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Biotransformation of Toxic Metal Compounds by Fungi

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Abstract

In nature, fungi are saprotrophic degraders of organic substances, and play an important role in biogeochemical cycle. Many fungi show distinguished ability to mobilize metals and metalloids from insoluble compounds such as metal phosphates, sulphides, carbonate, oxide and mineral ores by secretion of fungal metabolites (e.g. organic acid). They can also immobilize metal ion by extracellular precipitation as metal oxalate complexes. Metal transformation by insoluble metal oxalate formation is a process of marked environmental significance associated with fungal survival, bioremediation, mineral weathering and metal detoxification. Predicated on the ability of fungi in both mobilization and immobilization, it is plausible to exploit fungal ability to transform metals and metalloids for biotechnological application for metal recovery from smelter sludge, low grade ores, and other solid wastes.

Keywords: Biotransformation, Bioremediation, Metal, Metalloid, Fungi

1. Introduction

Nowadays, the heavy metals tend to give rise to the greatest amount of elements of concern with regard to human health such as Pb, As, Hg, Zn, Cu and Cd. Some are known as toxic metals in ecological system, but others are not known about biological functions. Heavy metal polluted in nature cause a widespread environmental problem resulting in harmful effects on human health when exposure in an amount that cannot be processed by organisms. Damage may cause adverse reactions in different organs and biological functions, including reproduction and inactivation of enzymes [1-3]. Chemical and physical methods for removing heavy metal could be employed to remedy such problem; however, they are too extremely expensive to be used in large-scale application. Therefore, to ameliorate the problem, bioremediation could be a potential strategy to remove heavy metal. [4-5]. As aforementioned, fungi play a major role in ecological system as decomposers and involved in biogeochemical cycle; therefore, they are powerful solubilizing agents [6]. Fungal-based bioremediation could be a promising tool to transform toxic metals and metalloids into the non-toxic form. This review will provide details in understanding the fungal role and mechanisms in toxic metals transformation.

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2. Mechanisms of metal and metalloid amelioration

Many metals are micronutrient and essential for fungal physiology such as Zn, Cu, Co, Mn and Fe, but all can exert toxicity when present above certain threshold concentrations in bioavailable forms. Other heavy metals such as Cd, Pb, and Hg, have no known biological function, but can be accumulated by fungi [7]. Despite apparent toxicity, many fungi survive, grow, and flourish in apparently metal-polluted locations, and a variety of mechanisms, both active and incidental, contribute to tolerance. Fungi possess many properties that influence heavy metal toxicity, including organic and inorganic precipitation, intracellular compartmentalization and the production of metal-binding proteins, while major constituents of fungal cell walls (e.g. chitin, melanin) show significant metal-binding abilities [7-8].

Fungi interact with metal and their compounds in various ways depending on the metal species, organism and environment. They are able to restrict toxic metal entry into cells by (1) sorption of metals in the mycelium, (2) reduction of metal mobility as a result of hydrophobicity of the fungal cell wall, (3) secretion of chelating agent e.g. oxalate, and (4) accumulation of metals on the external mycelium by exopolysacchrides and other extracellular metabolites [9-10]; the mechanisms of metal resistance and metal amelioration are illustrated in figure 1. Moreover, metal-tolerant fungi can survive due to their ability for intracellular chelation, e.g. by metallothioneins and phytochelatins and metal sequestration within vacuoles. The fungal vacuole functions in the regulation of cytosolic metal ion concentration and the detoxification of potentially toxic metal ions [11-13].

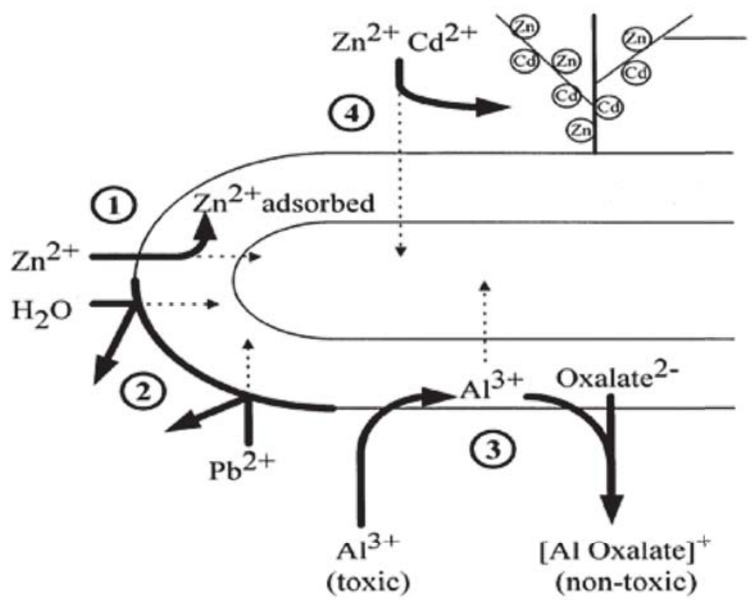

Figure 1 Mechanisms of metal resistance and metal amelioration (Adapted from Jentschke and Godbold [9]).

3. Metal Transformation

Metal-containing mineral rocks are biologically unavailable; nevertheless, fungal processes dissolve metal minerals, thereby increasing metal bioavailability and potential toxicity, whereas others immobilize them and reduce bioavailability. However, it should be realized that there is no necessarily any direct relationship between bioavailability and toxicity; this is especially valid for fungi where acidic pH values can increase chemical availability of metals but greatly reduces toxicity [7]. The balance between solubilization and immobilization is contingent on the involved organisms and the physicochemical attributes of their environment. As well as being an integral component of biogeochemical cycles for metals and associated elements, these processes may have potential in the treatment of metals contaminated wastes [14].

3.1 Metal solubilization

Fungi can solubilize insoluble metal compounds through bioleaching by generating metabolites such as organic acids and siderophore [15]. Solubilization is an important process to release phosphate and micronutrient into the soil environment. This can occur by protonation of the anion of the metal compound, decreasing its availability to the cation, with the proton translocating ATPase of the plasma membrane and the production of organic acids being sources of protons [7, 15]. Organic acids are primary metabolites, which are produced by fungi and function in chemical attack of minerals, providing protons as well as a metal chelating anion [6, 16]. Fungal-derived carboxylic acids play a key role in chemical attack of mineral rock surfaces [17]. For example, citrate and oxalate can form stable complexes with a large number of metals. Many metal citrates are highly mobile and not readily degraded [18]. Oxalic acid can act as a leaching agent for those metals that form insoluble oxalate complexes. In addition, other excreted metabolites with metal complexing properties, e.g. amino acids, enzymes and siderophores, might be associated with the formation of complexes (Figure 2). Siderophores are the most common name, which means the acquisition of iron by fungi and bacteria, and the most common fungal siderophore is ferrichrome [15]. Many fungi are able to leach metals from industrial waste and by products, low-grade ores and metal-bearing minerals [19-21].

A large number of fungi can solubilize heavy metals from solid substrates. *Aspergillus niger* and *Penicillium* sp. are the strains most commonly used for biohydrometallurgical treatments. Generally, *Aspergillus* spp. and *Penicillium* spp. are known to be very efficacious producers of organic acids either from the tricarboxylic acid (TCA) cycle such as citric acid and oxalic acid or derived from glucose (e.g. gluconic acid) [23].

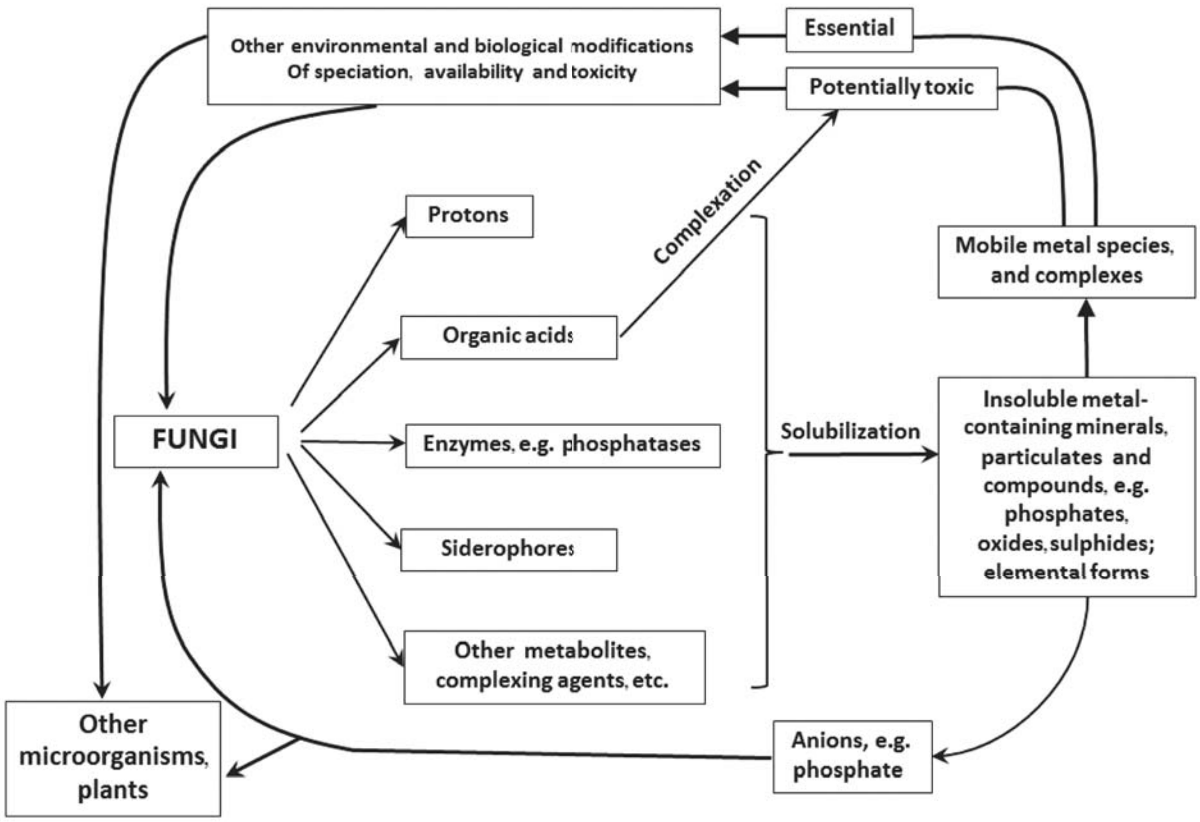

Figure 2 Diagrammatic representation of the mechanisms involved in fungal solubilization of insoluble metal compounds [22].

3.2 Metal immobilization by formation of mycogenic crystals

Fungi have been shown to precipitate a number of organic and inorganic compounds such as oxalates carbonates and oxides and this can lead to formation of mycogenic crystals [15]. Precipitation, including crystallization, will immobilize metals in the soil and therefore limiting bioavailability, as well as lead to release of nutrients like sulfate and phosphate [24]. Fungi can produce metal oxalates with a variety of different metals and metal-containing minerals such as Zn, Pb, Cu and Cd (Figure 3). The formation of oxalates containing potentially toxic metals may provide a mechanism whereby oxalate-producing fungi can tolerate environments containing high concentrations of toxic metals. Metal immobilization by insoluble metal oxalate formation is a process of marked environmental significance both regarding fungal survival, biodeterioration, pathogenesis, soil weathering, mineral formation and metal detoxification [25-27].

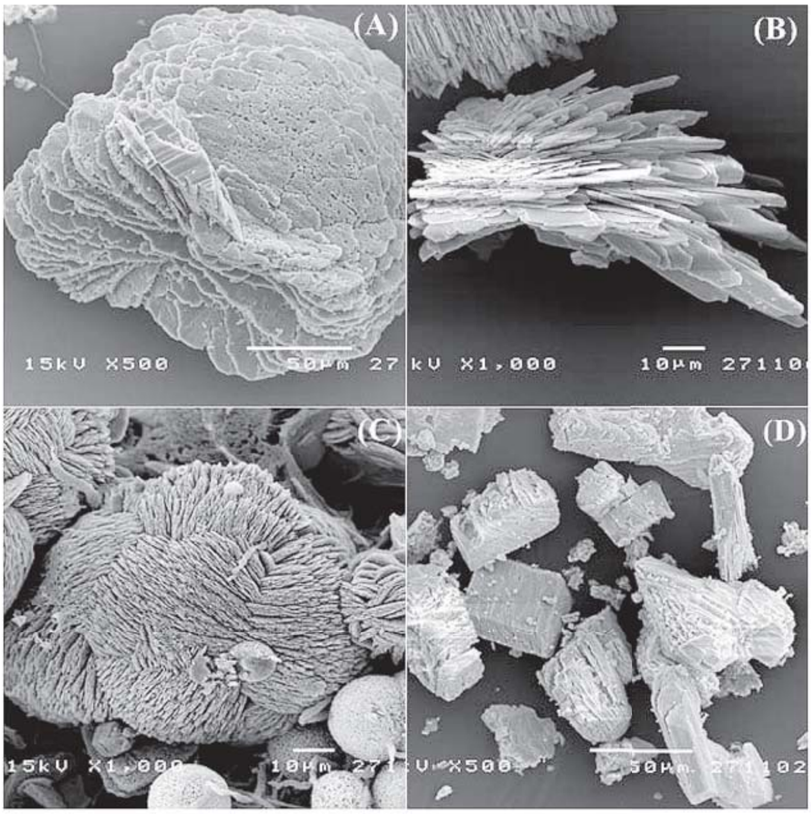

Figure 3 Scanning electron micrographs of insoluble metal oxalate crystals. (A) Zinc oxalate produced by *Aspergillus* spp., (B) Lead oxalate produced by *Aspergillus* spp., (C) Copper oxalate produced by *Aspergillus niger*, (D) Cadmium oxalate produced by *Penicillium* spp. Scale bar markers: (A, D) 100 µm; (B, C) 10 µm [28].

4. Conclusion

Fungi show the distinguished ability to transform metal compounds through acidolysis in which organic acids produced by fungi are directly involved in the metal solubilization and immobilization. Especially, oxalic acid plays an important role in metal immobilization process transforming toxic metals into metal oxalate complexes (non-toxic form). This review provides the strong evidence that fungi could detoxify heavy metals and metalloids by solubilization and immobilization; however, whether this is a process of significance *in situ* remains to be ascertained.

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