

APPLICATION OF BIOSORBENTS IN SEPARATION OF HEAVY METALS

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Abstract

Extensive industrialization increases release of harmful pollutants to the environment which might have potential for bioaccumulation via the food chain. Biosorption is a physico-chemical and metabolically independent process involving absorption, adsorption, ion exchange, surface complexation and precipitation. It removes heavy metals from solution with the help of biological material. It is ideal as compared to conventional method due to the cost effectiveness and environment friendly nature. This review summarizes the various biosorbents and immobilized techniques used for removal of the radioactive metals

Keywords: biosorption; adsorption; immobilization; radioactive waste; microorganisms

1. Introduction

The safe disposal of heavy metal wastes becomes a serious problem with the advancement in the nuclear energy sector (Gupta et al. 2018). The radionuclides releasing from nuclear plants and mining operation causes a serious threat to the environment due to their long-lived property and probability of leaching of these radionuclides from geological repositories and mines (Farnan et al. 2007).

Radionuclides and heavy metals are harmful to the human health due to their high transfer rate, increased solubility, lengthy half-lives and effortless assimilation in living organisms (Wang and Chen 2009). So radionuclide and heavy metal pollution is a matter of concern. The conventional treatment methods are either unsuccessful or highly costly for degradation of these radio wastes. Before discharging into the environment heavy metals can be removed by using different physico-chemical and biological processes (Gadd 2009). The sewage and water purification treatments which are categorized under biological process have been used since long due to the potential role of microorganisms in detoxifying organic and inorganic pollutants (Gadd 2000, 2007).

Due to its simple procedure, equivalent operation to conventional ion exchange technology, apparent efficiency and accessibility of biomass and waste bio-products biosorption has been considered as an emerging technology for removal of pollutants and/or recovery from solution (Volesky 2001, 2007; Tsezos, 2001; Wang and Chen, 2006; Mack et al., 2007). Physico-chemical attachment of one substance to another is called Sorption whereas physico-chemical removal of substances from solution by biological material called Biosorption (Gadd, 2009). therefore involves A solid phase (biosorbent) and a liquid phase (solvent: normally water) containing the dissolved or suspended species needs to be sorbed (sorbate) is involved in the biosorption process.

In the present review various biosorbents along with their mode of action and mechanism are discussed briefly. This will give future insight in finding novel approaches for removal of heavy metals and radio wastes from environment.

2. Types of biosorbent

Microbial biomass such as bacteria, cyanobacteria, yeast, fungi, algae, waste biomass from food industry and biotechnological processes, active sludge, plant and wood waste biomass, biomass containing chitin and chitosan can be used as a biosorbents. The mechanism of biosorption is described in figure 1.

2.1. Algal Biosorbent

During the manufacturing of additive products in the cosmetic and pharmaceutical industries algae plays a vital role. It is also preferred for the adsorption of heavy metal ions and other lethal pollutants from industrial waste water due to its high adsorption ability and easy availability (Mehta & Gaur 2005; Liu & Guo 2001). The probable use of algae in the management of nuclear waste has been explored and a variety of algal species both from marine and freshwater origins have been discovered (Gupta et. al.).

Red, brown and green algal biomass have cellulose, carrageenan, and alginate, respectively as their constituents with functional groups like $-\text{COOH}$, $-\text{OH}$, $-\text{NH}_2$, and $-\text{SH}$ causing selective binding of metal ions (González et al. 2011).

Algae *C.reinhardtii*, *Scevedesmus spp.*, *S. platensis*, *Chlorella spp.* as well as *Tetraselmis spp.* remove Cd^{2+} efficiently (Sbihi et al. 2012). Spirulina as well as *Chlorella spp.* algae show potential for Pb^{2+} removal. The immobilized cells, i.e., *C. reinhardtii* also significantly removed lead (Bayramoglu et al. 2006). *P. lanceolatum* algae are a potential candidate to remove zinc metal up to 118.66 mg g^{-1} (Sbihi et al. 2012).

Biosorption capacity of Red algae (*Ceramium virgatum*) biomass for total chromium was found to be 26.5 mg/g at pH 1.5 and 10 g/L biomass dosage, 90min equilibrium time and 20°C . The biosorption process was feasible, spontaneous and exothermic at $20\text{--}50^\circ\text{C}$ and followed pseudo-second-order kinetics (Sarı & Tuzen 2008).

Freshwater green algae (e.g., *Chlorella spp.*, *Cladophora spp.*, *Scenedesmus spp.*, *Chlamydomonas reinhardtii*), brown algae (*Sargassum natans*, *Fucus vesiculosus*, *Ascophyllum nodosum*, *Laminaria japonica*), and blue-green algae (like *Microcystis aeruginosa* and *Oscillatoria*) have the potential for metal biosorption (Mehta & Gaur 2005).

Majority of algal species have the capacity to absorb maximum Pb as compared to others (Tiem 2002; Davis, Volesky, and Mucci, 2003). Due to the high alginate content brown algae like *Ascophyllum*, *Sargassum*, etc., sorb more metal than other algae.

2.2. Bacterial biosorbents

The unicellular prokaryotic micro-organism, bacteria found ubiquitously in soil and water. The functional groups such as carboxyl, phosphonate, amine and hydroxyl present in the bacterial cell wall is responsible for metal binding (Vijayaraghavan & Yun 2008).

Various findings have been published on bioaccumulation and biosorption of heavy metals and dyes from industrial wastewater by bacteria. A number of bacteria genera including *Cellulosi microbium* (Elwakeel et al. 2012), *Arthrobacter*, *Citrobacter*, *Escherichia*, *Corynebacterium*, *Micrococcus*, *Pseudomonas*, *Thiobacillus*, *Zooglea* (Nakajima & Suruta 2004), *Sargassum* (Picardo et al. 2006), *Mycobacterium* (Andres et al. 1993), *Streptomyces* (Li et al. 2016; Yi et al. 2017), *Nocardia* (Nakajima, Tsuruta 2004), *Myxococcus*, *Deinococcus* (Andres et al. 1993), and *Geobacillus* (Ozdemir et al. 2012) have been identified for the purpose of nuclear waste management.

The uranium biosorption by an aerobic bacterial strain *Streptomyces sporoverrucosus* isolated from a potential disposal site were evaluated. Approximately 60% of total uranium absorbed at an initial concentration of 10 mg/L and the dynamic biosorption process followed a pseudo second-order. Uranium accumulated on cell walls and within the cells of *S. sporoverrucosus* and bound to functional groups amino, phosphate and carboxyl present in the cells (Li et al. 2015).

Biosorption of radioactive thorium was investigated using a dry biomass of *Sargassum filipendula* as the biosorbent material. The uptake capacity varied from 20 to 100%, depending on the solution concentration (Picardo et al. 2006).

Cells harvested from the stationary growth phase of lyophilized *Streptomyces longwoodensis* exhibited remarkably high biosorption capacity for uranium (0.44 g U/g dry weight) at pH 5. The uranium uptake was alike both for cell wall and the cytoplasmic fraction (Friis and Keith 1985).

Among eighteen different species of bacteria *Micrococcus luteus*, and *Arthrobacter nicotianae* have showed high adsorption capacity for thorium and uranium respectively. Thorium and uranium was adsorbed rapidly by the cells of *Micrococcus luteus* and affected by the solution pH, and obeyed the Langmuir adsorption isotherm in a competitive manner (Nakajima & Tsuruta 2004).

Thorium was removed from aqueous solutions by using living and dead *Cellulosi microbium cellulans* isolated from radioactive waste. The sorption of thorium by living and dead *C. cellulans* are 151.94 and 220.56 mg/g respectively and followed pseudo-second-order model (Elwakeel et al. 2012).

Bacteria plays a major role as a selective sorbent, adding high surface/volume ratio with an abundance of potentially active sorption centres due to its complex cell wall. The biosorption ability of *Bacillus subtilis* biomass immobilized in calcium alginate, in batch mode towards Cd(II) ions was 251.91 mg/g (Ahmad et al. 2014).

Bacillus drentensis MG 21831T biomass was immobilized effectively in polysulfone and had a highly porous structure and successfully adsorbed Pb(II) and Cu(II) ions (Seo et al. 2013).

In a study *Bacillus* strain CR-7 was isolated from soil and characterized by using multiple metal and antibiotic resistance (Xu et al. 2011). The biosorption capacity was increased by immobilization of thermally deactivated biomass with 0.1 M NaOH solution. A new biocomposite was manufactured by spinning the mixture of waste *Escherichia coli* biomass/polysulfone in N,N-dimethylformamide into water, which recovered ruthenium and Pd(II) ions (Kim et al. 2016).

Staphylococcus aureus treated with iron oxide magnetic nanoparticles, n-Fe₃O₄, with phthalic acid as a exterior coating and protective material (Mahmoud et al. 2016). Under most favourable

conditions, the biocomposite exhibited utmost biosorption capacities both for Ni(II) and Cu(II) ions.

Bacillus drentensis MG 21831T biomass was immobilized productively in polysulfone and had a highly porous structure and successfully adsorbed Pb(II) and Cu(II) ions (Seo et al.2013).

2.3. Fungal biosorbents

The eukaryotic organism fungi have chitin in their cell wall attached with amine, imidazole, phosphate, sulphate, thiol and hydroxyl groups accountable for metal sequestration. Fungal biosorbents are preferred owing to their low cost, easy cultivation and non-pathogenic nature. Various fungi *Aspergillus*, *Fusarium*, *Trichoderma*, *Rhodotorula*, *Saccharomyces*, *Rhizopus*, *Lentinus*, *Trametes*, *Talaromyces*, *Phanerochaete*, *Ganoderma*, *Pleurotus*, *Penicillium*, *Debaryomyces*, *Aplysina*, *Kluyveromyces*, *Candida*, and *Gibberellin* has been explored for their biosorption potential against heavy metals both in their native and modified form (Gupta et. al. 2018). The complexity of fungal cell wall is due to the presence of chitins, glucans, mannans and proteins along with other polysaccharides, lipids and pigments e.g. melanin. This variation in structural mechanism allows binding of metal ions with varying degree. Living mycelium becomes an efficient technology for elimination of toxic metals due to reusability of biomaterial, low operating cost, simple fermentation cultivation, the enhanced selectivity for specific metals, short operation time, release of non- toxic secondary compounds (Yang et. al. 2015)

Powdered biomass of lake-harvested water-bloom, cork, dry/wet bacterial biomass, spores and fungal mycelia, fungal biomass and dried alga biomass has been studied for uranium uptake (Kulshrestha and Venkobachar, 2008). In *Rhizopusarrhizus*, Uranium attach to the amine N of chitin, adsorped in the cell wall and further precipitation of hydroxylated derivatives (Fomina and Gadd 2013). Uranium biosorption by fungus followed pseudo-second-order kinetics by displaying a complicated multilayer phenomenon of biosorption (Akhtar et. al. 2007). Fungus had great potential to uptake copper (II), uranium (VI) and thorium (IV) ions by producing special metabolites (Yang et al. 2015). Thorium (IV) uptake by *A. fumigatus* was pH dependent and maximum sorption observed at pH 4.0. Thorium originates from the nuclear industry, from power stations during lignite burning, ore processing and from fertilizers. Various fungal biomass such as *Rhizopusarrhizus*, *Penicillium spp.*, *Aspergillus spp.*, involved in Thorium uptake (Bhainsa et. al. 2008).

The fungal cell wall is composed up of a micro-fibrillar layer and an amorphous layer and the presence of carboxyl and phosphate groups makes it negatively charged. The amino groups poorly participated in the metal-ion retention due to the inadequate protein content in the cell wall (Volesky 2003).

The micromycetes of the *Aspergillus*, *Rhizopus*, *Trichoderma*, etc. are the frequently used fungal biomass (Dhankhar&Hooda 2011). Micromycetes are preferred due to their rapid growth on cheap culture media, and production of abundant biomass (Sağ&Kutsal 2001).

Trichoderma viride biomass immobilized in calcium alginate into a continuous packed-bed column studied for biosorption of Cr(VI), Ni(II) and Zn(II) ions. The recovery efficiency for

Cr(VI), Ni(II) and Zn(II) ions was found to be 40.1%, 75% and 53%, respectively (Kumar et al.2011).

Live and dead *Trichoderma sperellum* biomass immobilized in calcium alginate for Cu(II) biosorption (Tan and Ting 2012). *Trichoderma rezeanum* biomass was immobilized onto Calcium alginate and the resulting biosorbent was removed uranium from aqueous solutions in continuous mode (Akhtaret al.2009).

Penicillium citrinum biomass, isolated from copper polluted sites, was cultivated and immobilized in calcium alginate. The highest biosorption capacity for the immobilized biomass was found to be 25 mg/g, and 22.7 mg/g for the free biomass at an initial concentration of copper ions ranged from 20 to 90 mg/l (Verma et al. 2013).

Thermally deactivated *Penicillium fellutinum* biomass immobilized in sodium bentonite for the removal of Ni (II) and Zn (II) ions. Under optimized conditions, the maximum biosorption capacities found to be 111 mg/g, 0.476 mg/g for Ni(II) and Zn(II) ions respectively (Xiao et al. 2013).

Aspergillus niger biomass was immobilized into Ca-alginate gel showed that the biosorption of uranium(VI) ions strongly dependent on pH of the solution (Ding et al. 2012).

2.4. Yeast cell biosorbent

Various organic compounds and their polymers, such as glucan (28%), mannan (31%), proteins (13%), lipids (8%), chitin and chitosan (2%) are the major constituents of yeast cell wall (Brady et al.1994). *Saccharomyces cerevisiae*, are the most usually studied biosorbents both in free or immobilized form due to their easy cultivation (Wang et al. 2006).

Co-immobilization of *Janiarubens* biomass with *S. cerevisiae* on mesoporous silica gel effectively biosorbedTh(IV) ions and the capacity was 26.95 mg/g (Goketal. 2011).

Ethylenediamine-modified yeast biomass coated with magnetic chitosan microparticles (EYMC) efficiently removed Pb(II) ions from aqueous solutions in a batch system (Li et al. 2013).

Immobilized waste biomass *S. cerevisiae* in Ca-alginate along with graphene oxide (GO) and PVA-Ca-alginate-graphene oxide in CaCl₂-boric acid solution removed U(VI) from aqueous solutions. U(VI) was adsorbed unevenly from the cell surface and the carboxyl and hydroxyl groups may be involved in U(VI) binding by yeast cells (Chen & Wang 2016).

S. cerevisiae biomass immobilized onto the surface of chitosan-coated magnetic nanoparticles removedCu(II) from aqueous solutions (Peng et al. 2010).

A biosorbent of immobilized *S. cerevisiae* biomass in magnetic chitosan microspheres removed Sr(II), Co(II), and Cs(I) from one- and two-component solutions (Yin et al. 2017 a;Yin et al. 2017 b). Immobilized dead *S. cerevisiae* biomass on titania nanopowder, and glutaraldehyde as a cross-linker have shown 162.07 mg/g of biosorption (Choudhury et al.2017). *Rhodotorulaglutinis* biomass enhanced biosorption capacity when supported on the nanoparticles of iron oxide (Balet al.2012).

3. Conclusion

Biosorption becomes commercially unsuccessful due to its complex process. So more focus should be given to enhance biosorption capacity, selectivity, kinetics and re-use. Although the raw

biosorbents are cheap and abundant but their poor adsorption performance becomes a problem. Immobilization with organic and inorganic functional group onto the biosorbent's surface may enhance the adsorption capacity but cost-to-performance ratio and biodegradability are the limitations. Before choosing immobilization technique the factors mechanical strength, chemical resistance, regeneration, reuse of the immobilized biomass and the mass transfer should be taken into account. Yeast and fungal biomasses (*Saccharomyces* sp., *Rhizopus* sp., *Aspergillus* sp.) should be given special attention due to their ability to bind both cations and anions, low cost and availability. So the future research must be targeted to shift biosorption from laboratory studies to its large-scale application for separation of radionuclide.

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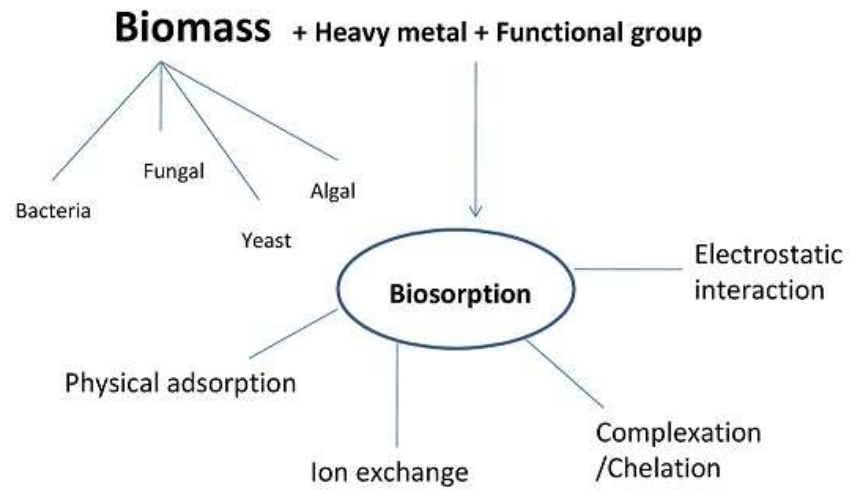


Fig. 11.1: Mechanism of biosorption