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Removal of heavy metals from waste water using different biosorbents

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ABSTRACT

The discharge of waste water containing heavy metals like Cr, Cd, Cu from tanneries, electroplating units, metal processing industry etc is the major cause for metal pollution which in turn causes adverse effects in the environment. The conventional methods available for removal of heavy metal are costly and also produce some toxic sludge. This has lead to the invention of new technology like biological removal of heavy metal. In this paper use of various biosorbents like plants, microbes and their derived products were reviewed with context to metal removal. Various modes of operation and reactor types, adsorption kinetics with respect to growth condition and metal sorption were also given importance.

Key words: Biosorption, bioremediation, heavy metal, bioreactors, immobilization, isotherms.

INTRODUCTION

Industrial revolution has lead to the increased use of heavy metal like Cr, Cu, Cd, Pd, Zn etc. Heavy metals such as Cr, Cu, Cd, Pd, Zn are essential for the plants and microbes as they form part of many enzymes and proteins[1]. The effluents from metal processing industries and tanneries are released into the environment without proper treatment or untreated. These metals accumulate on the soil and are persistent and pose a severe threat to the environment. Elevated level of both essential and non essential metals has lead to toxicity to living organisms. To protect themselves from metal poisoning plants and microbes have developed a mechanism by which the metal entering their cells are inactivated or transformed to nontoxic forms. The conventional methods available for metal removal are chemical treatment like precipitation, reverse osmosis and thermal treatment. Chemical treatment of metal results in production of sludge which is much more dangerous than metal solution. Other methods like reverse osmosis are efficient but costly, these limitations has resulted in innovation of new techniques like biosorption and bioremediation. Literature review reveals that various plants like aquatic plants[1,3], neem bark, husk, microbial sources like algae, fungi, yeast [4,5], bacteria can be used as efficiently used as biosorbent for heavy metal removal. The biosorbents have advantage over conventional methods in low cost, high efficiency, regeneration.

Biosorption is the recent trend for removal of recalcitrant elements. It utilizes the ability of biological materials to accumulate heavy metals from wastewater streams by either metabolically mediated or physic-chemical pathway of uptake[1]. Metabolically inactive biomass due to their unique chemical composition sequesters metal ions and metal complexes from solution. Metal sorption by inactive biomass is advantageous that it does not need the maintenance of specific growth conditions[2]. Bioremediation utilizing plants or microbes for removal of heavy metal is a suitable alternative for conventional methods, but require the maintenance of special growth conditions. Bioremediation is aesthetically pleasing and makes environment green as the entire process is solar energy driven making it cost effective and environment friendly.

Immobilization is the process by which the whole cell or the metabolites like enzymes are attached on to an inert, insoluble material like calcium alginate, polyurethane foam, etc. immobilization gives the advantage that the microbes can with stand increased stress like change in pH , temperature. Immobilized microbes were tested in their efficiency for metal removal. Various microbes on different support matrix have been reviewed.

Mechanism of metal uptake by biosorbents

It is necessary to know the mechanism by which biological materials accumulate metals. Microbial cells contain a large number of metal binding sites called ligands. Biomass cell wall contains polysaccharides proteins and lipids which offer functional groups to bind metal ions[4]. The mechanism by which biological materials remove metals is not completely understood. The performance of the biosorbent depends on the ionic state of the biomass. The uptake of metals by biomass is a two step process, the cells of biomass contains proteins and polysaccharides which offer a lot of binding site for heavy metals. The first step is the stoichiometric interaction between the cell components and the metal ions. The second step is the accumulation of heavy metal on the binding sites.[15]

Biosorption is a complex process comprosing of ion exchange, chelation and adsorption by physical forces, entrapment in capillaries. Acetamide groups of chitin, amino and phosphate groups of nucleic acid, amide and sulfhydryl groups of proteins are well known examples of chemical groups that attract metals in biomass. The steric and conformational effects also have a major role in binding capacity of biomass.

Plants as biosorbents

Removal of heavy metals from aqueous solutions using plants and plant derived biomass is a viable option when cost of removal is a major criterion. Large numbers of works have been performed with various plant based biomass. *Eicchornia crassipes*, sawdust, bael fruit, wheat straw have been reviewed as biosorbents.

Reed

Reed contains lignin and cellulose as their cellular component which has the ability to adsorb heavy metal ions from metal solutions. Bounheng *et al*., 2006 studied the use of reeds as biosorbent for removal of heavymetals. Reeds are cut into small pieces and washed with distilled water and dried to 60°C and ground to homogenous powder. Pretreatment of reed is done treatment with acid and alkali. 0.05g of reed sorbent so prepared was treated against metal solution at a pH range of 2-3 and for 3h in a shake flask. Plasma absorption spectroscopic studies showed 64% removal of heavy metals[6].

Saw dust

Saw dust from work shops were investigated for removal of Cr. The pretreatment step involves the washing of saw dust with distilled water and dried at room temperature for 8h. Batch study was performed with addition of various concentration of saw dust to flasks containing Cr solutions (1000mgL^{-1}) at 25°C. The concentration of the chromium is determined by spectrometric method. Tarun *et al.,* 2009 reported 42.52 mg g^{-1} adsorption of chromium for a pH range of 1. Various adsorption isotherms were also studied. Langmuir isotherm was found to best fit the results[7].

Sunflower stem waste

Sunflower stem was sundried and ground in ball mill and washed with distilled water, oven dried at 60°C and sieved to 300 µm. Pretreatment was done with water and formaldehyde. Batch adsorption study was done with treatment of (1000mgL^{-1}) of chromium solution in a flask with a solution pH of 2 for (0.2 mg of biosorbent/ 50ml of chromium solution. The solution was centrifuged at 400 rpm for 10 mins and the chromium concentration in the supernatant was studied using atomic absorption spectroscopy. SEM studies

Table 1: Comparison of various biosorbents

Biosorbent	Metals	Adsorption capacity	Reference
Sacchromyces	Cu	96%	Manuels *et al.,*
cerevisiae	Ni		2007
	Zn		
	Cd		
A.niger	Cd	7.06 mmol/g	Paula marques 2006
	Cu	97.5%	Wan Xia Ren 2009
	Cd	88.2%	
	Pb	26	
	Zn	14.5	
Arthrobacter sp	Cd	33%	F.Pagnaelli 2003
R.oryzae	Cu		
Living		19.4mg/g	
Non living		43.7mg/g	Kuber 2007
Mucor rouxii	Pb	17	Yan 2003
	Zn	4.89	
	Cd	6.94	
	Ni	5.74	
P.chrysogenum	Cd		Skowruski 2001
Phanerochaete chrysosporium	Pb	2	Say etal
Chlorella vulgans	Cd	111mg/g	Asku 2001
Scenedemus incrassatula	Cr		
Olive pomace	Cd(II)	0.100mmmollg	H. Gao,
Reed	Pb	0.082mmmollg	B. Southichak,
Laminoria	CD	1.67	Yinghiu liu
japonica	Cu	1.62	
	Zn	0.91	
	Ni	1.22	
Gelidium	Cu	0.571 g^{-1}	Vitar J.P. Vilar
Fucus vesiculous	Pb, Cu	Model equation was arrived	Y.N. Mata
Candida albicans	Pb	833mg/g	Zubyde beysul
Yeast biomass	Cu	2.59mg/g	Corneliu
Aspergillus foetidus	Cr	2mg/g	Prasanjit 2005
Aureobasidium pullalans	Cu	18 mg/g	Ahluwalia 2003
Cladosporium resinae	Cu	24mg/g	Ahluwalia 2003
Pleurotus sapidus	Hg	127mg/g	Skowronski 2001
R.oligosporus	Cr	126mg/g	Ariff etal 1999
Aphanothece halophytica	Zn	133mg/g	Incharoenskadi 2002
Dunaliella	Cr	58.3	Domenz and asku 2002
Pachymenopis	Cr	225mg/g	Lee 2000
Bacillus firms	Pb mg/g	467 mg/g	Salehizadeh 2003
B.coagulants	Cr	30.7	Srinath 2002
B.megaterium	Cr	39.9	Srinath 2002

revealed Sunflower stem has large surface area for binding of large number of adsorbates[8].

Bael fruit

Bael fruit was dried to 110°C in hot air oven and and reduced to size range of 600-800 µm. Chemical activation was done with 88% orthophosphoric acid. Batch kinetic study was performed for various pH range from 1-8 and various chromium concentration (50-125mg/L) with a predetermined time of 240 min in a orbital shaker. The batch studies were conducted by varying one parameter at a time. The samples were filtered using 42 number whatman filter paper and analyzed in a flame absorption spectrophotometer. Maximum removal of chromium was obtained at pH2 and the removal efficiency decreased 91.9% to 85.9 with increase in initial concentration of chromium from 50-125mgL^{-1} [9].

Wheat straw

Cd and Cu removal b wheat straw was studied with various pH from 4 to 7 and varying metal concentrations 130 and 60 % removal of cd and cu respectively was reported with the increase in pH from 4 to 7, temperature also was studied as a significant parameter. Experimental studies revealed maximum removal at 25 to 30°C. Langmuir and Freundlich isotherm suited well for Cd. The study proposes wheat straw as a low cost biosorbent for heavy metals removal[10].

Microbial biomass

Microbe's posses a large number of polysaccharides in their cell wall which helps in accumulation of metal ions. This mechanism is similar to that of ion exchange method of removal heavy metal with the advantage that cost of biomass is cheaper and can be regenertated easily.

Table 2: Various reactors for biological removal of metals

Bioreactor	Metal	Total feed	Total removed	Reference
Airlift	CdCr	32.01mmol 18mg/l	25.02mmol 6mg/l	P.Marques 2007
Fixed bed	Cd	3.39mmol	1.14mmol	P.Marques 2007
Membrane reactor	Cu	1.5mmol	0.5mmol	F.Pagnelli
Biocolumn reactor (GAC)	As	12.5 ppm	12.4ppm	P.Mondal 2007
Batch reactor GAC (Ralstonia eutropha)	As		8%	P.Mondal 2007
Soil bioreactor(97% of Cr VI was reduced to Cr III which is less toxic compared with CrVI)	Cr	4320mg	127mg	Jeya Singh 2004
Bench scale column	Cr	Monod Inhibition constant was derived		T.Shasidhar 2006

Algae

Chladophora albida was investigated as a potential sorbent for chromium removal in batch experiments[11]. The biomass was prepared by washing the algae with distilled water and oven drying at 60°C. Chromium removal rate was found to increase with increase in temperature and decrease in pH. The optimum pH was found to be 5. Results for removal of chromium with algae were 100% (28.09mg L^{-1} initial concentration) efficient and the author has emphasized on the regeneration of column as a scopeful future study.

Scenedesmus incrassatulus was studied for the removal of chromium. The micro alga was cultivated in a agar- nitrate modified basal medium. The well grown colony was picked and used for inoculating the photobioreactor. Culture conditions were as follows: temperature, 25 ± 2°C; air flow rate, 997 ml min^{-1}. Cr solution was added into the photobioreactor up to 1 mg Cr(VI) l^{-1}. Cr concentration in the feeding medium was verified every 3 d using an atomic absorption spectrometer. The algal suspension was filtered through a Millipore filter paper and the concentration of chromium was measured using atomic absorption spectrometer. 43% removal efficiency was reported[12].

Bacteria

Bacteria may uptake and accumulate a significant amount of metal ions resulting in the transfer of metal ions to a matrix. Suspensions of dead biomass of actinomycetes from industrial fermentation was mixed with waste water the biosorption of Cd occurred due to negatively charged sites in the bacterial cells[13]. *Arthrobacter sp* was protanated with 0.1 N HCl and titrated with 0.1 NaOH. Biosorption tests were conducted for Cu and cd removal at different pH 4- 5. Subsequent addition method was employed (SAM) was employed. The equilibrium time for each metal was calculated as 30 min.

Fungal biomass

Cu uptake by *R. oryzae* in Erlenmeyer flask containing 25 mL of Cu solution was studied in an environmental shaker at 150 rpm. The performance of biomass was found to be maximum at pH 4- 6. Alkali treatment (NaOH) of the biomass resulted in higher amount of Cu removal as alkali neutralized the protons in the native biomass making more binding sites available for Cu ions[14]. Nonliving waste biomass of *A. niger* attached to wheat bran was used as biosorbent for removal of Zn and Cu from aqueous solution and metal uptake was found to be a function of the initial metal concentration, biomass loading and pH. Alkali treatment of *A. niger* biomass was found to sequester Cd, Cu, Zn effectively to 10% of its weight. *Neurospora, Fusarium* and *Penicillium* was also studied but *A. niger* gave better results in removal of Cd, Cu,Zn. Dry cells of *R. arrhius* were used for removal of Fe, Pb, Cd ions from waste water. Higher adsorption rate and adsorption capacity was obtained in a batch reactor. The maximum adsorption rate obtained was 100-150mgL^{-1} at pH 5 and 30°C.

Bioremediation

Sacchromyces cerevisiae was immobilized by entrapment in a matrix of polysulfolane. A fixed bed reactor and an airlift reactor were compared for their effective removal of Cd from dilute aqueous solutions. A liquid recirculation flow rate of 0.027. dm^{-3} min^{-1} in fixed bed reactor and an air injection flow rate of 0.1vvm was studied. Maximum removal of Cd was obtained in both reactor at pH 4-5. Airlift reactor gave superior results of 7.06 mmol Cd g biomass^{-1}.[4]. This result gives an idea that bioremoval of metal can be done in continuous reactor arrangements.

Removal of chromium using a suspended growth system and an aerobic and anoxic attached growth system was done using *Arthobacter rhombi*[16]. Synthetic wastewater was employed for the study purpose. The results obtained were encouraging for the use of bioreactors for metal removal. The aerobic suspended growth system resulted in 95% removal of chromium (20 mg/mL initial concentration). Further biokinetic parameters were also studied[16]. The authors have presented a biokinetic equation for metal removal using MATLAB.

$$\mu = \left[\frac{\mu_{max} S}{K_s + S}\right]\left[\frac{k_i}{k_i + Cr}\right]$$

k_i the inhibition constant, μ_{max} is the maximum specific growth rate, μis the specific growth.

CONCLUSION

Metals can be removed over broad range of pH, temperature and initial concentration. The cost of the process is lesser compared to other techniques. Low concentration of heavy metals in effluents can be easily and effectively removed using biosorbents. Literature review reveals that a particular biosorbent can be used to remove a wide range of metals. Fungi and algae are found to have more metal removal capacity than bacteria. Biological sorbents are applicable all kinds of industrial effluents, the biggest advantage is that their ability to remove heavy metals from effluents containing low concentrations of metals. The use of immobilized microbes rather microbes in free nature is recommended as immobilized microbes has the advantage of withstanding high stress and metal load. A hybrid system consisting of a microorganism attached on to a support and its usage in a reactor is recommended as the specific condition required for bioremediation can be maintained inside a bioreactor thereby enhancing efficient removal.

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