



Review Article

BIOSORPTION OF HEAVY METALS USING ALGAE: A REVIEW

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Various algal species can be used for removing heavy metals like Cd, Cu, Ni, Pb, and Zn from aqueous solutions successfully. Biological removal of metals is possible by both living and non living algal biomass. Algal biosorption is dependent on various parameters such as pH, biomass concentration, temperature, contact time and initial concentration of metal ion in the solution. The potential metal binding groups present on the cell surface of the algal species are carboxylate, amine, imidazole, phosphate, sulfhydryl, sulphate and hydroxyl. Algae found in large quantities in sea as well as in fresh waters serve as basis for newly developed metal biosorption process, as a very competitive means for the detoxification of metal bearing industrial effluents.

Keywords: Biosorption, Biosorbent, Algae, Immobilization, Modeling

INTRODUCTION

Toxic heavy metal contamination in wastewaters is a worldwide problem. These metals are detected either in their elemental state or bound in various salt complexes. Metals in their elemental state are not subjected to further biodegradative process. Their persistence in water bodies even in smaller or undetectable amounts may become elevated to such an extent that they start exhibiting toxic characteristics through natural processes such as bio-magnification. Metal recovery from industrial wastewater is important not only in view of environmental issues, but also on the technological aspects. Metals of technological importance or of economic value

may be removed or recovered at their source using appropriate treatment systems. Most of the heavy metals are soluble in water and form aqueous solutions and consequently cannot be removed by ordinary physical means of separation. Chemical reduction, precipitation, electro chemical treatment, ion-exchange, reverse osmosis, etc., are the commonly used procedures for metal removal from solutions. Due to the significant disadvantages of incomplete metal removal, high energy requirements, toxic sludge or other waste products generation and more over the high expense of chemical resins, there is an increasing demand for eco-friendly technologies using low cost alternatives. Certain

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species of microbial biomass are considered to retain relatively high quantities of metal by means of passive process called biosorption. Removal of metal ions by micro-organisms takes much attention due to its applications in environmental protection. A large number of micro-organisms belonging to various groups, viz., bacteria, fungi, yeast, cyanobacteria and algae have been reported to bind a variety of heavy metals to different extents. The role of various algal species in the removal and recovery of heavy metals by biosorption is reviewed here.

SOURCES OF HEAVY METALS

Various industries produce and discharge waste containing different heavy metals into the environment such as mining and smelting of metallic ferrous, surface finishing industry, energy and fuel production, fertilizer and pesticide industry and application of metallurgy, iron and steel electro plating, electrolysis, electro osmosis, leather working, photography, electrical appliance manufacturing, metal surface treating, aerospace and atomic energy installation (Jianlong and Canchen, 2009). The sources of heavy metal contamination include urban industrial aerosols, solid wastes from animals and agricultural chemicals.

BIOSORPTION

Biosorption is defined as the capacity of a substrate to retain metallic species, ionic forms and/or ligands from fluids in the molecular structure of the cell wall. The biosorption mechanisms include extracellular and intracellular bonds, as well as complex interactions that depend on the type of metal and the biosorbent structure (Davis *et al.*, 2003).

Biosorption can be defined as the removal of

metal or metalloid species, compounds and particulates from solution by biological material (Gadd, 1993). Large quantities of metals can be accumulated by a variety of processes dependent and independent on metabolism. Both living and dead biomass as well as cellular products such as polysaccharides can be used for metal removal.

Biosorption utilizes the ability of biological materials to accumulate heavy metals from wastewater by either metabolically mediated or physico-chemical pathways of uptake (Gupta *et al.*, 2008).

ALGAE AS BIOSORBENT

Algae are special interest for and the development of new biosorbent material due to their high sorption capacity and ready availability in practically unlimited quantity. According to statistical review on biosorption, algae have been used as biosorbent material 15.3% more than other kinds of biomass and 84.6% more than fungi and bacteria. Brown algae among the three groups of algae (red, green and brown) received the most attention. Higher uptake capacity has been found for brown algae than for red and green algae (Brinza *et al.*, 2007).

Biosorbent possesses metal sequencing property and can be used to decrease the concentration of heavy metals ions in solution from ppm to ppb level. Biosorbent behavior for metallic ions is a function of the chemical make up of the microbial cells of which it consists (Volesky and Holan, 1995). Seaweeds from the oceans produced are inexpensive sources of biomass. Marine algae especially brown algae was investigated for metal removal (Davis *et al.*, 2003). Great efforts have been made to improve bio-sorption process including immobilization and

reuse optimization. In bio-sorption various algae were used and investigated for their biosorptive efficiency. A thin rigid cell wall is surrounding the algal cell which is complex in nature. Metal bio-sorption by biomass mainly depends on the component on the cell wall especially through cell surface and spatial structure of the cell wall.

IMMOBILIZED ALGAL BIOSORBENT

Immobilization technology is one of the major elements for the practical application of biosorption, especially by dead biomass. Free microbial cells are not suitable for packing in columns in that due to their low density and size they tend to plug the bed, resulting in large drops in pressure. Support matrices suitable for biomass immobilization include alginate, polyacrylamide, polyvinyl alcohol, polysulfone, silica gel, cellulose and glutaraldehyde (Wang, 2002).

For application of biosorption in industries, it is important to utilize an appropriate immobilization technique to prepare commercial biosorbents that retains the capacity of microbial biomass to adsorb metals during the continuous treatment process. The immobilization of the biomass on solid structures would create a biosorbent material with the right size, mechanical strength, rigidity and porosity necessary for use in practical processes. The immobilized materials can be used in a manner similar to ion exchange resins and activated carbons such as adsorption – desorption cycles (Veglio and Beolchini, 1997).

BIOSORPTION BY DEAD ALGAL BIOMASS

The non-living *Sargassum* sp. has been shown

to absorb various metal ions, such as cadmium, chromium and copper (Eneida Sala *et al.*, 2002). In the batch studies, *Sargassum* seaweed has been found to biosorb chromium. pH had an important effect of the biosorption capacity. Biosorbent size did not affect the biosorption capacity and rate. Cadmium and copper uptake by six different *Sargassum* species was studied by Davis *et al.* (2003). Maximum biosorptive capacities were found to be 0.9 m.mol/g for *Sargassum* sp., 0.89 for *S. filipendula*, 0.93 for *S. vulgare* and 0.8 for *S. fluitans*. Cu uptake by *Ascophyllum nodosum* showed a q_{\max} of 0.037 m.mol/g (Table 1).

The biosorption of metal ions Pb and Cu by Red algae *P. palmate* was studied by Prasher *et al.* The q_{\max} for Lead was found to be 15.17 mg/g and for copper 6.65 mg/g. Dried biomass of Marine *Fucus spiralis*, *Fucus vesiculosus* and *Ulva* species were studied for their metal uptake capacities. Biosorption of metal ions strongly depended on pH. Increase in pH showed higher metal uptake capacities. Studies on kinetic behavior of biosorption shows a rapid initial sorption period and a later longer equilibrium period. The equilibrium time varied from 10 min to 60 min for the three marine biomass used. Sorption of metals by Blue green algae *spiralina* reached equilibrium with 5-10 min.

Studies on biosorption of lead by Gupta *et al.* (2008) showed the effect of pH on lead adsorption capacity of green algae *spirogyra*. As pH increased from 2.99 to 7.04, the adsorption capacity of lead was found to change. Study on uptake of metals Cu, Zn, Cd and Ni by *Chlorella vulgaris* conducted by Fraile *et al.*, were also found to be pH dependent. Higher metal uptake was noticed at higher pH ranges. Blue green algae *spirulina* species was also found to be pH

Table 1: Biosorption of Metal Ions by Various Algal Species

Biomass type	Metal Studied	Biosorptive Capacity		Reference
		mg/g	m.mol/g	
<i>Sargassum</i> sp.	Cadmium		0.9	Davis et al. (2000)
<i>S. filipendula</i>	Cadmium		0.89	Davis et al. (2000)
<i>S. vulgare</i>	Cadmium		0.93	Davis et al. (2000)
<i>Ascophyllum nodosum</i>	Cu		0.037	Alhakawati et al. (2004)
<i>Sargassum filipendula</i>	Lead		1.35	Vieira D et al. (2007)
<i>P. palmata</i>	Pb	15.17		Prasher et al. (2004)
<i>P. palmata</i>	Cu	6.65		Prasher et al. (2004)
<i>Chlorella vulgaris</i>	Ni	60.2		Z Aksu (2002)
<i>Fucus vesiculosus</i>	Cu	114.9		E L Cochrane et al. (2006)
<i>Fucus spiralis</i>	Cadmium	114.9		E Romera et al. (2007)
	Ni	50.0		
	Zn	53.2		
	Cu	70.0		
	Lead	204.1		
Immobilized Algal Biomass (mg/g)				
<i>Spirulina platensis</i> in alginate gel	Cd	70.92		N Rangasayatom et al. (2004)
<i>Spirulina platensis</i> in silica gel	Cd	36.63		
<i>Scenedesmus quadricauda</i> in Ca alginate	Cu	75.6		Gulay et al. (2009)
	Zn	55.2		
	Ni	30.4		
Immobilized algal consortium on silica gel	Pb	15.95		Rajiv Kumar et al. (2009)

dependent from the report by Katarzyna *et al.*, The studies on copper removal by *Ascophyllum nodosum* showed that the adsorptive capacity of the biomass depended on pH (Alhakawati *et al.*, 2004)

Biosorption is also affected by biomass concentration. *Chlorella vulgaris* showed best sorption at lower biomass concentrations for uptake of metals. Romera *et al.* studied

biosorption of Cd, Ni, Zn, Cu, Pb on six different algal species. Best results were obtained at low biomass concentration. The process was found to be dependent on pH. Aksu also conducted batch studies on uptake of Ni by *Chlorella vulgaris*. In this study temperature variation was taken into consideration and higher Nickel uptake was observed at 45°C. The maximum biosorptive capacity was found to be 60.2 mg/g. Gupta

reported the effect of temperature on lead removal by *spirogyra* species. For an increase in temperature from 298 K to 318 K, the maximum amount of metal adsorbed increased from 96.4 to 104 mg/g at 150 mg/L.

The biosorption of the heavy metal ions on the cell surface occurs by ion exchange process. Brown marine alga *Sargassum vulgare* was found to uptake metals like Cd, Ni, Pb by the main chemical groups on their surface such as carboxyl, amino, sulfhydryl and Sulfonate (Gaur and Dhankhar, 2009) studied the biosorption of zinc metal ion by *Anabaena variabilis*. The study revealed the presence of carboxyl, hydroxyl, amino, amide and imine groups are responsible for biosorption of Zn^{2+} ions. Thomas A Davis *et al.* (2003) in their review stated that Brown algae has proven to be the most effective and it is the properties of cell wall constituents such as alginate and fucoidan which are chiefly responsible for heavy metal chelation. Chetty *et al.* conducted batch studies on biosorption of lead by brown marine algae *Anthophycus longifolius*. *A. longifolius* treated 20 L of 5 mg/L and 8.7 L of 150 mg/L of lead solution.

BIOSORPTION BY IMMOBILIZED ALGAL BIOMASS

Immobilization is a general term that describes different forms of cell attachment or entrapment on either manual or natural materials. Silica gel has been extensively used for immobilization of algal cells or biomass.

The removal of cadmium by *Spirulina platensis* immobilized on alginate gel and silica gel was studied (Rangasayathorn *et al.*, 2004). The maximum biosorption capacities for alginate and silica immobilized cells were 70.92 and 36.63 mg/

g. Adsorption of alginate immobilized cells was pH dependent while that of silica immobilized cells was not affected by pH. These immobilized cells could be repeatedly used in the sorption process up to five times.

The potential use of the immobilized *Scenedesmus quadricauda* in Ca-alginate to remove Cu, Zn and Ni was evaluated by Gulay *et al.* The q_{max} values for Cu, Zn and Ni were 75.6 mg/g, 55.2 mg/g and 30.4 mg/g. The sorption process followed second order kinetics. The efficiency of immobilized brown alga *Fucus vesiculosus* in alginate xerogels for uptake of heavy metals was studied by Mata *et al.* It was found that immobilization increased the kinetic uptake and intra particle diffusion rates of the metals. Lead uptakes up to 370 mg Pb/g was observed in cross linked *Fucus vesiculosus* and *Ascophyllum nodosum* in a test conducted by Holan and Volesky (1993).

COMPARISON WITH OTHER BIOSORBENTS

Both living and dead cells are capable of metal adsorption. The use of dead biomass seems to be a preferred alternative due to the absence of toxicity limits, absence of requirements of growth media and nutrients in the feed solution and the fact the biosorbed material can be easily adsorbed and recovered, the regenerated biomass can be reused, and the metal uptake reactors can be easily modeled mathematically (Narsi R Bishnoi and Garima, 2004).

Rajiv Kumar and Dinesh Goyal compared systems using algal consortium as dried immobilized biomass in continuous mode and live biomass under batch conditions on removal of lead ion. Live biomass was found to remove 17% of lead after 15 days of incubation with

$q_{\max} = 33.31$ mg/g where as immobilized biomass exhibited 92.5% lead removal and q_{\max} of 15.95 mg/g.

In the work of Horvathova *et al.* (2009), the sorption capacity of *Chlorella kessleri* as non-immobilized algal power and as immobilized form in sodium alginate was compared. The maximum sorption capacities for non-immobilized algal power was found to be 37.24 mg/g for Cu and 40.23 mg/g for Zn. Whereas for immobilized cells q_{\max} was found to be 24.6 mg/g for Cu and 35.38 for Zn.

Metal removal capacity of algal biomass is compared with other biosorbents. Cochrane *et al.* compared the biosorption capacity of *Fucus vesiculosus* to remove copper with crab carapace and peat. *Fucus vesiculosus* showed q_{\max} of 114.9 mg/g in comparison with crab carapace of q_{\max} 79.4 mg/g and peat with q_{\max} 71.4 mg/g.

MODELLING OF BIOSORPTION – ISOTHERM AND KINETIC MODELS

The basic technique that assists in evaluating the metal uptake by different biosorbents is the construction of biosorption isotherm curves. The methodology is based on equilibrium sorption experiments extensively used for screening and quantitative comparison of new biosorbent materials. The generation of novel biosorbent materials and its regeneration for reuse can be effectively done using Experimental Methodologies and recent research results.

ISOTHERM MODELLING

The biosorption of metals by spirulina species was studied, Langmuir equation from adsorption

rate equation was derived assuming first order kinetics pattern (Chojnacka *et al.*, 2005). Reaction rate constants were determined by non-linear regression. Alhakawati studied the removal of copper by *Ascomyllum nodosum* and showed that their data fitted the langmuir equation with R^2 values greater than 0.96.

Studies on biosorption of lead by the algal biomass of *Spirogyra* species fitted the Langmuir isotherm accurately (Gupta *et al.*, 2008). Biosorption of cadmium on *Spirulina platensis* immobilized on alginate and silica gel fitted well with the langmuir isotherm (Rangasayatorn *et al.*, 2004).

The biosorption isotherms for the metals Lead, copper and cadmium on alginate xerogel with and without *Fucus vesiculosus* fitted well with the langmuir model. Studies on removal of zinc by the cyanobacterium *Anabaena variabilis* was conducted and the Freundlich and Langmuir isotherms were applied to the equilibrium data and it fitted well with the Freundlich isotherm.

KINETIC MODELING

To describe the reaction order of adsorption systems numerous kinetic models have been suggested based on solution concentration. The most widely used kinetic models to describe the biosorption process are the first order equation of Lagergren and pseudo second order equation.

The sorption capacity of *Chlorella vulgaris* for the metals Cu, Zn, Cd and Ni was investigated by Fraile *et al.* sorption isotherms fitted well to the Langmuir model, for both single metal and two metal systems. Freundlich, Langmuir and Redlich – Peterson isotherm models were applied to the equilibrium data of nickel biosorption by *Chlorella vulgaris* (Z. Aksu) Equation data fitted well with the models.

The adsorption – equilibrium was represented with Langmuir, Freundlich and Dubinin-Radushkevich adsorption isotherms for uptake of Cu, Zn and Ni ion by immobilized *Scenedesmus quadricauda* in Ca – alginate. The adsorption of metal ions followed second order kinetic equation. The study on *Fucus vesiculosus* to uptake Cu (E.L.Cochrane) followed pseudo second order rate model. Langmuir and Freundlich isotherm models were used to describe the sorption equilibrium data.

CONCLUSION

The biosorptive capacity of algal biomass for the removal of heavy metals depends on various parameters. pH is the most important factor as increase in pH showed higher metal uptake capacities. Biosorbent size did not affect the biosorption capacity and rate. The biosorption of heavy metal ions on the cell surface occurs by ion exchange process. The technique of immobilization of algal biomass increased the kinetic uptake rates of the metals. Due to the significant advantages of using algal species as biosorbent, it can be used as an alternative eco-friendly technology among the conventional ion exchange processes.

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