# Recent Advancements in Bioremediation of Metal Contaminants

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# Chapter 11
# Fungi-Mediated Detoxification of Heavy Metals

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## ABSTRACT

*Heavy metal pollution is one of the major environmental problems today. Therefore, the elimination of heavy metal ions from wastewater is important to protect public health. The use of biological material in the removal and recovery of toxic metals from industrial wastes has gained important credibility during recent years. Several microorganisms including bacteria, algae, yeast, and fungi have been reported to effectively accumulate or adsorb heavy metals through biosorption. Fungal biomaterial has been proved to be efficient as a biosorbent. High percentage of the cell wall material and availability of fungal biomass as a by-product of various antibiotic and food industries makes it an obvious choice. Thus, the chapter deals with detoxification of heavy metals from contaminated sources using biomaterials with special reference to fungi.*

## INTRODUCTION

Rapid improvement in industrialization has made human life comfortable, but it has also brought along with it a disruption of environmental balance. Heavy metals produced as a byproduct of many such industrial processes is toxic, and its accumulation in the environment can lead to severe health hazards in human beings. It can also harm the eco-system by accumulating in the food chain. Environmental heavy metal pollution can be primarily associated with the following causes:

- Seepage and overburdens generated from mines- associated with mining operations
- Effluents produced from electroplating plants
- Effluents produced from Coal-based power plants
- Byproducts produced from nuclear reactors

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Heavy metals due to their non-biodegradable nature pose severe threat to the environment as it cannot be removed from the system once it enters; these metals may also seep in to the soil contaminating the ground water sources. Hence, removal or de-toxification of the accumulated heavy metal from the environment is a major challenge for the environmental scientists.

Several techniques are available for treatment of the effluents which are physiochemical in nature. However, the major drawbacks of these processes are their high operational cost, high energy consumption and lack of efficiency with respect to complete removal of the metal concerned. The problems mentioned for the physico-chemical methods could be reduced with the use of biological organisms.

Out of the several biological methods known for removal of metals from aqueous solution bioaccumulation and biosorption have been proved to be effective (Volesky and Holan, 1995). However, biosorption using dead biomass have been preferred over bioaccumulation. Biosorption has a few advantages over active cellular accumulation like: absence of toxicity limits, possibility to regenerate and recycle of biomass, easy absorbance and recovery of the sorbed biomaterial.

Several biological substances are being used for the process of biosorption. Among the known biological materials, microbes have gained importance because they are ubiquitous in nature and can be grown and manipulated easily. A number of microbial organisms have been used as a biosorbent.

Fungi pose a suitable material for biosorption among the microbes, as it is a common product of industrial processes like food, brewing and distillation; biomass content of fungal cells are high, it is comparatively easier to handle and can regenerate within a short span . Thus fungi can serve as an effective biomaterial for heavy metal removal from aqueous solution.

## HEAVY METAL POLLUTION

**Heavy metals** occur naturally in the environment like many other metallic elements and have an atomic weight higher than the molecular weight of water. They occur in the earth crust naturally and do not interact with the normal biotic system. However, they may get introduced in to the environment via (1) natural phenomenon like volcanic eruptions, forest fire, deep sea vents etc. and (2) anthropogenic events like mining, industrial effluents, smelters etc. In recent times magnified exposure of the heavy metals are happening in the regular life of the biotic elements through anthropogenic acivities involving their indiscriminate use in industrial, domestic, agricultural, medical and technological sectors.

Heavy metals may have some biological roles and are known as **essential metals** (zinc, nickel, copper). These metals are required in very low concentration and can be detrimental to life forms in a slightly higher concentration. The other heavy metals like lead, cadmium, mercury etc. are not known to have any role related to biological organism and are known as **non-essential metals**.

The heavy metals are systemic toxicants and cause various adverse health issues in human and animals. The adversity however is dependent on the chemical nature, time of exposure and dose of the metal concerned. It has also been reported that co-exposure to metal/metalloid mixture cause more severe effects on human health (Wang et. al., 2008).

## CONVENTIONAL METHODS OF HEAVY METAL REMOVAL

There are several known and tested physico-chemical methods of heavy metal removal from the environment like:

**Physical Methods:** Reverse osmosis, electro-dialysis, ultra-filtration, ion exchange

**Chemical Methods:** Chemical precipitation, electrochemical treatment, oxidation/reduction

**Biological Methods:** Phyto-remediation

These well known processes come with some major disadvantages that include high reagent and energy requirement, low cost efficiency, generation of toxic sludge and inability for complete metal removal. There is definitely a need to find out better alternative for these processes. Biosorption of metals using microbial organisms could be a solution to these problems.

## BIOSORPTION OF HEAVY METALS

The process of removal of metal or metalloid species, compounds and particulates from solution using a biological material can be defined as biosorption (Gadd, 1993). There are several reports of accumulation and desorption of heavy metals by microorganisms. Different groups of microbes have been used for this purpose, members of bacteria, algae, yeast and fungi either in living state or in dead condition have been used for heavy metal removal (Huang *et. al.*, 1988, Antunes *et. al.*, 2003, Sag *et. al.,* 2003; Prasenjit and Sumathi, 2005, Mala *et. al.,* 2006, Gupta *et. al.*, 2007). Microbial biomass as an adsorbent has gained importance in recent times as a potential alternative technique in contrast to the already existing metal removal processes (Ozturk, 2007). Usage of biological substrate is associated with a number of advantages: (a) these microbes has a diverse kind of biologically active sites for heavy metal binding especially on their cell wall, (b) they are of small and uniform size and (c) there is very less chance of interference in their case as compared to alkali and alkali-earth metals and ion exchange resins (Madrid and Camara, 1997).

Biosorption basically involves the process of adsorption of a dissolved solid (sorbate) from a liquid containing the dissolved solid (solvent) on to a biological material (sorbent). There is a high affinity of the sorbent for the sorbate species facilitating its removal from the aqueous phase by different mechanisms. The absorption of sorbate on to the surface of the sorbent keeps on increasing until it reaches a state of equilibrium that exists between the adsorbed solid present in solution to that present adhered to the sorbent (Das *et. al.*, 2008).

**Advantages of Biosorption:** Biosorption has some advantages over the conventional metal removal processes (Sahin and Ozturk 2005; Alluri *et. al.* 2007): The major advantages are as follows:

- Cheaper source of biomass
- Multiple heavy metal uptake during metal interaction
- Treatment of a large volume of waste possible with the same set of biomass
- Highly selective for removal of heavy metal
- Is active in different conditions of physical parameters like time, temperature, pH and chemical parameters like interference of co-ions, concentration of sorbate or sorbent etc.
- Easy and cheap recovery of metal from metal loaded biomass
- Reduced production of waste or toxic material

## BIOSORPTION MECHANISM: MODES OF METAL UPTAKE

Metal sorption is a complicated mechanism and there are several controlling factors of the process, like, the nature of biomass (living or dead), type of biomaterials, properties of metal solution chemistry, ambient conditions such as pH, temperature, concentration of biomass etc. (Das *et. al.*, 2008).

The process by which the heavy metal adheres to the surface of the biomaterial can be of three types: 1) metabolism dependent biosorption, 2) metabolism independent biosorption and 3) bioaccumulation of metal species (Gadd, 1990; Sag and Kutsal, 2001).

1) Metabolism dependent biosorption

This process is exhibited by living cells. Metal biosorption is active, where the metal ion binds to the cell surface (essentially the cell wall) by a single process or a combination of processes viz. physical adsorption or inorganic micro-precipitation, formation of coordination complex, ion excahange and so on (Volesky, 1990; Wang *et. al.*, 2000). The process involves the association of the heavy metal with the cellular metabolic process of the microorganism, however the metal concerned remains primarily adhered to the cell surface.

2) Metabolism independent biosorption

Metal binding to the cell surface could be passive and can occur in either living or non-living microorganisms. Non-viable biomass exhibits a higher affinity for metallic ions as compared to the living biomass (Ilhan *et. al.*, 2004). The process can be due to ionic interaction or simple physiochemical adsorption. The functional groups present on the cell surface as a mosaic often play the key role in the process the major functional groups reported to be involved include carboxyl (-COOH), phosphate (-PO4), thiol (-SH), amide ($-NH_2$)and hydroxide (-OH) (Volesky, 1990).

3) Metal accumulation

Metals can also be a part of cellular metabolism (Pabst *et. al.*, 2010; Campbell *et. al.*, 2002). Active metal sorption involves metabolic uptake of metal ions into the inner parts of the cell.

## FUNGAL BIOMASS AND METAL UPTAKE

Biosorption being a surface phenomenon may depend on polarity and surface area of the biosorbent. A high content of cell-wall material with a large number of sites for binding of metals in fungi thus makes it a suitable choice as a biosorbent. (Gadd, 1990).

The fungal cell wall provides mechanical strength to the cell and it is the interface of the cell with the external environment. It contributes to 30% of the dry mass of the cell. It is an extremely complex structure consisting of an elastic framework. It is like a mosaic of different functional groups.

The fungal cell wall presents a multi laminate, micro fibrillar structure and reveals two phases: i) the outer layer and ii) an inner layer of microfibrillar nature. The cell wall is primarily made up of polysaccharide, which contributes to 80% of the cellular dry weight, in the polysaccharide different proteins are anchored in different ways.

The chief components commonly found in fungal cell wall are as tabulated in Table: 1.

*Table 1. Chief Components of Fungal Cell Wall*

| Component Nature | Component Name |
|---|---|
| Fibrillar component | Cellulose |
| | β-glucan |
| | Chitin |
| Matricial component | Glucoproteins |
| | Chitosans |
| | α-glucan |
| | Lipids |
| | Ingorganic salt |
| | Pigments |

The composition of the cell wall material varies between the different fungal species. Studies mediated by electron microscopy reveals that in case of the mycellial members, chitin, is the primary wall component contributing to nearly 30% of the cellular dry weight, whereas, yeast, has a more complex cell wall composition, containing glucan, mannan, proteins and lipid. Different metal binding groups are also known to be present in fungal cell wall (Dhankar and Hooda, 2011).

## MODELLING OF BIOSORPTION

Adherence of the metals to the active binding sites on the available biomass continues to an equilibrium state where the amount of metal ions distributed in the sorbent and solution phase maintains a balance, therefore, detailed information on adsorption equilibrium is necessary to understand and optimize the process of metal biosorption.

### Isotherm Models

Adsorption equilibrium may be defined as the capacity of the adsorbent for the adsorbate.

To obtain the equilibrium value the amount of metal adhering to the sorbent (qe) is plotted against the final concentration of the metal present in solution (C).

$$Qe=V\ [Ci-C]/S$$

V = volume (L) of solution contacted with the sorbent; Ci = initial concentration of the sorbate ($mgL^{-1}$) and C = final concentration of the sorbate ($mgL^{-1}$); S = amount of biosorbent ($mgL^{-1}$).

Out of different isotherm models available to describe equilibrium sorption distribution, Langmuir and Freudlich models are by far the most commonly used.

**Langmuir model**: $\mathbf{Q_{eq} = Q_{max}.(b).C_{eq}/1+(b).C_{eq}}$ (Langmuir, 1918)

**Freundlich model**: $\mathbf{Q_{eq} = K(C_{eq})^{1/n}}$ (Freundlich, 1906)

Where, Qeq is the amount of metal ion biosorbed at equilibrium per unit weight of biomass; Ceq is the metal ion concentration at equilibrium; Qmax and b are Langmuir model constants and K and n are Freundlich model constants.

## Sorption Kinetics

The sorption kinetics describes uptake of the solute that finally controls the time of residence of a sorbate at the solid-solution interface. This will ultimately provide information about the pathways, as well as the mechanism of the process (Ho and McKay, 2000). The most commonly used models are:

**The pseudo-first-order equation** (Lagergren, 1898):

$$\text{Log } (q_e - q_t) = \log q_e - (k_{ad}/2.303)t$$

Where, $k_{ad}$ ($min^{-1}$) = rate constant of pseudo-first-order adsorption process.

The values of $k_{ad}$ were calculated from the plots of log ($q_e$ - $q_t$) vs. time (t).

**The pseudo-second-order equation** (Ho and McKay, 1999):

$$t/q_t = 1/kq_e^2 + (1/q_e)t$$

Where, k = rate constant, $q_t$ is the metal uptake capacity at time.

With the help of the above mentioned models the phenomenon of biosorption could be statistically established with respect to its energy consumption and viability.

## FACTORS CONTROLLING FUNGAL BIOSORPTION

Metal sorption by microbial biomass is known to be affected by several factors like, nature of the biomass, the type of the metal used and the ambient environmental factors. The major factors influencing the process of biosorption include metal ion concentration, biomass concentration in aqueous phase, temperature and pH (Das *et. al.*, 2008). Growth, nutrition, and age of the biomass, can also influence the process due to changes in cell wall composition, extracellular product formation, cell size, etc.

## Temperature

The biosorption reactions are generally exothermic in nature and the adsorption rate has an inverse relation with the incubation temperature. Ahalya *et. al.* (2003) reported that a temperature within a range of 20°C -35°C is most suitable for metal biosorption, higher temperature often affects the cell surface topography and thus reduces its capacity to adhere to metal particles.

## pH

pH of the aqueous phase has a very important role to play in the biosorption processes. The process is highly dependent on the changes in pH gradient in almost all kinds of biological systems used for the process including bacteria, algae, and fungi (Das *et. al.*, 2008). Generally, for most of the biomass types, metal uptake declined with the decrease of the pH of the solution from 6.0 to 2.5. Metal removal from solution has been recorded to be negligible at a pH below 2.0. However, a contrasting condition has been reported by RajaRao and Bhargavi (2013), where, metal uptake was augmented with an increase in the pH of the solution from 3.0 to 5.0. pH is also known to be affect the active metal binding sites, solubility of the metal, solution chemistry, activity of the functional groups present on the cell wall and the competition between co-ions. It has been reported that, there is an increase in the density of the negative charge present on the cell surface when there is an increase in the pH of the solution. The reason may be attributed to the process of de-protonation of the active metal binding sites leading to an increased rate of biosorption (Martinez-Juarez *et. al*., 2012). In addition, optimum value of the pH is a major controlling factor for metal sorption.

## Biomass Concentration

Biomass concentration also plays a major role on biosorption of metal from aqueous solution (Modak and Natarajan, 1995). Metal sorption is more with a low density of biomass as compared to higher density at equilibrium; therefore, cellular electrostatic interaction plays a vital role in metal uptake (Gourdon *et. al.*, 1990). When the concentration biomass is low, metal uptake increases, whereas, there is a sharp decline in the rate of biosorption with higher concentration of biomass as crowding leads to interference between the active metal binding sites (Malkov and Nuhoglu, 2005). High biomass concentration often posses restriction over the access of the metal ions to the binding sites (Fourest and Roux, 1992). The initial concentration however, provides an important driving force which helps the metal in solution to overcome all mass transfer resistance between the aqueous and solid phases and hence adsorb to the surface of the biomaterial (Zouboulis *et. al.*, 1997). An optimum concentration of biomass has been reported to facilitate biosorption, however, a concentration higher than that of the optimum may adversely affect biosorption (Gadd and White, 1985).

## Metal Ion Concentration

The concentration of the metal ion in solution has an impact on the rate of biosorption. With a high concentration of the solute in solution, the rate of biosorption is augmented. When the initial metal ion concentration is low, due to greater available sites for metal binding the process of sorption becomes independent of the metal concentration in solution. The contrast happens when the metal ion concentration increases in solution, then the attachment of the solute to cell surface is dependent on the initial metal ion concentration. Biosorption of Chromium was reported to increase with an increase in metal concentration from 2 to 6 mM, using *Aspergillus* sp. and *Rhizopus* sp. isolated from waste water (Ahmed *et. al.*, 2005). It is thus absolutely essential to identify the maximum saturation potential of a biosorbent, for which the highest possible intial metal ion concentration has to be determined, for execution of a successful biosorption process.

## Pre-treatment of Biomass

Physical pretreatment of the biomass by autoclaving, boiling and drying may interfere with the process of biosorption (Pal *et. al.*, 2006), while treatment with chemicals of alkaline nature has been reported to augment the process of metal sorption (Wang and Chen, 2006). Physical as well as chemical pretreatments are known to affect the cellular permeability and electric potential thereby exposing the metal binding groups making them accessible for the metal ions. Pre treating agents like alkali, acid, detergents and heat have been used for the purpose of cell surface modification (Ahalya *et. al*., 2003). Presence of both physical and chemical factors can affect biosorption in both positive as well as negative ways. Biosorbents are prepared by pre-treating the biomass by different methods. Effective metal biosorption on to cell surface depends on certain properties of the biomass like, number of active sites present on the cell surface, accessibility of the site for the metal and the chemistry involved in between the metal and the biosorbent (Ahluwalia and Goyal, 2005).

The physical factors affecting the cell-surface modification include heatng/autoclaving, freezing, lyophilization and drying of the cell, whereas, chemicals that affect the surface properties of a cell include detergents, organic solvents, alkali and acids. This kind of pre-treatment modifies the surface of the cell by either masking the functional groups present on the cell surface, removing them completely or by modifying the active metal binding sites (Vieira and Volesky, 2000). Removal of Cd has been studied by nine species of fungi in batch and continuous reactors, where, the pre-treating chemicals were used on the biomass for modification of the active metal binding stuctures viz. carboxyl, amino and phosphate (Huang *et. al.*, 1998). Illhan *et. al.,* (2004) studied the effect of pre-treatment on biosorption capacity of *Penicillium lanosa-coeruleum*, and reported that pre-treatment by heating or by using chemicals like NaOH and detergent augmented biosorption of Pb and Cu whereas, glutaraldehyde pretreatment improved biosorption of Ni. Kogrej and Pavko, (2001), used immobilized *Rhizopus nigricans* for removal of Pb from aqueous solution. Effect of pre-treatment on Pb biosorption capacity was studied by *Aspergillus versicolor*, *Penicillium verrucosum* and *Metarrhizium anisopliae* var. *anisopliae* by Cabuk *et. al.* (2005).

## METAL ELUTION POST BIOSORPTION FROM LOADED FUNGAL BIOMASS

Desorption is a process where the metal loaded biomass is eluted and it is made suitable for biosorption again. Desorption is very important when the used biomass is expensive or not readily available. The phenomenon is strongly dependent on the mechanism involved in biosorption and the nature of biosorbent. The eluant should not cause any damage to the biomass; it should also be environmentally compatible and effective. Dilute mineral acids such as sulfuric acid, hydrochloric acid and different organic acids (citric, acetic, gluconic, tartaric) and complexing agents (EDTA, thiosulfate) has been used for the purpose (Akthar *et. al.*, 1996). Interaction of the eluant with the biosorbent material should be restricted as far as possible in order to minimize the damage of the biosorbent and favour its reuse. The technology also ensures the possibility of recovery of valuable metals such as silver, gold, platinum, cadmium etc. which if disposed in to the environment may again get accumulated in the ecosystem and cause the same problem.

Several microbes both in living and non-living forms are capable of sorbing several toxic materials from solution including heavy metals. Use of algae, bacteria and fungi, as biosorbents of heavy metals are ample.

**Fungal biomaterial** has been proved to be efficient as biosorbent. List of fungal members reported to act as metal biosorbents are presented in Table 2.

*Table 2. List of fungal members reported as metal bio-sorbents*

| Organism | Metal sorbed | Reference |
|---|---|---|
| *Sacchromyces cerevisae* | Mn | Fadel *et. al.*, 2015 |
| *S. cerevisae* | Pb, Zn, Cr, Co, Cd and Cu | Farhan and Khadom, 2015 |
| *Paecilomyces lilacinus*<br>*Mucoromycote sp.* | Cd | Xia *et. al.*, 2015 |
| *Aspergillus niger* | U | Wang *et. al.*, 2017 |
| *A. niger,*<br>*A. flavus* | Cu and Pb | Iram and Abrar, 2015 |
| *A. niger* | Cu and Ni | Rao and Bhargavi, 2013 |
| *A. niger* | Cu and Ni | Javaid *et. al.*, 2011 |
| *A. niger* | Cr | Sadhana Mala *et.al.*, 2006 |
| *A. niger* | Cu, Ni, Cr, and Zn | Filipovic-Kovacevic *et. al.*, 2000 |
| *A. fumigatus* | Pb, Cr, Cd and Zn | Shazia *et. al.*, 2013 |
| *A. aculeatus* | Cd | Pandey and Banerjee, 2012 |
| *A. versicolor* | Cr, Cu and Ni | Tastan and Donmez, 2010 |
| *A. flavus* | Cr | Deepa *et. al.*, 2006 |
| *A. foetidus* | Cr | Prasenjit and Sumathi, 2005 |
| *A. flavus,*<br>*A. fumigatus,*<br>*Cladosporium sp.,*<br>*Candida albicans*<br>*Mucor rouxii,*<br>*Helminthosporium sp.,* | Hg | Martinez-Juarez *et. al.*, 2012 |
| *Aspergillus sp.,*<br>*Rhizopus sp.* | Cd, Cr, Co, Cu and Ni | Ahmad *et. al.*, 2005 |
| *Aspergillus niger,*<br>*Penicillium chrysogenum*<br>*Rhizopus oryzae* | Zn and Co | Tahir *et. al.*, 2017 |
| *Aspergillus* sp. | Cr and Ni | Congeevaram *et. al.*, 2007 |
| *Aspergillus sp.* | Cr | Sen and Ghosh Dastidar, 2007 |
| *Aspergillus* sp. | Cr | Srivastava and Thakur, 2006 |
| *P. lanosa-coeruleum* | Pb, Cu and Ni | Ilhan *et. al.*, 2004 |
| *P. cyclopium* | Cu and Co | Tsekova *et. al.*, 2006 |
| *Mucor racemosus* | Cu, Zn, Pb | El-Morsy *et. al.*, 2013 |
| *M. rouxii* | Ni, Zn, Pb and Cd, | Yan and Viraraghavan, 2008 |
| *Pleurotus eous* | Pb, Cr and Ni | Suseem and Mary, 2014 |
| *Morganella morganii* | Cr | Ergul-Ulger *et. al.*, 2014 |
| *Talaromyces helicus* | Cu | Romero *et. al.*, 2006 |
| *Agaricus microsporous* | Cd, Hg and Cu | Garcia *et. al.*, 2005 |
| *Phanrochaete chrysosporium* | Cr | Marandi, 2011 |
| *Phanrochaete chrysosporium* | Ni and Pb | Ceribasi and Yetis, 2001 |
| *Morteriella* sp. | Co | Pal *et. al.*, 2006 |
| *Rhizopus oryzae,*<br>*R. oligosporus,*<br>*R. arrhizus,*<br>*A. oryzae* | Cd | Yin *et. al.*, 1999 |
| *R. arrhizus* | Cr and Fe | Sag and Kutsal, 1996 |
| *R. stolonifer,*<br>*Macrophomina phaseolina* | Pb, Cd, Cu and Zn | Fawzy *et. al.*, 2017 |
| *Volvariella volvacea* | Pb, Cd, Co, and Cu | Purakayastha and Mitra, 1992 |

## APPLICATIONS OF FUNGAL BIOMATERIAL AS BIOSORBENT

Bioremoval of Cr(VI) has also been executed by development of consortium of the organisms isolated from the Sukinda chromite mines (Samuel *et.al.*, 2012).

## COST EFFECTIVENESS OF SORPTION USING FUNGAL BIOMASS

Fungi are naturally available raw material in metal rich soil; they are ubiquitous and play significant role in the ecosystem as a decomposer, nutrient recycler and bio-transformer. The biomass produced in fermentation and other industrial processes can act as a source of very good and cheap biosorbent. A combination of biosorption with metabolically dependent processes like bioreduction and bioprecipitation called intrabiological hybrid technologies can be used in reactor designing. Improved mathematical models justifying the dynamics of the process and computer simulations could also be used in future for better understanding and improvement of the process.

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