Chapter 2
Potential of Biosorption Technology

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Abstract Heavy metal removal from inorganic effluent can be achieved by conventional treatment such as chemical precipitation, ion exchane or flotation, however each treatment has its limitation. Recently, sorption, namely biosorption has become one of the alternative treatments. Basically, sorption is a mass transfer process by which a substance is transferred from the liquid phase to the surface of a solid, and substance becomes bound by physical and/or chemical interactions. Due to large surface area, high sorption capacity and surface reactivity of sorbents, sorption can be utilized as low-cost alternative to conventional processes. For example, materials locally available in large quantities such as natural materials, living or dead biomass, agricultural waste or industrial byproducta can be used as biosorbents with quite little processing. This chapter discusses the significance of the heavy metal removal from waste streams and provides brief oveview of the potential of biosorbents and biosorption technology. Considered are various aspects of utilization of microbial and plant derived biomass in connection with biosorption and the possibility of exploiting such material for heavy metal removal form solutions.

Keywords Heavy metals • Biomass • Biosorption • Biosorbent • Bioavailability

2.1 Significance of Metal Recovery—Industrial and Environmental View

Heavy metal pollution is one of the most important environmental problems today. Various industries produce and discharge wastes containing different heavy metals into the environment, such as mining and smelting of metalliferous ores, surface

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finishing industry, energy and fuel production, fertilizer and pesticide industry and application, metallurgy, iron and steel, electroplating, electrolysis, electro-osmosis, leatherworking, photography, electric appliance manufacturing, metal surface treating, aerospace and atomic energy installation etc. (Wang and Chen 2009). Among these, the following four appear as the main priority targets, particularly in the industrialized world (Volesky 2007):

1. acid mine drainage (AMD)—associated with mining operations;
2. electroplating industry waste solutions (growth industry);
3. coal-based power generation (throughput of enormous quantities of coal);
4. nuclear power generation (uranium mining/processing and special waste generation).

Three kinds of heavy metals are of concern, including toxic metals (such as Hg, Cr, Pb, Zn, Cu, Ni, Cd, As, Co, Sn, etc.), precious metals (such as Pd, Pt, Ag, Au, Ru etc.) and radionuclides (such as U, Th, Ra, Am, etc.) (Wang and Chen 2009, 2006).

Methods for removing metal ions from aqueous solution mainly consist of physical, chemical and biological technologies. Conventional methods for removing metal ions from aqueous solution involve chemical precipitation, chemical and electro coagulation, filtration, ion exchange, electrochemical treatment, membrane technologies, adsorption on activated carbon, zeolite, evaporation etc. However, chemical precipitation and electrochemical treatment are ineffective, and also produce large quantity of sludge required to treat with great difficulty. Ion exchange, membrane technologies and activated carbon adsorption process are extremely expensive when treating large amount of water and wastewater containing heavy metal in low concentration, they cannot be used at large scale. The advantages and disadvantages of the conventional metal removal technologies were summarized by Volesky (2001).

The development and implementation of cost-effective process for removal/recovery of metals is essential to improve the competitiveness of industrial processing operations. Disadvantages, together with the need for more economical and effective methods for the recovery of metals from wastewaters, have resulted in the development of alternative separation technologies (Volesky and Naja 2007).

In recent years there has been a trend toward the implementation of passive treatment schemes. These take advantage of naturally occurring geochemical and biological processes to improve water quality with minimal operation and maintenance requirements. Biological removal includes the use of microorganisms (fungi, algae, bacteria), plants (live or dead) and biopolymers and may provide a suitable means for heavy metals treatment from wastewater.

Microoorganisms react with metals and minerals in natural and synthetic environments, altering their physical and chemical state, with metals and minerals also able to affect microbial growth, activity and survival. In addition, many minerals are biogenic in origin, and the formation of such biominerals is of global geological and industrial significance. Microbes can somehow interact with all elements found in the periodic table (including actinides, lanthanides, radionuclides). The elements can be accumulated by or be associated with microbial biomass depending on the context and environment. Microbes possess transport systems for essential metals; inessential metal species can also be taken up. Microbes are also capable of mediating metal and mineral bioprecipitation, e.g. by metabolite production, by changing the physico-chemical microenvironmental conditions around the biomass, and also by the indirect release of metal-precipitating substances from other activities, e.g. phosphate from organic decomposition or phosphate mineral solubilization. Microbial cell walls, outer layers, and exopolymers can sorb, bind or entrap many soluble and insoluble metal species as well as e.g. clay minerals, colloids, oxides, etc. which also have significant metal-sorption properties. Redox transformations are also widespread in microbial metabolism, some also mediated by the chemical activity of structural components.

Metals exhibit a range of toxicities towards microbes, and while toxic effects can arise from natural geochemical events, toxic effects on microbial communities are more commonly associated with anthropogenic contamination or redistribution of toxic metals in aquatic and terrestrial ecosystems. Such contamination can arise from aerial and aquatic sources, as well as agricultural and industrial activities, and domestic and industrial wastes. In some cases, microbial activity can result in remobilization of metals from waste materials and transfer into aquatic systems (Gadd 2010, 2009; Violante et al. 2008). It is commonly accepted that toxic metals, their chemical derivatives, metalloids and organometals can have significant effects on microbial populations and, under toxic conditions, almost every index of microbial activity can be affected (Giller et al. 2009).

There is a number of mechanisms involved in detoxification and transformation of metals depending on the organism and the cellular environment; mechanisms may be dependent on and/or independent of metabolism. A variety of mechanisms may be involved in transport phenomena contributing to decreased uptake and/or efflux. A variety of specific or non-specific mechanisms may also effect redox transformations, intracellular chelation and intracellular precipitation. Biomineral formation (biomineralization) may be biologically induced, i.e. caused by physico-chemical environmental changes mediated by the microbes, or biologically controlled. The mechanism by which microorganisms remove metals from solutions are: (1) extracellular accumulation/precipitation; (2) cell-surface sorption or complexation; and (3) intracellular accumulation (Muraleedharan et al. 1991). Among these mechanisms, extracellular accumulation/precipitation may be facilitated by using viable microorganisms, cell-surface sorption or complexation which can occur with alive or dead microorganisms, while intracellular accumulation requires microbial activity (Asku et al. 1991). Although living and dead cells are both capable of metal accumulation, there are differences in the mechanisms involved, given on the extent of metabolic dependence (Gadd and White 1990).

The major mechanisms of microbial metal transformations between soluble and insoluble metal species include chemolithotrophic leaching, chemoorganotrophic leaching, rock and mineral bioweathering and biodeterioration, biocorrosion, redox mobilization, methylation, complexation (with microbial products such as extracellular polymers (EPS) and metallothionein like proteins) in case of soluble metal species while for latter case we speak about biosorption, accumulation, biomineral formation, redox immobilization, metal sorption to biogenic minerals and formation of metalloid nanoparticles (Roane et al. 2005). The relative balance between such processes depends on the environment and associated physico-chemical conditions and the microbe(s) involved as well as relationships with plants, animals and anthropogenic activities. Chemical equilibria between soluble and insoluble phases are influenced by abiotic components, including dead biota and their decomposition products, as well as other physico-chemical components of the environmental matrix, e.g. pH, water, inorganic and organic ions, molecules, compounds, colloids and particulates. Solubilization can occur by chemolithotrophic (autotrophic) and chemo-organotrophic (heterotrophic) leaching; siderophores, including phytosiderophores released by plants, and other complexing agents; redox reactions; methylation and demethylation; and biodegradation of organo-radionuclide complexes. Immobilization can occur by biosorption to cell walls, exopolymers, other structural components and derived/excreted products; precipitation can be a result of metabolite release (e.g. sulfide, oxalate) or reduction; transport, accumulation, intracellular deposition, localization and sequestration; and adsorption and entrapment of colloids and particulates. The overall system is also affected by reciprocal interactions between biotic and abiotic components of the ecosystem such as abiotic influence on microbial diversity, numbers and metabolic activity; ingestion of particulates and colloids (including bacteria) by phagotrophs; and biotic modification of physico-chemical parameters including redox potential, pH, O_2, CO_2, other gases and metabolites, temperature, and nutrient depletion. An important role play also plants and their metabolites in extraction influencing the composition of bacterial composition in soil (Uhlík et al. 2009; Macek et al. 2009). Plant biomass itself can exhibit improved metal accumulation capacity (Kotrba et al. 2009).

The combined effects of above mentioned parameteres influence so called speciation of the metals. At high pH metals are predominantly found as insoluble mineral phosphates and carbonates while at low pH they are more commonly found as free ionic species or as soluble organometals. Also redox potential of an environment influences metal speciation. Redox potential is established by oxidation/reduction reactions in the environment (reactions that are relatively slow), particularly in soils, but also metabolic activities of microorganisms play essential roles in establishing redox potential as well.

In contrast to metal speciation, metal bioavailability is determined by the solubility of metal species present and the sorption of metal species by solid surfaces including soil minerals, organic matter and colloidal materials. Organic matter is a significant source of metal complexation. Living organisms, organic debris and humus sorb metals, reducing metal solubility and bioavailability. Organic matter consists of humic and nonhumic material. Nonhumic substances include amino acids, carbohydrates, organic acids, fats etc. Humics consist of high molecular weight compounds altered from their original structures. Anionic functional groups bind cation metals, sequestering metal activity. Some organic complexing agents form soluble complexes with metals while others form insoluble structures. In latter case toxic metal concentrations in water phase may be reduced to nontoxic levels.

Metal bioavailability generally increases with decreasing pH. This is due to the presence of phosporic, sulfuric and carbonic acids which solubilize organic and particulate bound metals. For example solubility can increase in surface layers where plant exudates, microbial activity, moisture and leaching lower the pH (Roane et al. 2005).

2.2 Biosorption—A Suitable Approach for Heavy Metal Removal

Numerous strategies have potential applicability in the removal of metals, however only few field-based studies were performed. Biohydrometallurgy is a recent technical area that is based on specific interactions between microorganisms and minerals to extract metals from raw materials. The technological breakthroughs must allow the integration of innovative biotechnology-based processes for recovery and/or removal of metals from primary materials such as ores and concentrates, secondary materials such as mining wastes, metallurgical slags, and combustion/power plant ashes. The investigated biotechnologies, covering all the aspects of the application of biohydrometallurgy, have included bioleaching, biooxidation, biosorption, bioreduction, bioaccumulation, bioprecipitation, bioflotation, bioflocculation, and biosensors. They should give consideration for eco-design and a reduced impact on environment.

One such important and widely studied alternative is biosorption, where certain types of biomass are able to bind and concentrate metals from even very dilute aqueous solutions. Microbial biomass provides a metal sink, by biosorption to cell walls, pigments and extracellular polysaccharides, intracellular accumulation, or precipitation of metal compounds in and/or around cells, hyphae or other structures. All microbial materials can be effective biosorbents for metals except for mobile alkali metal cations like Na^+ and K^+, and this can be an important passive process in living and dead organisms (Gadd 1993).

A biosorption-based process offers a number of advantages when compared to the conventional methods used. However, for all practical priority reasons, the metal biosorption studies are focusing on mainly anthropogenic point sources of metal releases into the environment (Volesky 2007). The process of biosorption has many attractive features including the selective removal of metals over a broad range of pH and temperature, its rapid kinetics of adsorption and desorption and low capital and operation cost. Biosorbent an easily be produced using inexpensive growth media or obtained as a by-product from industry. It is desirable to develop biosorbents with a wide range of metal affinities that can remove a variety of metal cations. Alternatively a mixture of non-living biomass consisting of more than one type of microorganisms can be employed as biosorbents (Ahluwalia and Goyal 2007).

Based upon the metal binding capacities of various biological materials, biosorption can separate heavy metals from various waste material including wastewater (Vilar et al. 2007; Pavasant et al. 2006). Biosorption can be characterized as the removal of heavy metals using a passive binding process with nonliving microorganisms including bacteria, fungi, and yeasts (Parvathi et al. 2007), and other biomass types that are capable of efficiently collecting heavy metals. Obviously, some of the advantages biosorption has over conventional treatment methods include low cost, high efficiency for dilute concentration solutions, a minimal amount of chemical and/or biological sludge, no additional nutrients required and the possibility of biosorbent regeneration and metal recovery (Vilar et al. 2007). The sorption of heavy metals onto these biomaterials is attributed to their constituents, which are mainly proteins, carbohydrates and phenolic compounds, since they contain functional groups such as carboxyls, hydroxyls and amines, which are able to attach to the metal ions (Choi and Yun 2006).

Heavy metal accumulation in aquatic organisms, which is an active process involving metabolic activity within living organisms, has been studied by several researchers since 1978 (Braek et al. 1980; Duddridge et al. 1980; Hart et al. 1979; Macka et al. 1979; Wong et al. 1978). Biosorption onto biomass, an entirely different process from bioaccumulation, was pioneered by Volesky's group from McGill University in 1981 (Tsezos and Volesky 1981). At present, the biosorption field has been enriched by a vast amount of studies published in different journals. Although at the beginning most researchers focused their efforts upon heavy metal accumulation and concentration within living organisms (Lesmana et al. 2009), upon noticing that dead biomass possesses high metal-sorbing potential (Volesky 1990), their interest shifted to biosorption (Selatnia et al. 2004; Yetis et al. 2000; Zhou 1999; Bossrez et al. 1997; Asthana et al. 1995; Volesky and Prasetyo 1994; Holan et al. 1993; Volesky et al. 1993; Niu et al. 1993; Fourest and Roux 1992). The research efforts directed towards the use of inactive and dead biomass for removal of heavy metals from aqueous solution then resulted in viable method for removing these pollutants. Nonliving biomass of algae, aquatic ferns and seaweeds, waste biomass originated from plants and mycelial wastes from fermentation industries are potential biosorbents for removal of heavy metals from aqueous solution and wastewater. Their efficiency depends on the capacity, affinity and specificity including physico-chemical nature.

Several reviews are available that discuss the use of biosorbents for the treatment of water and wastewater containing heavy metals (Demirbas 2008; Nurchi and Villaescusa 2008; Vijayaraghavan and Yun 2008; Romera et al. 2006; Davis et al. 2003; Kratochvil and Volesky 1998; Zouboulis et al. 1997; Lovley and Coates 1997; Veglio and Beolchini 1997; Volesky and Holan 1995; Wan Ngah and Hanafiah 2008). Biosorbents for the removal of metals mainly come under the following categories: bacteria, fungi, algae, plants, industrial wastes, agricultural wastes and other polysaccharide materials. In general, all types of biomaterials have shown good biosorption capacities towards all types of metal ions. Most studies of biosorption for metal removal have involved the use of either laboratory-grown microorganism or biomass generated by the pharmacology and food processing industries or wastewater treatment units (Agarwal et al. 2006; Chang and Hong 1994; Rao et al. 1993; Macaskie 1990; Rome and Gadd 1987; Townsley et al. 1986; Tsezos and Volesky 1981). Therefore, this promotes environment eco-friendliness. The physiological state of the organism, the age of the cells, the availability of micronutrients during their growth and the environmental conditions during the biosorption process (such as pH, temperature, and the presence of certain co-ions) are important parameters that affect the performance of a living biosorbent. Potent metal biosorbents under the class of bacteria are represented by genera including *Bacillus, Pseudomonas* and *Streptomyces* and fungi including *Aspergillus, Rhizopus* and *Penicillium* etc. Since these microorganisms are used widely in different food/pharmaceutical industries, they are generated as waste, which can be attained free or at low cost from these industries. Another important biosorbent, which has gained momentum in recent years, is seaweed. Marine algae, popularly known as seaweeds, are biological resources, which are available in many parts of the world. Algal divisions include red, green and brown seaweed; of which brown seaweeds are found to be excellent biosorbents). This is due to the presence of alginate, which is present in gel form in their cell walls. Also, their macroscopic structure offers a convenient basis for the production of biosorbent particles that are suitable for sorption process applications. Recently, numerous approaches have been made for the development of low-cost sorbents from industrial and agricultural wastes. Of these, crab shells, activated sludge, rice husks, egg shell and peat moss deserve particular attention (Vijayaraghavan and Yun 2008). The efficiency of metal concentration on the biosorbent is also influenced by chemical features of metal solution.

Equilibrium studies, that give the capacity of the adsorbent and the equilibrium relationships between adsorbent and adsorbate are described by adsorption isotherms which is usually the ratio between the quantity adsorbed and the remaining in solution at fixed temperature at equilibrium. Freundlich and Langmuir isotherms are the earliest and simplest known relationships describing the adsorption equation (Hussein et al. 2005).

Excellent removal capabilities were apparent for several biomasses. More than a few factors, such as pH, temperature, adsorbent dose, etc. significantly affect the biosorption capacities. On the other hand, utilization of them in industrial-scale applications is still some distance from reality. While most available biomasses have the capability to sequester heavy metals from solutions, not all of them fit as alternative adsorbents in real wastewater treatment plants. Several vital characteristics are available and need to be listed to render the materials valuable enough as an industrial adsorbent.

1. High adsorption capacity.
2. Available in large quantities at one location.
3. Low economic value and less useful in alternative products.
4. Attached metals can be easily recovered while biosorbent is reusable.

There is no doubt that many biosorbents and/or alternative adsorbents as mentioned in a scientific literature have a high adsorption capacity to the extent that even some are better than commercially available adsorbents. Looking from this perspective only, it seems that most biosorbents and/or alternative adsorbents have potential for industrial application. Yet, several biomasses that have low binding capacity in nature still widely exist. Their adsorption capacity normally can be improved by pretreatment or modification using physical or chemical methods. Chemically, modification is usually performed by adding some chemicals such as acid, alkali or other oxidizing and organic chemicals, while in the physical method, pretreatment is facilitated by heat, autoclaving, freeze-drying and boilling. Unfortunately chemical activation methods are not favorable, because the advantage of environmentally friendly (waste for waste treatment) and cost effective procedure, is lost. Unused chemicals represent more serious problems and commonly necessitate expensive waste treatment facilities (Lesmana et al. 2009).

Huge markets already exist for cheap biosorbents. Electroplating and metal finishing operations, mining and ore processing operations, smelters, tanneries and printed circuit board manufacturers are a few of the industries in which metal-bearing effluents pose a problem. The potential application for biosorption appears to be enormous. It can easily be envisaged that cheaper biosorbents would open up new, particularly environmental, markets so far non-accessible to ion-exchange resins because of their excessive costs, which make them prohibitive for clean-up operation applications. These considerations clearly demonstrate the economic feasibility and potential of the biosorption process for heavy metal removal/recovery purposes. It should be pointed out that there is a potential added benefit of metal-recovery as an *additional source of revenue* generated by a water treatment that *must* be carried out anyway (from a regulatory and environmental point of view).

2.3 Conclusions

The use of microbial and plant biomass and other biological mechanisms naturally used for heavy metal detoxification and removal, offer promising alternatives to traditional technologies in the treatment of heavy metals. The new biological-based technologies need not necessarily replace conventional treatment approaches but may complement them.

At present, information on different technological approaches is inadequate to accurately define parameters for scale up of processes and design perfection including reliability and economic feasibility. To provide an economically viable treatment, the appropriate choice of technology and proper operational conditions have to be identified.

Probably one of the most studied approaches is biosorption which offers an economically feasible technology for efficient removal and recovery of metal(s) from aqueous solution. The process of biosorption has many attractive features including removal of metals over quite broad range of pH and temperature, its rapid kinetics of adsorption and desorption and low capital and operation cost. Biosorbent can easily be produced using inexpensive growth media or obtained as a by-product from industry (Ahluwalia and Goyal 2007). Biosorption allows significant cost savings in comparison with existing technologies, can be more effective in many cases than its closest rival, ion exchange can be easily converted to the biosorption process. Additional cost reduction results from the possible recovery of heavy metals (Volesky and Naja 2007). Also being aware of the hundreds of biosorbents able to bind various pollutants, sufficient research has been performed on various biomaterials to understand the mechanism responsible for biosorption. Therefore, through continued research, especially on pilot and full-scale biosorption process, the situation is likely to change in the near future, with biosorption technology becoming more beneficial and attractive than currently used technologies (Vijayaraghavan and Yun 2008).

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