

Review

Biosorption: An eco-friendly alternative for heavy metal removal

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Accepted 13 November, 2007

Heavy metals occur in immobilized form in sediments and as ores in nature. However due to various human activities like ore mining and industrial processes the natural biogeochemical cycles are disrupted causing increased deposition of heavy metals in terrestrial and aquatic environment. Release of these pollutants without proper treatment poses a significant threat to both environment and public health, as they are non biodegradable and persistent. Through a process of biomagnification, they further accumulate in food chains. Thus their treatment becomes inevitable and in this endeavor, biosorption seems to be a promising alternative for treating metal contaminated waters. This technology employs various types of biomass as source to trap heavy metals in contaminated waters. The biosorbent is prepared by subjecting biomass to various processes like pretreatment, granulation and immobilization, finally resulting in metal entrapped in bead like structures. These beads are stripped of metal ions by desorption which can be recycled and reused for subsequent cycles. This technology out- performs its predecessors not only due to its cost effectiveness but also in being eco-friendly i.e., where other alternatives fail.

Key words: Biosorption, biomass, biosorbents, pretreatment, immobilization.

INTRODUCTION

Water bodies are being overwhelmed with bacteria and waste matter. Among toxic substances reaching hazardous levels are heavy metals (Regine and Volesky, 2000). Heavy metals of concern include lead, chromium, mercury, uranium, selenium, zinc, arsenic, cadmium, silver, gold, and nickel (Ahalya et al., 2003). Heavy metal pollution in the aquatic system has become a serious threat today and of great environmental concern as they are non-biodegradable and thus persistent. Metals are mobilized and carried into food web as a result of leaching from waste dumps, polluted soils and water. The metals increase in concentration at every level of food chain and are passed onto the next higher level—a phenomenon called bio-magnification (Paknikar et al., 2003). Heavy metals even at low concentrations can cause toxic

city to humans and other forms of life, its adverse effects on human health are quite evident from Table 1. The toxicity of metal ion is owing to their ability to bind with protein molecules and prevent replication of DNA and thus subsequent cell division (Kar et al., 1992). To avoid health hazards it is essential to remove these toxic heavy metals from waste water before its disposal. Main sources of heavy metal contamination include urban industrial aerosols, solid wastes from animals, mining activities, industrial and agricultural chemicals. Heavy metals also enter the water supply from industrial and consumer water or even from acid rain which breaks down soils and rocks, releasing heavy metals into streams, lakes and ground water.

Techniques presently in existence for removal of heavy metals from contaminated waters include: reverse osmosis, electro dialysis, ultrafiltration, ion-exchange, chemical precipitation, phytoremediation, etc. However, all these methods have disadvantages like incomplete metal removal, high reagent and energy requirements,

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Abbreviations: Cd Te- cadmium tellurium.

Table 1. Types of heavy metals and their effect on human health

Pollutants	Major sources	Effect on human Health	Permissible level (ppm)
Arsenic	Pesticides, fungicides, metal smelters	Bronchitis, dermatitis	0.02
Cadmium	Welding, electroplating, pesticide fertilizer CdNi batteries, nuclear fission plant	Kidney damage, bronchitis, gastrointestinal disorder, bone marrow, cancer	0.06
Lead	Paint, pesticide, smoking, automobile emission, mining, burning of coal	Liver, kidney, gastrointestinal damage, mental retardation in children	0.1
Manganese	Welding, fuel addition, ferromanganese production	Inhalation or contact causes damage to central nervous system	0.26
Mercury	Pesticides, batteries, paper industry,	Damage to nervous system, protoplasm poisoning	0.01
Zinc	Refineries, brass manufacture, metal Plating, plumbing	Zinc fumes have corrosive effect on skin, cause damage to nervous membrane	15

generation of toxic sludge or other waste products that require careful disposal (Ahalya et al., 2003). With increasing environmental awareness and legal constraints being imposed on discharge of effluents, a need for cost-effective alternative technologies are essential. In this endeavor, microbial biomass has emerged as an option for developing economic and eco-friendly waste water treatment process.

Biosorption can be defined as “a non-directed physico-chemical interaction that may occur between metal /radionuclide species and microbial cells” (Shumate and Stranberg, 1985). It is a biological method of environmental control and can be an alternative to conventional contaminated water treatment facilities. It also offers several advantages over conventional treatment methods including cost effectiveness, efficiency, minimization of chemical/biological sludge, requirement of additional nutrients, and regeneration of biosorbent with possibility of metal recovery.

The biosorption process involves a solid phase (sorbent or biosorbent; usually a biological material) and a liquid phase (solvent, normally water) containing a dissolved species to be sorbed (sorbate, a metal ion). Due to higher affinity of the sorbent for the sorbate species the latter is attracted and bound with different mechanisms. The process continues till equilibrium is established between the amount of solid-bound sorbate species and its portion remaining in the solution. While there is a preponderance of solute (sorbate) molecules in the solution, there are none in the sorbent particle to start with. This imbalance between the two environments creates a driving force for the solute species. The heavy metals adsorb on the surface of biomass thus, the biosorbent becomes enriched with metal ions in the sorbate.

Mechanisms involved in biosorption can be classified taking into account various criteria that are, based on cell metabolism, they are classified as metabolism dependent and non- metabolism dependent while based on location of the sorbate species it is classified as extra cellular accumulation/precipitation, cell surface sorption /precipitation and intra cellular accumulation. The adsorbed ions are transported across the membrane in the same mechanism by which metabolically important ions such as potassium, magnesium, and sodium are conveyed. These mechanisms comprise (i) physical adsorption e.g., electrostatic interaction has been demonstrated to be responsible for copper biosorption by bacterium *Zooglea ramigera* and alga *Chorella vulgaris* (Aksu et al., 1992), (ii) ion exchange e.g., biosorption of copper by fungi *Ganoderma lucidium* and *Asperigillus niger* (Muraleedharan and Venkobachr, 1990), (iii) complexation e.g., biosorption of copper by *C. vulgaris* and *Z. ramigera* takes place through both adsorption and formation of co-ordinate bonds between metals and amino or carboxyl groups of cell walls (Aksu et al., 1992). Various biosorption mechanisms mentioned above can take place simultaneously. Figure 1 shows a generalized schematic process of biosorption for heavy metal removal.

A successful biosorption process requires preparation of good biosorbent. The process starts with selecting various types of biomass. Pretreatment and immobilization are done to increase the efficiency of the metal uptake. The adsorbed metal is removed by desorption process and the biosorbent can be reused for further treatments.

SELECTION AND TYPES OF BIOMASS

While choosing the biomass for metal biosorption, its origin is a major factor to be taken into account. Biomass

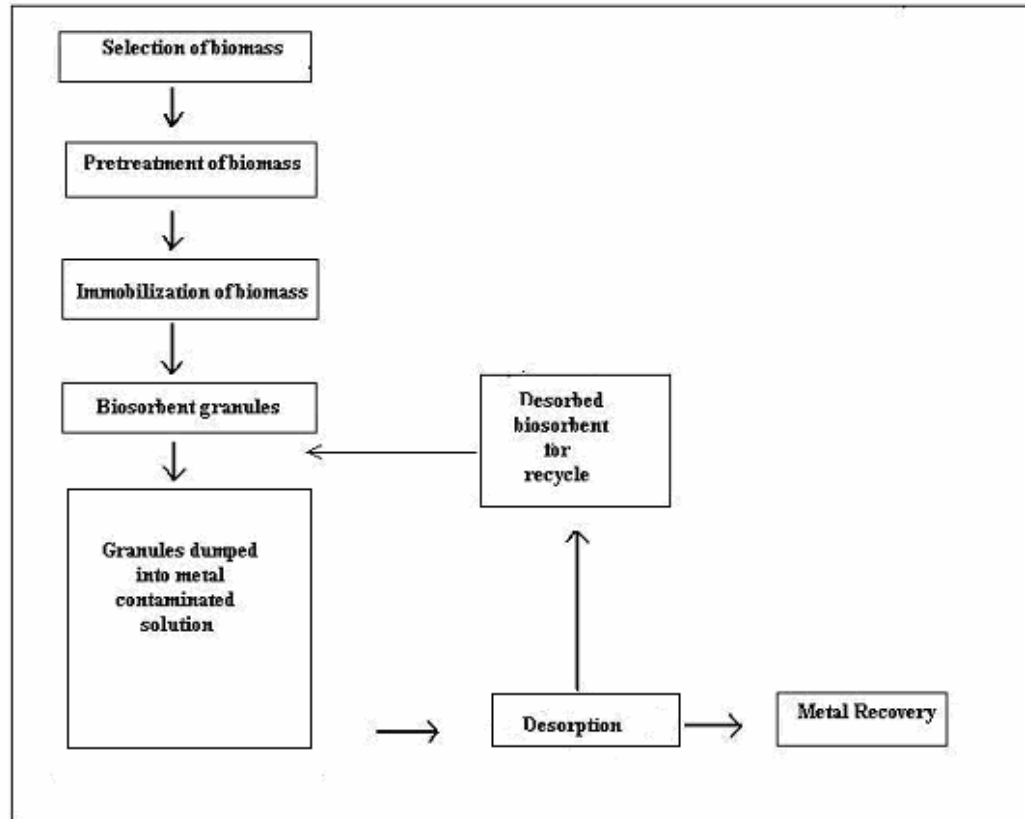


Figure 1. Schematic representation of biosorption procedure.

can come from, activated sludge or fermentation waste from industries like those of food, dairy and starch. Also, organisms (e.g., bacteria, yeast, fungi and algae) coming from their natural habitats are good sources of biomass. Fast growing organisms that are specifically cultivated for biosorption purposes (e.g., crab shells, seaweeds) (Regine and Volesky, 2000) can be used as biosorbents. Apart from the microbial sources even agricultural products such as wool, rice, straw, coconut husks, peat moss, exhausted coffee (Dakiky et al., 2002), waste tea (Ahluwalia and Goyal, 2005), walnut skin, coconut fibre, cork biomass (Chubar et al., 2003), seeds of *Ocimum basilicum* (Melo and D'Souza, 2004), defatted rice bran, rice hulls, soybean hulls and cotton seed hulls (Teixeria et al., 2004), wheat bran, hardwood (*Dalbergia sissoo*) sawdust, pea pod, cotton and mustard seed cakes, (Saeed et al., 2002) are also proven as good biomass sources. However, sea weeds, molds, yeasts, bacteria have been tested for metal biosorption with encouraging results (Regine and Volesky, 2000).

Seaweeds

Seaweeds are large group of marine benthic algae. They

offer several advantages for biosorption because of their larger surface area. This feature offers a convenient basis for the production of biosorbent particles suitable for sorption process. They contain many polyfunctional metal-binding sites for both cationic and anionic metal complexes. Potential metal cation-binding sites of algal cell components include carboxyl, amine, imidazole, phosphate, sulphate, sulphhydryl, hydroxyl and chemical functional groups contained in cell proteins and sugars (Crist et al., 1981). Brown algae stand out as very good biosorbent of heavy metals (Romera et al., 2006). Their cell walls contain fucoidin and alginic acid. The alginic acid offers anionic carboxylate and sulfate ions at neutral pH. Table 2a shows examples of various heavy metals adsorbed by seaweeds.

Fungi and yeasts

The majority of fungi show filamentous or hyphal growth. Cell walls of fungi present a multi-laminate architecture where up to 90% of their dry mass consists of amino or non-amino polysaccharides. The fungal cell walls can be considered as a two phase system consisting of chitin framework embedded on an amorphous polysaccharide

Table 2a. Heavy metal adsorbing capability of various sea weeds.

Algae	Metal adsorbed	Reference
<i>Chlorella emersonii</i>	Cd	Arkipo et al. (2004)
<i>Sargassum muticum</i>	Cd	Loderro et al. (2004)
<i>Ascophyllum sargassum</i>	Pb,Cd	Volesky and Holan (1995)
<i>Ulva reticulata</i>	Cu(II)	Viajayaraghavan et al. (2004)
<i>brown sea weeds</i>	Cr	Yeoung-Sang et al. (2001)
<i>Ecklonia species</i>	Cu(II)	Park et al. (2005)

Table 2b. Some fungal species used in metal biosorption.

Fungi	Metal adsorbed	Reference
<i>Phanerochaete chrysosporium</i>	Ni(II),Pb(II)	Haluk and Ulki (2001)
<i>Aspergillus niger</i>	Cd	Barros et al. (2003)
<i>Aspergillus fumigatus</i>	Ur(VI)	Bhainsa and D'Souza (1999)
<i>Aspergillus terreus</i>	Cu	Ruchi et al. (2003)
<i>Penicillium chrysogenum</i>	Au	Niu and Volesky (1999)

Table 2c. Various yeast species used for metal biosorption.

Yeast	Metal adsorbed	Reference
<i>Saccharomyces cerevisiae</i>	Uranium	Volesky and May-Phillips (1995)
<i>Saccharomyces cerevisiae</i> , <i>Kluyveromyces fragilis</i>	Cadmium	Bashar et al. (2003)
<i>Saccharomyces cerevisiae</i>	Methyl mercury and Hg(II)	Madrid et al. (1995)

matrix (Yan and Viraraghavan, 2000). The cell walls are rich in polysaccharides and glycoproteins such as glycans [β -1-6 and β -1-3 linked D-glucose residues], chitin (β -1-4 linked N-acetyl-D-glucosamine), chitosan (β -1-4 linked D-glucosamine), mannans (β -1-4 linked mannose) and phosphormannans (phosphorylated mannans). Various metal binding groups, viz amine, imidazole, phosphate, sulphate, sulfhydryl and hydroxyl are present in the polymers (Crist et al., 1981). *Saccharomyces cerevisiae* can remove toxic metals, recover precious metals and clean radio-nuclides from aqueous solutions to various extents. *S. cerevisiae* is a product of many single cell and alcohol fermentations, it can be procured in large quantity at low cost. *Saccharomyces* has the ability to differentiate between different metals such as selenium, antimony and mercury based on their toxicity. This property makes *S. cerevisiae* useful in analytical measurements (Wang and Chen, 2006). Tables 2b, 2c show examples of heavy metals adsorbed by various fungi and yeast respectively.

Bacteria

A great deal of heterogeneity exists among different

bacterial species in relation to their number of surface binding sites, binding strength for different ions and the binding mechanisms (Paknikar et al., 2003). Cell walls of bacteria and cyanobacteria are principally composed of peptidoglycans which consist of linear chains of the disaccharide N-acetylglucosamine, β -1,4-N-acetylmuramic acid with peptide chains. Gram positive cell walls and surfaces have a negative charge density owing to the peptidoglycan network, a macromolecule consisting of strands of alternating glucosamine and muramic acid residues, which are often N-acetylated. Carboxylate groups at the carboxyl terminus of individual strands provide bulk of anionic character to the cell wall. The phosphodiester of teichoic acid and the carboxyl groups of teichuronic acid contribute to the ion exchange capacity of cell walls (Paknikar et al., 2003). Table 2d shows examples of various heavy metals adsorbed by bacteria.

PRETREATMENT OF BIOMASS

Biosorbents are prepared initially by pretreating the biomass with different methods. The importance of any given group of biosorption of a certain metals by a certain

Table 2d. Bacterial species exploited in metal biosorption.

Bacteria	Metal adsorbed	Reference
<i>Bacillus polymyxa</i>	Cu	Philip and Venkobachr (2001)
<i>Bacillus coagulans</i>	Cr(VI)	Srinath et al. (2003)
<i>Eschereria coli</i>	Hg	Weon et al. (2003)
<i>Eschereria coli</i>	Cu,Cr,Ni	Churchill et al. (1995)
<i>Pseudomonas species</i>	Cr(VI),Cu(II),Cd(II),Ni(II)	Muraleedharan et al. (1991)

biomass depends on various factors such as the number of sites in the biosorbent material, the accessibility of the sites, the chemical state of the site (i.e., availability) and affinity between site and metal (i.e., binding strength) (Regine and Volesky, 2000). Biomass can be pretreated directly however, if it is larger in size (seaweeds), they are sized into fine particles or granules and they are further treated in several ways. Methods involved in pretreatment include heat treatment, detergent washing, employing acids, alkalies, enzymes, etc. Heat treatment and detergent washing expose additional metal binding groups (Gadd et al., 1988); enzymes destroy unwanted components and increase sorption efficiency (Ting and Teo, 1994). In case of alkali pretreatment, bioadsorption capacity of *Mucor rouxii* biomass was significantly enhanced in comparison with autoclaving, while pretreatment of biomass with acid resulted in decreased bioadsorption of heavy metals (Kapoor and Viraraghavan, 1998; Yan and Viraraghavan, 2000). This can be attributed to binding of H⁺ ions to biomass after acid treatment resulting in reduced heavy metals adsorption.

IMMOBILIZATION OF BIOMASS

Microbial biomass consists of small particles with low density, poor mechanical strength and little rigidity. However, biosorbents are hard enough to withstand the application pressures, water retention capacity, porous and/or "transparent" to metal ion sorbate species, and have high and fast sorption uptake even after repeated regeneration cycles, also because of immobilization, the biosorbent will have better shelf-life and offers easy and convenient usage compared to free biomass, which is easily biodegradable (Volesky and May-Phillips, 1995). Hence, the biomass is to be immobilized before being subjected to biosorption. The principal techniques available for application of biosorption are based on (i) adsorption on inert supports e.g., activated carbon was used as a support for *Enterobacter aerogens* biofilm (Scott and Karanjakar, 1992; Wei-Bin et al., 2006); (ii) entrapment in polymeric matrix e.g., polymers used were calcium alginate (Costa and Leite, 1991; Peng and Koon, 1993), polyacrylamide (Macaskie et al., 1987; Michel et al., 1986; Takehiko, 2004; Wong and Kwok, 1992)

polysulfone (Sudha and Abraham, 2003; Vijayaraghavan and Yeoung-Sang, 2007) and polyethylenimine (Wilke et al., 2006); (iii) covalent bonds to vector compounds (Holan et al., 1993; Mahan and Holcombe, 1992); (iv) cell cross-linking (Holan et al., 1993). However, the last two techniques are majorly employed for algal immobilization. Table 3 gives examples of various immobilization matrices used for the study of metal adsorption.

DESORPTION AND METAL RECOVERY

The regeneration of the biosorbent may be crucially important for keeping the process cost down and in opening the possibility of recovering the metals extracted from the liquid phase. For this purpose it is desirable to desorb the sorbed metals and to regenerate the biosorbent material for another cycle of application. The desorption process should yield the metals in a concentrated form, restore the biosorbent close to the original state for effective reuse with undiminished metal uptake and no physical changes or damages to the biomass. Dilute mineral acids (HCl, H₂SO₄, HNO₃) have been used for the removal of metals from biomass (De Rome and Gadd, 1987; Holan et al., 1993; Puranik and Paknikar, 1997; Zhou and Kiff, 1991) and also organic acids (Citric, acetic, lactic) and complexing agents (EDTA, thiosulphate, etc) can be used for metal elution without affecting the biosorbent (Mattuschka and Straube, 1993).

The technology also has some novel applications like recovering economic heavy metals like silver, tellurium, cadmium, etc, from waste cadmium tellurium photovoltaic cells, which if disposed into landfill sites, may pose severe environmental and health hazards. It can also be used to remove heavy metals like mercury, arsenic, lead, etc sequestered in food and food products caused due to metal accumulation in plants.

CONCLUSION

Despite the fact that the technology also suffers inherent disadvantages like early saturation of biomass, little bio-

Table 3. Various immobilization matrixes used with biomass for metal adsorption

Immobilization matrix	Biomass types	Metal adsorbed	Reference
Calcium alginate	<i>Chryseomonas luteola</i> <i>Laminaria digitata</i> <i>Bacillus cereus</i> <i>Luffa cylindrical</i>	Cu, Ni Cu, Cd, Pb Pb Cd	Guven et al. (2005) Sergios et al. (2006) Paul et al. (2006) Iqbal et al., 1997
Polyurethane	<i>Pseudomonas aeruginosa</i> <i>Ascophyllum nodosum</i> <i>Asperigillus niger</i> <i>Phanerochaete chrysosporium</i> <i>Asperigillus terreus</i> <i>Rhizopus delemar</i>	Ur Cu Cu Pb, Cu, Cd Fe, Cr, Ni Co, Cu, Ni	Hu and Reeves (1997) Alhakawati and Banks (2004) Tsekova and Ilieva (2001) Pakshirajan and Swaminathan (2006) Dias et al. (2002) Kolishka and Galin. (2002)
Silica	Algasorb <i>Saccharomycete</i> <i>Asperigillus niger</i>	Cu, Ni, Ur, Pb Cu, Zn, Fe, Ni, Pb Cr, Cu, Zn, Cd	Beveridge and Fyfe (1985) Fan and Xiaotao (2002) Baytak et al. (2005)
Polyacrylamide	<i>Citrobacter</i> , <i>Pseudomonas maltophilia</i>	Ur, Cd, Pb, Au	Macaskie and Dean (1989) Takehiko (2004)

logical control over the characteristics of biosorbents. It offers several advantages including cost effectiveness, high efficiency, minimization of chemical/biological sludge, and regeneration of biosorbent with possibility of metal recovery. In countries, with the rush for rapid industrial development coupled with lack of awareness about metal toxicity there is an urgent need for developing an economical and eco-friendly technology which satisfies these demands when other conventional methods fail.

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