021). This phenomenon is widespread and represents an important part of biological, geological, and chemical cycles (Zhang et al., 2022). Some bacteria are capable of precipitating oxides, sulfates, and phosphates in the form of minerals (Arias, Cisternas, and Rivas, 2017). However, carbonate deposition is more important for the biomineralization of heavy metals.

Thus, the microorganism *Terrabacter tumescens* forms mineral carbonates of nickel, copper, lead, cobalt, zinc, cadmium, and calcium due to the production of the enzyme urease, which hydrolyzes urea. Through this process, the pH of the soil increases, and carbonates are formed, which leads to the mineralization of soluble heavy metal ions present in the soil environment (Li et al., 2016). Currently, many studies are now focused on ureolytic bacteria that have demonstrated very high removal rates of heavy metals from the environment (Zhao *et al.*, 2019), such as *Sporosarcina pasteurii*, *Stenotrophomonas rhizophila* and *Variovorax boronicumulans* (Jalilvand et al., 2020).

3.1.4. Biotransformation

Biotransformation is a process in which the interaction between bacteria and heavy metals results in the formation of less toxic metal compounds (Emenike et al., 2018). Many bacteria have been described for their ability to biotransform metals, such as *Micrococcus* and *Acinetobacter* species, that convert arsenic into a less soluble and less toxic form (Pande et al., 2022). Also noteworthy are strains of the genus *Alcaligenes* that transform elemental mercury into its monovalent compounds (Gupta and Nirwan, 2015).

3.1.5. Bioleaching

Bioleaching is a method based on the ability of certain microorganisms to convert heavy metals into soluble and extractable compounds (Sarkodie et al., 2022). The bacteria used in this process can mobilize potentially toxic metals in the soil through autotrophic and heterotrophic leaching. Acidophilic microorganisms involved in autotrophic leaching (species of the genera *Acidithiobacillus, Thiobacillus*) (Pande et al., 2022) oxidize iron (II) and reduce elemental sulfur. The end products of these reactions, ferric iron, and sulfuric acid, reduce soil pH, which leads to an increase in the solubility of metals. The mobilization of metals through heterotrophic bioleaching is achieved through the formation and release of organic acids (oxalic, gluconic, malonic, etc.), which increase the solubility of potentially toxic metals due to their chelation (Wang et al., 2021). In addition, heterotrophs such as *Pseudomonas aeruginosa* can produce biosurfactants and siderophores to bind and remove toxic metals from contaminated soil (Feng et al., 2021). Bioleaching can be used to recover metals from mining and metallurgical wastes (Fomchenko and Muravyov, 2020).

3.1.6. Methylation

Methylation is a process by which pollutants, including potentially toxic metals, are converted into volatile compounds by the enzymatic activity of microorganisms (Tarfeen et al., 2022). Bacteria of the genera *Pseudomonas, Escherichia, Clostridium, and Bacillus* have a significant ability to convert mercury, selenium, arsenic, and lead into gaseous form.

3.2. Limitation of the use of microbiological remediation

Despite the obvious advantages (discussed at the beginning of this section), the widespread use of bacteria for bioremediation of the environment from potentially toxic metals has a number of limitations. For example, it is necessary to provide optimal conditions for bacterial activity, which is achieved by implementing additional agrotechnical measures (fertilization, irrigation, plowing, etc.), which result in additional costs. The next disadvantage is the resistance of microorganisms only to certain pollutants. Many strains that are promising agents of environmental biotechnology cannot be used in the bioremediation of disturbed areas due to their pathogenicity for humans and animals. Furthermore, there is a problem of maintaining sufficient numbers of introduced bacteria in an open ecosystem. Nevertheless, some of these limitations could be overcome.

4. Conclusion

Plants and microorganisms can be widely used to reduce mine soil pollution. Microbial remediation and phytoremediation are attracting more and more attention due to their relatively low cost and environmental friendliness. A large number of studies related to the investigation of mine plants and microorganisms and their utilization for mine cleanup demonstrate the high efficiency of bioremediation. These studies contribute to the rapid development of bioremediation technologies. The joint use of plants and microorganisms for cleaning mine soils also has great prospects.

Further development of bioremediation technologies will be associated with wider implementation of the research findings in practice, as also possible use of biotechnology in phytoremediation and increasing resistance to environmental pollution (Gladkov et al., 2023; Gladkov and Gladkova, 2023, 2024). An individual approach is necessary when using bioremediation in field conditions. This is because types of organisms, environmental factors, toxicants, and their concentrations, as well as features of the contaminated site, play an important role in the effective use of bioremediation. To achieve greater effectiveness of phytostabilization, for example, microtopography, which accounts for different soil characteristics, should also be considered along with plant species (Shahrokh et al., 2023). The faster-growing plants with a high capacity for the accumulation of toxicants need to be identified for the use of phytoextraction (Ojuederie and Babalola, 2017). Thus, the successful practical application of mine bioremediation requires a complex interdisciplinary approach associated with biological, ecological, biotechnological, and geographic-geological areas.

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