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Biosorption of Cr (VI) from aqueous solution using untreated and NaOH treated biomass of *Penicillium citrinum*

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Absract

In the present investigation, untreated and Sodium Hydroxide (NaOH) treated biomass of *Penicillium citrinum* was used as an inexpensive and efficient biosorbent for Cr (VI) removal from its aqueous solution. The fungal biomass was immobilized in sodium alginate to increase the biosorption surface area. Biosorption experiments were carried out at different pH, contact time, biosorbent dose and initial metal ion concentration. Biosorption equilibrium was established after 60 minutes and at equilibrium NaOH treated biomass showed maximum removal as compared to untreated biomass. The NaOH treated biomass showed maximum removal efficiency at 50 ppm concentration i.e. 89.34% and it was found to decrease with further increase in initial metal ion concentration. The equilibrium adsorption data fitted well to Freundlich and Langmuir adsorption isotherms.

Keywords: Biosorption; Heavy metal; *Penicillium citrinum;* Cr (VI); NaOH

Introduction

Modern civilization with high-tech life style depends upon the use of a myriad of natural and man-made compounds that contain one or more heavy metals. Release of these metals from natural deposits as well as due to anthropogenic activities has made them to reach unexpected levels in natural biogeochemical cycles. The accumulation of metals in an aquatic environment has direct consequences to man and ecosystem (Akinlua and Asubiojo, 2006). Heavy metal pollution represents an important environmental problem due to their non-biodegradability, toxicity and accumulation throughout the food chain which leads to serious ecological and health problems (Malik, 2004). Heavy metals are removed traditionally by physico-chemical processes-ion exchange, reverse osmosis, precipitation, solvent extraction, membrane technologies and electrochemical treatments. These techniques have significant disadvantages including incomplete metal removal, the need of expensive monitoring equipments and some physical methods not suitable to remove heavy metal concentration in order of 1–100 mg (Volesky and Holon, 1995). Biosorption has evolved as an attractive technology using inactive and dead biomass to remove heavy metals from aqueous solutions (Soylak *et al.*, 2006).

Metal removal abilities of various species of bacteria, algae, fungi and yeasts have been investigated by several workers (Yetis *et al.*, 2000, Akhtar *et al.*, 2008 and Aksu and Balibek, 2010). Biosorption consists of several mechanisms, mainly ion exchange, chelation, adsorption, and diffusion through cell walls and membranes (Kuyucak and Volesky, 1988), which differ depending on the species used, the origin and processing of the biomass and solution chemistry. Binding sites for metal ions localized at cell surface include carboxylic, hydroxylic and phosphate groups of lipids, proteins, and polysaccharides (Selatnia *et al.*, 2004).

Some reports are available on the use of immobilized biomass for the removal of metal contaminants from their aqueous wastes (Yalcinkaya, 2002, Aryca *et al.*, 2004, Soylak *et al.*, 2006 and Razek *et al.*, 2009). Calcium alginate, a popular entrapment agent in immobilization technology, has been one of the most extensively investigated biopolymer for binding heavy metals from dilute aqueous solutions (Lu *et al.*, 2006). Polyacrylamide gel has been successfully used as immobilizing matrix for removal of many metals.

Chromium compounds are widely used in industries like textile, leather, cement, catalysts and fertilizers. Two stable forms of chromium persist in the environment, Cr (III) and Cr (VI) that have contrasting toxicities, mobility and bioavailability (Bishnoi *et al.*, 2007). Toxic kinetics of Cr (VI) show higher rate of penetration into biological membranes as compared to Cr (III) (Vankar and Bajpa, 2008). Exposure to Cr (VI) causes cancer in digestive tract and lungs and may cause epigestric pain, nausea, vomiting, severe diarrhea and hemorrhage. It is therefore essential to remove Cr (VI) from waste water before disposal.

In the present investigation attempts were made to use encapsulated dead biomass of *Penicillium citrinum* in polymeric matrices such as alginate and to evaluate its metal binding efficiency for the removal of Cr (VI) from its aqueous solution.

Material and Methods

Isolation of the strain: Fungal strain *Penicillium citrinum* was isolated from soil sample collected from a tannery situated in Uttar Pradesh, India in Oct, 2005 by using Rose Bengal culture medium.

Preparation of biosorbents: For the production of biomass, *Penicillium citrinum* was cultivated in liquid broth medium on incubator cum shaker. The *Penicillium citrinum* spores were transferred to 250 ml conical flask filled with 100 ml of nutrient broth (pH 5.0) followed by incubation for 3-4 days at 30 ± 2^{o}C temperature and 120 rpm in incubator cum shaker. The biomass was harvested by filtering through muslin cloth after 4 days of incubation. It was then washed thoroughly with deionized water to remove the growth medium sticking on its surface. After washing, the biomass was autoclaved at 15 psi pressure in an autoclave for 15 min. After that, the 50% biomass was treated with 0.1 N NaOH solution for 15 min, while rest 50% was used in untreated form. Untreated as well as NaOH treated biomass was dried in oven at 60°C and powdered. Then the powdered biomass was sieved through standard sieve to obtain particle of size up to 0.3 mm. For the immobilization of biomass in polymeric matrix of sodium alginate, 3% (W/V) slurry of sodium alginate was prepared in hot (60°C) distilled water. After cooling, 3% (W/V) biomass was added and stirred on magnetic stirrer. The alginate biomass slurry was introduced in 50 mM $CaCl_2.2H_2O$ for polymerization and bead formation using 5 ml syringe. The resultant beads were of 4 mm diameter. The fungal entrapped beads were cured in the solution for 1 hour and then washed twice with 200 ml sterile distilled water.

Preparation of stock solution: Stock solution of Cr (VI) of 1000 mg/l concentration was prepared by dissolving $K_2Cr_2O_7$ in deionized water. It was further diluted with distilled water to make solutions of different concentrations as desired in experiments.

Biosorption studies: Biosorption studies were conducted in batch mode to explore the biosorption capacity of immobilized biomass of *Penicillium citrinum*. The effect of pH (1.0 - 4.0), contact time (15 -120 min.), biosorbent dose (0.1 – 2.0 gm/100 ml) and initial metal ion concentration (10-150 ppm) on removal of Cr (VI) from its aqueous solution was studied using immobilized biomass. All the experiments (except metal ion concentration experiment) were performed with 50 ppm metal concentration. All biosorption experiments were conducted in triplicates using conical flask (250 ml) on an incubator cum shaker (120 rpm) at 30°C. The amount of metal uptake (mg/g) was obtained by using equation:

$$\mathbf{qe = \frac{(Co - Ce)\ V}{W}}$$

Where qe is equilibrium uptake (mg/g); Co is initial metal ion concentration (mg/l); Ce is equilibrium metal ion concentration (mg/l); V is the volume of the metal solution (l); W is the mass of the biosorbent (g).

Adsorption isotherms

The biosorption data obtained for Cr (VI) was plotted using Langmuir and Freundlich isotherms

Langmuir's isotherm model is valid for monolayer adsorption on to a surface containing a finite number of identical sites, which is represented as equation

$$\frac{Ce}{qe} = \frac{1}{Qob} + \frac{Ce}{Qo}$$

Where qe is the amount adsorbed at equilibrium (mg/g); Ce is the equilibrium concentration (mg/l); Qo and b are the Langmuir constants.

The Freundlich equation (Bai and Abraham, 2003) proposes an empirical model that is based on the sorption on heterogenous surface and has the form:

$$\text{Log } x/m = \log k + 1/n\log Ce$$

Where k (mg/g) and n are Freundlich isotherms constants; Ce is the equilibrium concentration (mg/l); x/m is the amount adsorbed (mg/g) and m is the adsorbent dose (g/l).

Results and Discussion

Effect of pH

The effect of pH on Cr (VI) biosorption was investigated at varying pH (1.0-4.0) for both untreated and NaOH treated biomass of *Penicillium citrinum* (Figure 1) Biosorption experiments were carried out at initial metal ion concentration (50 mg/l), biosorbent dose (0.5g/100ml), contact time (60 min.) and temperature (30°C). The equilibrium Cr (VI) sorption was favored by acidic pH i.e. 3 (both untreated & treated), further increase in pH decreased the Cr (VI) biosorption by *Penicillium citrinum*. At pH 3, NaOH treated biomass showed more removal of Cr (VI) i.e. 89% as compared to untreated biomass i.e. 84.36%. The reduction of Cr (VI) to Cr (III) is the reason behind this pattern of biosorption behaviour. At acidic pH, the predominant species of Cr (VI) are $Cr_2O_7^{2-}$, $HCrO^{4-}$ and $Cr_2O_4^{2-}$ and the surface of the sorbent becomes protonated and attracts anionic species of Cr (VI) (Congeevaram *et al*., 2007).

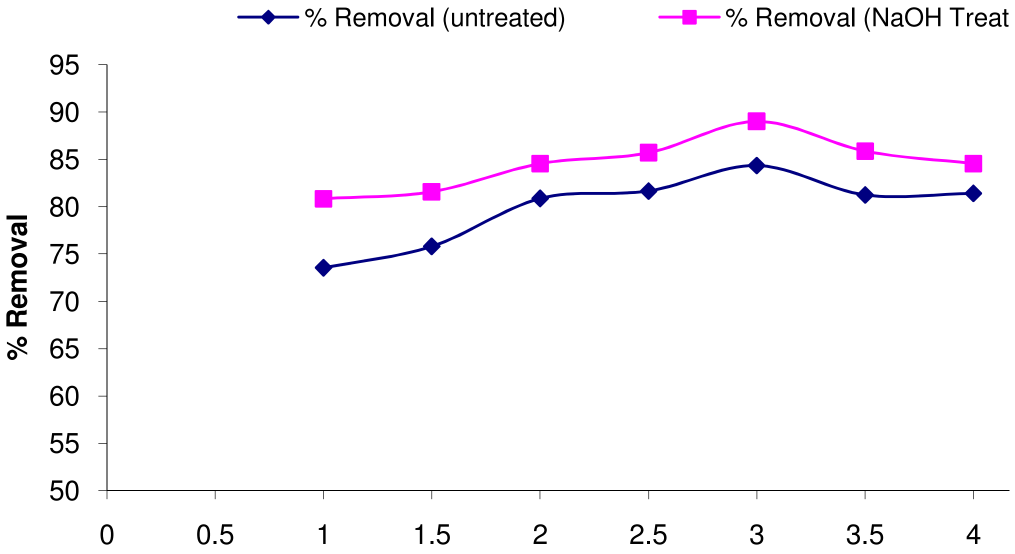

Figure 1 Effect of pH on Cr (VI) removal by untreated and NaOH treated biomass of *Penicillium citrinum*

The negatively charged active sites present on the biosorbent particles play a important role in effective removal of Cr (VI) ions from solutions under acidic pH. The negatively charged active sites got neutralized by exchange with chromium ions thereby decreased hindrance to diffusion to bound Cr (VI) ions under acidic conditions (Garg *et al*., 2004). With the increase in the pH, there is the reduction in electrostatic forces of attraction between Cr (VI) species and surface of the biosorbent which resulted in decrease in biosorption percentage consequently. Similar results were observed by Tewari *et al.,* 2005, Bishnoi *et al.,* 2008 and Chen *et al*., 2009.

Effect of Contact time

The effect of Contact time on Cr (VI) removal by untreated and treated biomass was investigated at optimized pH (3.0) by varying the contact time from 15 to 120 min. (Figure 2) while other parameters such as initial metal ion concentration, biosorbent dose and temperature were kept constant. In case of untreated biomass, the percentage removal of Cr (VI) was increased with increase in contact time from 78.28% to 87.83%. While in case of NaOH treated biomass percentage removal increased from 80.80% to 88.22%. Equilibrium was reached after 60 min. for both biosorbents and at equilibrium NaOH treated biomass showed maximum removal i.e 88.22% while in case of untreated biomass removal was 87.83%, thereafter no appreciable increase in percentage removal was observed. Therefore 60 min. was taken as optimized contact time for further experiments.

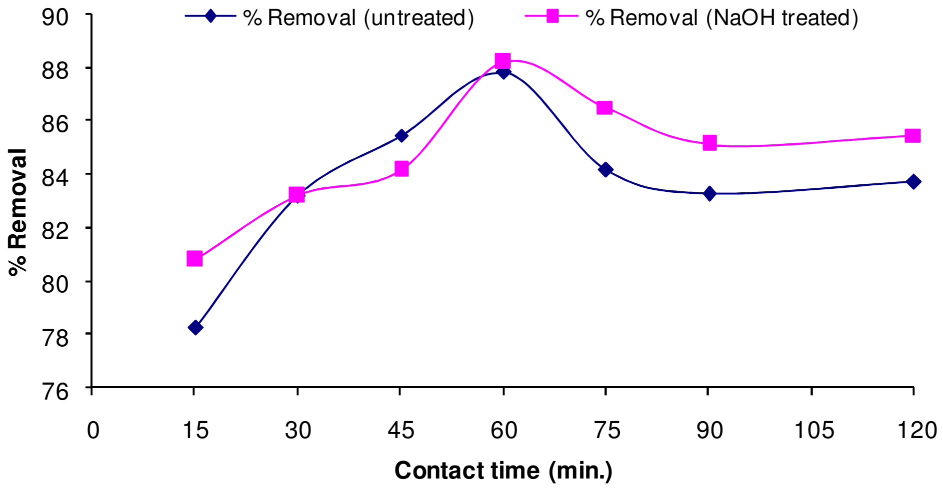

Figure 2 Effect of Contact time on Cr (VI) removal by untreated and NaOH treated biomass of *Penicillium citrinum*

It was observed that after certain time, the rate of removal was not as high as it was in initial time periods. The biosorption get slowed down in later stages because initially a large number of vacant surface sites may be available for biosorption and after sometime the remaining vacant sites may be difficult to occupy due to repulsive force between the solute molecules of the solid and bulk phase (Saravanane *et al*., 2002). Increase in percentage removal of chromium with increase in contact time was also observed by Mungasavalli *et al*., 2007, Priya *et al*., 2008 and El-Kassas & El-Taher, 2009 using CTAB treated *Aspergillus niger*,*Tamarindus indica* fruit nut testa and non-pathogenic marine fungus-*Trichoderma viride* respectively.

Effect of biosorbent dose

The effect of dose for both the biosorbents was studied at optimized pH and contact time by varying the biosorbent dose from 0.1 to 2.0 g/100 ml of aqueous solution. As shown in Figure 3, increase in percentage removal was observed with increase in biosorbent dose upto certain extent thereafter percentage removal became more or less constant. The percentage removal of Cr (VI) was observed to increase from 80.90 % to 88.40% for untreated biomass and from 80.80% to 89.0% for NaOH treated biomass. The optimum biosorbent dose observed was 0.5g/100ml for both the biosorbents. Similarly Mohanty *et al*., (2006) and Qaiser *et al.,* 2009 observed that the maximum removal of Cr (VI) occurred in initial stage, which gradually decreased and remained almost constant after an optimum period. 78% removal of Cr (VI) was observed by using acid treated *Tamarindus indica* fruit nut testa seed coat (Priya *et al*., 2008)

This can be attributed to the fact that with the increase in biosorbent dose, more and more surface become available for solutes to adsorb and this increases the rate of biosorption. Very slow increase in the removal beyond optimal dose is due to the attainment of the equilibrium between biosorbate and biosorbent at the existing operating conditions (Rao *et al*., 2002)

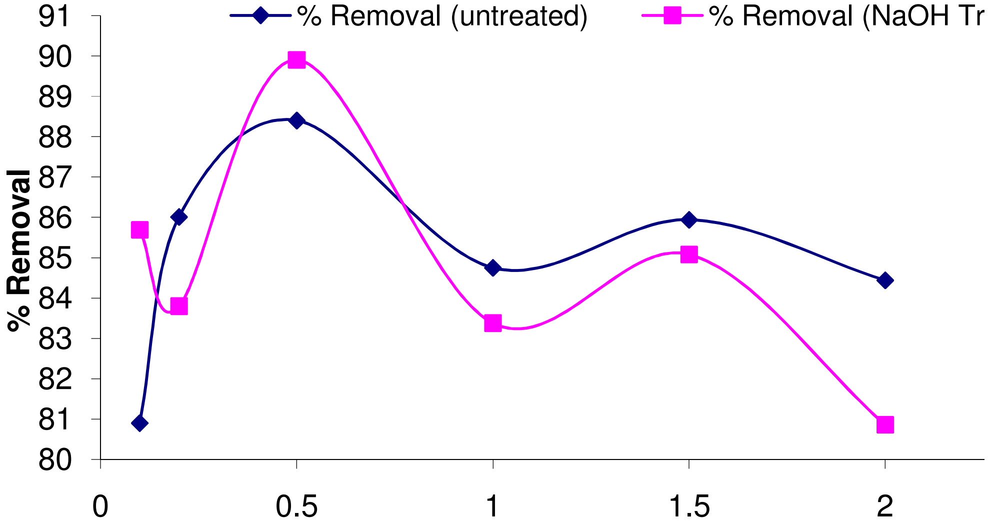

Figure 3 Effect of Biosorbent dose on Cr (VI) removal by untreated and NaOH treated biomass of *Penicillium citrinum*

Effect of Initial metal ion concentration

Effect of initial Cr (VI) ions concentration on its percentage removal was investigated at optimized conditions (pH, contact time and biosorbent dose) by untreated and NaOH treated biomass of *Penicillium citrinum*. The metal ion concentration was varied from 10 mg/l to 150 mg/l.

As evident from Figure 4, a significant increase in Cr (VI) ions removal was observed with increasing metal ion concentration from 10 to 50 ppm thereafter percentage removal decreased with further increase in metal ions concentration. Percentage removal increased from 68.56% to 88.32% and 76.5% to 89.34% for untreated and NaOH treated biomass respectively. Decrease in percentage removal after 50ppm concentration may be due to increase in number of competing ion for available binding sites and also due to the lack of binding sites for the complexation at higher concentration of metal ions (Garg *et al*., 2004).So 50 ppm concentration was taken as optimum concentration for both the biosorbents.

Increase in sorption rate of Cr (III) on fungal biomass was observed with increase in initial Cr (III) concentration from 455, 1076, 1630 and 2600 mg/l by Louhab *et al*., (2006).

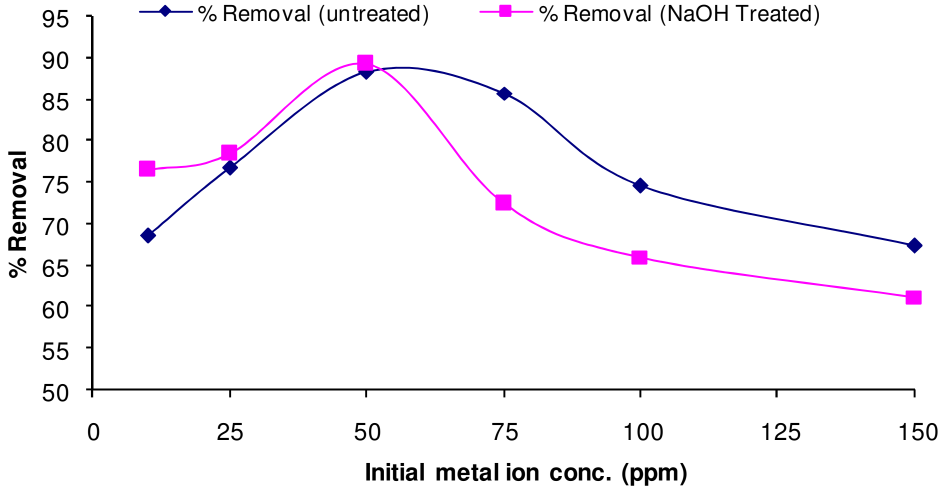

Figure 4 Effect of Initial metal ion concentration on Cr (VI) removal by untreated and NaOH treated biomass of *Penicillium citrinum*

Biosorption studies

The Langmuir and Freundlich adsorption models were used for mathematical description of biosorption of Cr (VI) ions and isotherms constants were determined to compare the adsorption capacity of immobilized biomass of *Penicillium citrinum.* Higher values of $R^2 \geq 0.90$ indicated that the biosorption data are well fitted to Langmuir and Freundlich isotherm (Table 1).

In case of Langmuir isotherm, value of Qo were 19.083 (untreated) and 15.15 (NaOH treated), which indicated a good adsorption capacity while lower value of b i.e 0.025 (untreated) and 0.004 (NaOH treated) indicated high affinity of biosorption of Cr (VI). The applicability of this model indicates the adsorption to be monolayer.

Table 1 Isotherm model constant and correlation coefficient for biosorption of Cr (VI) by untreated and NaOH treated biomass of *Penicillium citrinum*

P.citrinum	**Langmuir constant (mg/gm)**			**Freundlich constant (mg/gm)**		
	Q_0(mg/gm)	b	R^2	K(mg/gm)	n	R^2
Untreated biomass	19.083	0.025	0.8989	1.467	1.083	0.9444
NaOH treated biomass	15.15	0.004	0.9388	1.163	1.415	0.9306

In case of Freundlich isotherm, higher values of K and n i.e. 1.467 and 1.083 and 1.163 and 1.415 respectively for untreated and NaOH treated biomass, indicated a high biosorption capacity and higher intensity of biosorption.

Conclusion:

The higher biosorption efficiency of *Penicillium citrinum* makes it an effective biosorbent for Cr (VI) removal from its aqueous solution. So the biosorption using immobilized biomass of *Penicillium citrinum* can be used as an alternative technique for the removal of heavy metals from their aqueous solutions.

Authors' contributions: Dr. Asha Gupta, (Associate Professor) *contributed in experiment design, performance, editing and also corresponding author of the manuscript; Puneet Kaushik, (M.Tech student) performed experiments and helped in calculations.*

References:

Akhtar, N., Iqbal, M., Zafar, S.I, Iqbal, J., 2008. Biosorption characteristics of unicellular green alga *Chlorella sorokiniana* immobilized in loofa sponge for removal of Cr (III). *Journal of Environmental Science* 20, 231–239.

Akinlua, A., Asubiojo,O.I., 2006.Physico-chemical and trace metal characterization of battery factory wastwwater. *Journal of Applied Sciences* 6 (7), 1456-1462.

Aksu, Z., Balibek, E., 2010. Effect of salinity on metal-complex dye biosorption by *Rhizopus arhizus*. *Journal of Environmental Management* 91(7), 1546-1555.

Aryca, M.Y., Bayramoglu,G., Yilmaz,M., Bekta,S., Gencb,O., 2004.Biosorption of Hg^{+2}, Cd^{+2} and Zn^{+2} by Ca-alginate and immobilized wood-rotting fungus, *Funalia trogii.Journal of Hazardous Materials* 09, 191-199.

Bai, S.R., Abraham, E.T., 2003. Studies on chromium (VI) adsorption-desorption using immobilized fungal biomass. *Bioreource Technology* 87, 17-26.

Bishnoi, N.R., Kumar, R., 2008. Biosorption of Cr (VI) with *Trichoderma viride* immobilized fungal biomass and cell free Ca-alginate beads. *Indian Journal of Experimental Biology* 45, 657-664.

Bishnoi, N.R., Kumar, R., Kumar, S., Rani, S., 2007. Biosorption of Cr (III) from aqueous solution using algal biomass *Spirogyra* sp. *Journal of Hazardous Materials* 145, 142–147.

Chen, Y., Tang, G., Yu, Q.J., Zhang, T., Chen, Y., Gu,T., 2009.Biosorption properties of hexavalent chromium on to biomass of tobacco-leaf residues. *Environmental Technology* 30 (10), 1003–1010.

Conngeevaram, S., Dhanarani, S., Joonhong, P., Michael, D., Thamaraiselvi, K., 2007. Biosorption of chromium and nickel by heavy metal resistant fungal and bacterial isolates. *Journal of Hazardous Materials* 146, 270-277.

El-Kassas, H.Y., El-Taher, E.M., 2009. Optimization of Batch Process Parameters by Response Surface Methodology for Mycoremediation of Chrome-VI by a Chromium Resistant Strain of Marine *Trichoderma Viride. American-Eurasian Journal of Agriculture & Environmental Science* 5 (5), 676-681.

Garg, V.K., Gupta, R., Kumar, R., Gupta, R.K., 2004. Adsorption of chromium from aqueous solution on treated sawdust. *Bioresource Technology* 92, 79-81.

Kuyucak, N., Volesky, B., 1988. Biosorbents for recovery of metals from industrial solutions. *Biotechnology Letters* 10 (2), 137-142.

Louhab, K., Nacer, S., Bilango, G., 2006.Kinetics of chromium sorption on biomass fungi from aqueous solution.*American Journal of Environmental Sciences* 2 (1), 27-32.

Lu, W.B., Shi, J.J., Wang, C.H., Chang, J.S., 2006. Biosorption of lead, copper and cadmium by an indigenous isolate *Enterobacter* sp. J1 possessing high heavy-metal resistance. *Journal of Hazardous Materials* 134 (1-3), 80-86.

Malik, A., 2004. Metal bioremediation through growing cells. *Environment International* 30, 261-278.

Mohanty, K., Meikap, B.C., Biswas, M.N., 2006. Biosorption of chromium (VI) from aqueous solutions by *Eichhornia crassipes*. *Chemical Engineering Journal* 117, 71-77.

Mungasavalli, D.P., Viraraghvan, T., Jin, Y. C., 2007. Biosorption of chromium from aqueous solutions by pretreated *Aspergillus niger*. batch and column studies. *Collids and Surfaces A: Physicochemical Engineering Aspects* 301, 214-233.

Priya, A.J., Gajulapalli, S.R., Abburi, S., Boddu, V.M., 2008. Biosorption of Chromium, Copper, and Nickel Ions by *Tamarindus Indica* Fruit Nut Testa. *Bioremediation Journal* 12 (3), 145–155.

Qaiser, S., Saleemi, A.R., Umar, M., 2009. Biosorption of lead (II) and chromium (VI) on groundnut hull: Equilibrium, kinetics and thermodynamics study. *Electronic Journal of Biotechnology* 12 (4), 23-34.

Rao, M., Parvate, A.V., Bhole, A.G., 2002. Process development for the removal of copper and lead from aqueous solution using low cost material. *Journal of Environmental Pollution* 22 (1), 17

Razek, A.S., AbdelGhany, T.M., Mahmoud, S.A., ElSheikh, H.H., Mahmoud, M.S., 2009. The use of free and immobilized *Cunninghamella elegans* for removing cobalt ions from aqueous waste solutions. *World Journal of Microbiology & Biotechnology* 25, 2137-2145

Saravanane, R., Sundararajan, T., Reddy, S.S., 2002. Efficiency of chemically modified low cost adsorbents for the removal of heavy metals from wastewater. *Indian Journal of Environmental Health* 44, 78-87.

Selatnia, A., Madani, A., Bakhti, M.Z., Kertous, L., Mansouri, Y., Yous, R., 2004. Biosorption of Ni^{2+} from aqueous solution by a NaOH-treated bacterial dead *Streptomyces rimosus* biomass. *Mineral Engineering* 17, 903–911.

Soylak, M., Tuzen, M., Mendil, D., Turkelkul, 2006. Biosorption of heavy metals on *Aspergillus fumigatus* immobilized Diaion HP-2MG resin for their atomic absorption spectrophotometric determinations.*Talanta* 70 (5), 1129-1135.

Tewari, N., Vasudeven, P., Guha, B.K., 2005. Study on biosorption of Cr (VI) by *Mucor hiemalis. Biochemical Engineering Journal* 23, 185-192.

Vankar, P., Bajpa, D., 2008.Phyto-remediation of chrome-VI of tannery effluent by *Trichoderma* species. *Desalination* 222, 255-262.

Volesky, B., Holan, Z.R., 1995.Biosorption of heavy metals. *Biotechnology Progress* 11 (3), 235-250.

Yalcinkaya, Y., Arica, M.Y., Soyasal, L., Adil, O., Omer, G., Sema, B., 2002.The removal of Pb (II) by *Phanerochaete chrysosporium.Water Research* 34 (16), 4090-4100.

Yetis, U., Dolek, A., Dilek, F.B., Ozcengiz, G., 2000. The removal of Pb (II) by *Phanerochaete chrysosporium*. *Water Research* 34 (16), 4090-4100.