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Utilization of *Aspergillus terreus* for the Biosorption of Hexavalent Chromium Ions

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ABSTRACT

The heavy metal contamination of the water bodies is a worldwide environmental problem and its removal is a great challenge. This long term environmental hazard has received considerable attention in recent years. The use of low cost waste materials as adsorbents of heavy metal provides an eco friendly complimentary solution in removal of the dissolved metal ions and utilization of the waste materials. In the present investigation, biosorption of Cr (VI) ions was carried out using *Aspergillus terreus* dead biomass and the effect of various parameters such as pH, temperature, incubation time, initial metal concentration and initial biomass concentration which influenced the removal of Cr (VI) ions was studied. The experimental results showed that *Aspergillus terreus* is an effective biosorbent for the removal Cr (VI) ions. There was a strong influence of pH over biosorption process; especially over pH 1 it reached 54%. Similarly bisorption was observed higher when there was increase in the biomass concentration and decrease in initial metal concentration. Temperature also has a considerable impact on biosorption process, maximum at 27°C. Further, the untreated and treated biosorbent were characterized by FTIR spectral analyses and SEM micrograph to study the nature of bisorbent before and after the removal of Cr (IV) ions. The results of the present study revealed the potential use of *Aspergillus terreus* biomass as biosorbent for the removal of Cr (VI) from the aqueous environment.

Key words: Biosorption, *Aspergillus terreus*, biosorbent, FTIR, SEM

INTRODUCTION

The increase in industrial activities has maximized the environmental pollution and the deterioration of several ecosystems with the accumulation of many pollutants, especially heavy metals. Heavy metal released into the environment by technological activities or accidental, including chemical spills or improper land disposal tends to persist indefinitely accumulating and circulating throughout the food chain, leading to a serious problem for the mankind and the environment (Pagnelli *et al*., 2000).

Among the various heavy metals, chromium in the aquatic environment has been classified under Group A of human carcinogens by the United States Environmental Protection Agency (USEPA) (Costa, 2003). Chromium in the form of chromate and dichromate is extensively used in electroplating, metal finishing, leather tanning, nuclear power plants and textile industries.

(Barnhart, 1997). The trivalent (Cr^{3+} and $CrOH^{2+}$) and hexavalent ($HCrO_4^-$ and $Cr_2O_7^{2-}$) states of chromium were mostly observed in these industrial effluents. Cr (VI) is known to be highly toxic to both plants and animals, due to its strong oxidizing property and a potential carcinogen. Although Cr (III) is less toxic than Cr (VI) or nontoxic, long term exposure to a higher concentration of Cr (III) may cause symptoms such as allergic skin reactions (Rudolf and Cervinka, 2005). Therefore, the discharge of Cr (VI) to surface water has been regulated to <0.05 mg L^{-1}, according to USEPA, whereas the total chromium (containing Cr (III), Cr (VI) and other forms of chromium) to <2 mg L^{-1} (Baral and Engelken, 2005).

Commonly employed conventional methods to remove heavy metals from wastewaters, such as chemical precipitation, electro winning, membrane separations, evaporation and ion exchange may be technologically inapplicable or very expensive from an economic point of view. The drawback of conventional methods includes (1) utilization of expensive chemical reductants, (2) inadequate removal of chromate from wastewater to meet regulatory standards, (3) generating large volumes of toxic sludge which needs special storage facility and (4) inability in complete recovery of chromium in Cr (VI). For the above reasons, interest has arisen recently in the investigation of some unconventional methods and materials for scavenging heavy metal ions from industrial effluents (Cabatingan *et al*., 2001).

Biosorption of heavy metals is one of the most promising technologies which involve removal of toxic metals from industrial waste streams and natural waters through the use of biomaterials as a low-cost adsorbent. Biosorption is a process that uses non-living biomass as an adsorbent material, in contrast to bioaccumulation, which involves the application of living microorganisms (Zouboulis *et al*., 1997). It employs the application of divergent biomass such as seaweed (Yun *et al*., 2001), microalgae (Gupta *et al*., 2001), fungi (Sag and Kutsal, 2000), bacteria (Nourbakhsh *et al*., 2002) and various other plant materials (Gardea-Torresdey *et al*., 2000). Fungal biomass has a benefit over the other biomass as it can easily obtained in large quantities as a byproduct from industrial fermentation processes which can been used for the removal of chromium from wastewaters (Park *et al*., 2005; Khambhaty *et al*., 2009).

Different microorganisms (algae, bacteria, fungi and yeasts) are able to accumulate heavy metals and additionally, agricultural wastes have also been tested for metal sorption. The biosorption mechanisms can be metabolism independent and a function of the microbial cell activity. The cell walls consisting mainly of polysaccharides, proteins and lipids having functional groups such as carboxylate, hydroxyl, sulfate, phosphate, amide and aminogroups are responsible for the biosorption of chromate ions. The nature of microbial species and its physiological state to external physio-chemical conditions such as pH, temperature, initial metal concentration and inoculum concentration etc., has impact on heavy metal biosorption (Xu *et al*., 2004). In the present study, *Aspergillus terreus* dead biomass was screened for the biosrption of Cr (VI) and various parameters such as pH, contact time, initial Cr (VI) concentration, biomass concentration and temperature influencing Cr (VI) biosorption were also studied.

MATERIALS AND METHODS

Materials: All the reagents and media used in this study were purchased from Himedia Laboratories Pvt. Ltd, Mumbai, India and Sisco Research Laboratories (SRL) Pvt. Ltd. Mumbai, India.

The fungi, *Aspergillus terreus*, *Aspergillus flavus*, *Aspergillus niger* and *Aspergillus fumigatus* used in the present study was obtained from culture collection centre,

Centre for Advanced Studies in Botany, Guindy Campus, University of Madras, Chennai. The culture was maintained on Potato Dextrose Agar (PDA) slants at 27°C.

Preparation of metal solutions: Stock solution (1000 mg L^{-1}) of Cr^{6+} was prepared by dissolving 2.828 g of analytical grade of $K_2Cr_2O_7$, in double deionized water. Before mixing with the biosorbents, the stock solution was diluted based on the required concentration. The pH adjustment was carried out using 0.1 N HCl and 0.1 N NaOH solutions.

Preparation of fungal biosorbent: For biosorption study, the fungal strains were grown in the PDB medium for 5 to 7 days. The live fungi were killed by boiling in 0.5 N NaOH using water bath for 15 min. The mat was then washed with distilled water for about 6-7 times till the pH of the solution reached in the range of 7 to 7.2. The mat was dried in hot air oven at 50°C for 24 h. The dried dead fungal biomass was stored in a desiccator and used for further study.

Analytical estimation of chromium: A 0.25% w/v solution of diphenyl carbazide was prepared in 50% acetone. The sample solutions, 15 mL each of containing various concentrations of Cr (VI) were pipetted out into 25 mL standard flasks. To this 2 mL of 3 M H_2SO_4 was added followed by 1 mL of diphenylcarbazide and the total volume was made up to 25 mL using double distilled water. Chromium concentration was estimated by the intensity of the colour complex formed which was measured using a UV visible spectrophotometer. The absorbance was measured against a reagent blank at 540 nm. A linear plot was obtained indicating adherence to the Beer Lambert's law in the concentration range studied (Clesceri *et al*., 1998).

Determination of biosorption percentage: The percentage of Cr (VI) biosorption, (%R), which represents the metal uptake, was calculated from the difference in metal concentration in the aqueous phase before and after biosorption, according to the following equation. The biosorption efficiency (%) was calculated according to the following equation (Bajpai and Rai, 2010):

$$\%R = \frac{C_o - C_e}{C_e} \times 100$$

Where:

%R = Percent removal of chromium

C_o = Initial metal concentrations (mg mL^{-1})

C_e = Final metal concentrations (mg mL^{-1})

Metal biosorption experiments: All the experiments (except the effect of temperature on biosorption efficiency) were conducted at a constant temperature of 35±2°C to be representative of environmentally relevant conditions. In order to determine the biosorption ability, the dead fungal biomass (1 mg mL^{-1}) was mixed with a solution containing 1 mg mL^{-1} of Cr (VI) separately at pH 2.0 at 35±2°C for 24 h and the most promising fungal biomass was selected and used for further optimization studies.

Effect of pH on the biosorption of Cr (VI) was observed by varying the initial pH of the metal solution i.e., 1 to 10 using 0.1 N HCl or 0.1 N NaOH. The reaction mixture containing metal solution (1 mg mL^{-1}) and biomass (1 mg mL^{-1}) was incubated at 35°C for 6, 12, 18, 24, 30, 36 and

42 h to determine the optimum incubation time. Effect of temperature on the biosorption of Cr (VI) was studied using five different temperatures viz., 25, 27, 29, 31 and 35°C and incubated for 24 h. In order to determine the effect of initial Cr (VI) concentration on biosorption, solutions containing 1 to 10 mg mL^{-1} of chromium were used. The effect of initial biomass concentration on the Cr (VI) removal was also studied by employing 1 to 10 mg mL^{-1} of biomass in the solution containing metal (1 mg mL^{-1}). The flasks were agitated on a shaker at 120 rpm. The solution was sampled at regular intervals, filtered and the Cr (VI) concentration of the filtrate was analyzed for the residual concentrations of the metal ions using diphenylcarbazide assay method (Goyal *et al.*, 2003).

Characterization of biosorbents

Fourier transform-infrared spectroscopy: A raw sample of fungal biomass and biomass loaded with Cr^{6+} were analyzed using an infrared spectrophotometer (IR) Model 470 Shimadzu corporation adopting KBr disk technique. For the FTIR study, 25 mg of finely ground untreated and treated biomass of *Aspergillus terreus* was pelletized with KBr in order to prepare translucent sample disks (Khambhaty *et al.*, 2009).

Scanning electron analysis: The surface structure of biosorbent was analyzed by Scanning Electron Microscopy (SEM) S-3400 Hitachi. Untreated and metal-treated fungal biomass samples were mounted on aluminum stab sequenced by sputter coating with gold under vacuum to increase the electron conduction and to improve the quality of the micrographs (Khambhaty *et al.*, 2009).

RESULTS

Among the five species of fungi, the dead biomass of Aspergillus *terreus* showed maximum biosorption efficiency and was chosen for further optimization studies. The effects of various parameters like pH, incubation time and temperature on the removal efficiency of Cr (VI) ions using *Aspergillus terreus* dead biomass was investigated in the present study. Figure 1 shows the biosorption of Cr (VI) ions using fungal biomass when the pH of the medium was varied from 1 to 10. It was observed that pH 1 and 24 h of incubation was optimum for Cr (VI) biosorption. The results presented in Fig. 2 shows that biosorption of metal ions steadily increased from 12 to 36 h

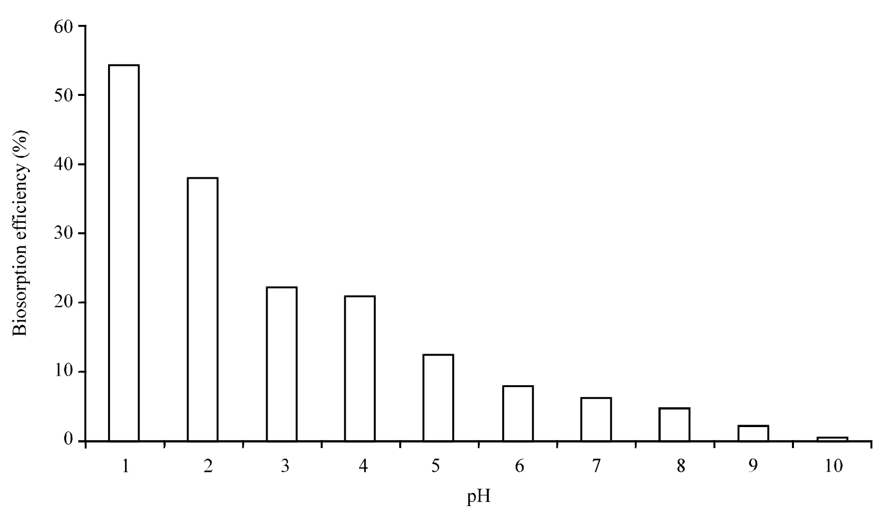

Fig. 1: Effect of Initial pH on biosorption

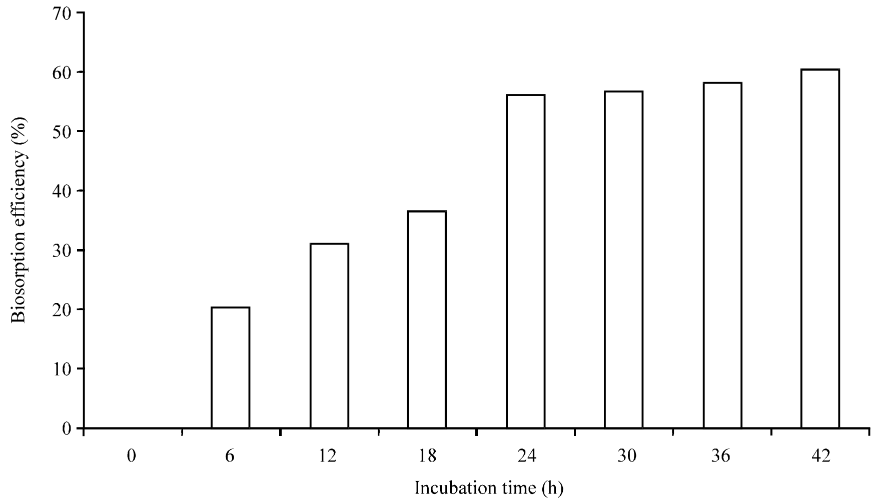

Fig. 2: Effect of incubation time on biosorption

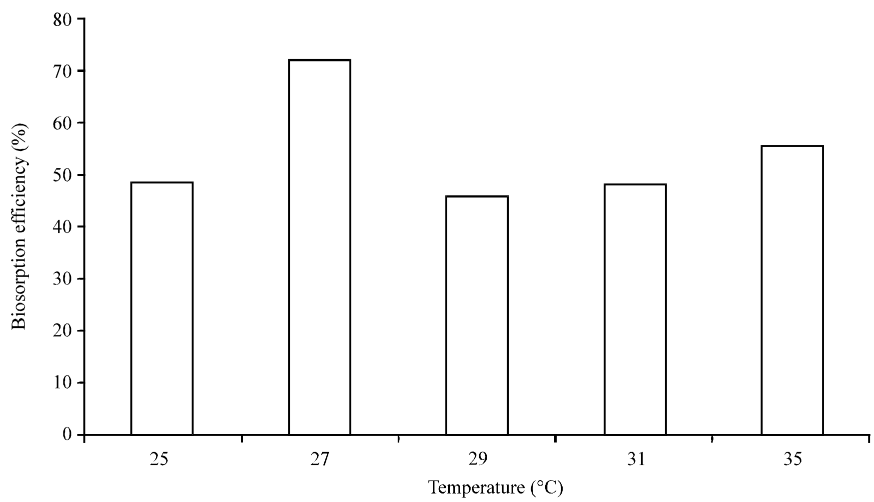

Fig. 3: Effect of temperature on biosorption

and the optimum was recorded at 24 h. Temperature plays a major role in the biosorption of hexavalent chromium ions. Based on the results, biosorption of Cr (VI) ions reaches maximum at 27°C (Fig. 3). The effect of initial metal concentrations on biosorption experiments using treated biomass is shown in Fig. 4. The effect of initial biosorbent concentration of the present study is shown in the Fig. 5. It was observed that increase in biosorbent dose from 1 to 10 mg mL^{-1} resulted in increase in biosorption rate of Cr (VI) ions. The FT-IR spectra are useful to study the binding states of functional groups and metal ions. The biosorption of chromium ions may depend on factors such as the quantity of sites, their accessibility, chemical state and affinity between site and metal. Fig. 6a and b show the absorption peaks, indicating the nature of the untreated and treated biomass. FTIR spectrum of control biomass (Fig. 6a) shows peaks ranges from 3430, 2932, 1638, 1542, 1402, 1155, 1047 and 628 cm^{-1} and treated fungal biomass shows 3389, 1638, 1402, 1231,

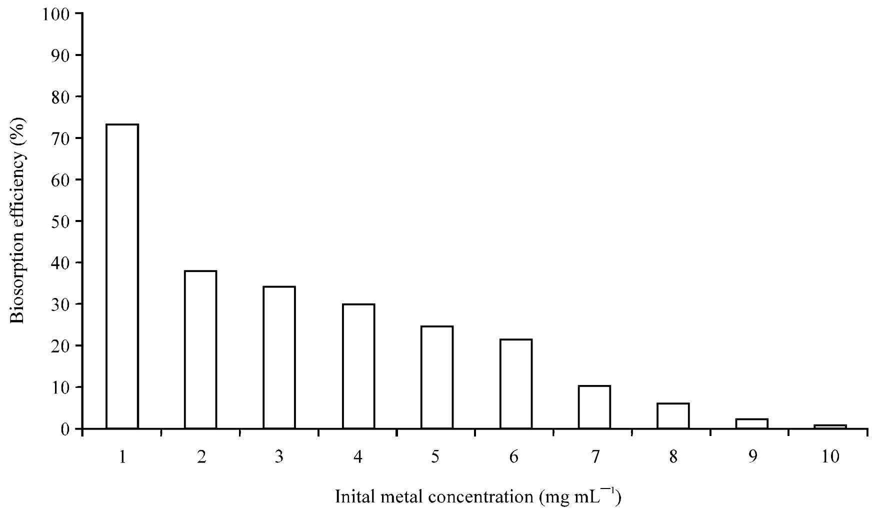

Fig. 4: Effect of initial metal ion concentration on biosorption

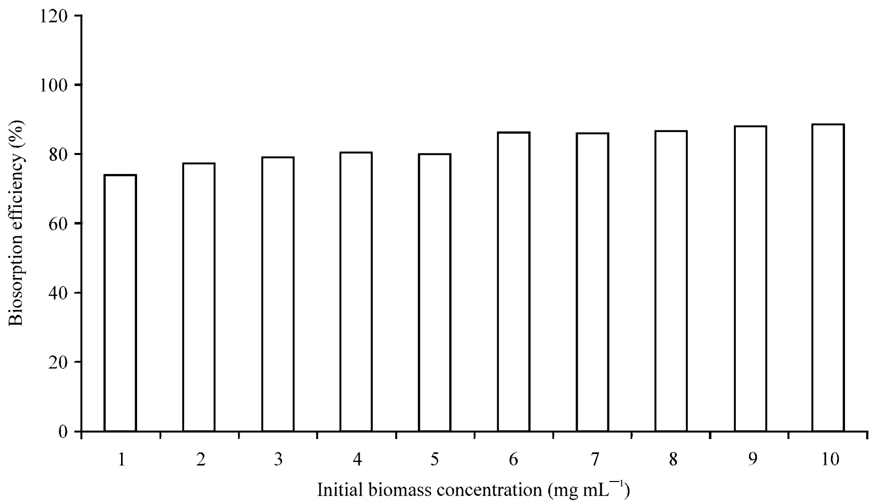

Fig. 5: Effect of initial biomass concentration on biosorption

1076, 930, 653 and 534 cm^{-1}. SEM micrographs of untreated and Cr (VI) loaded dead biomass of *A. terreus* biomass was presented in Fig. 7a and b. The micrograph shows the filamentous structure of the biosorbent and linear grooves and projections on the surface of *A. terreus* whereas the Cr (VI) loaded biomass shows significant changes in morphological structure due to the accumulation of metal deposited on the surface of the biomass.

DISCUSSION

The cell wall is made up of several components such as carboxyl, carbonyl, alcoholic and amino groups which determines the biosorption ability based on its protonation or unprotonation nature. Earlier studies on heavy metal biosorption have shown that pH was the single most important parameter affecting the biosorption process (Aksu *et al.*, 1991; Donmez *et al.*, 1999). At acidic pH, protonation of amino groups of the cell wall components enhance the biosorption capacities due to electrostatic binding of positively charged groups. The increased binding of Cr (VI) ions at low pH

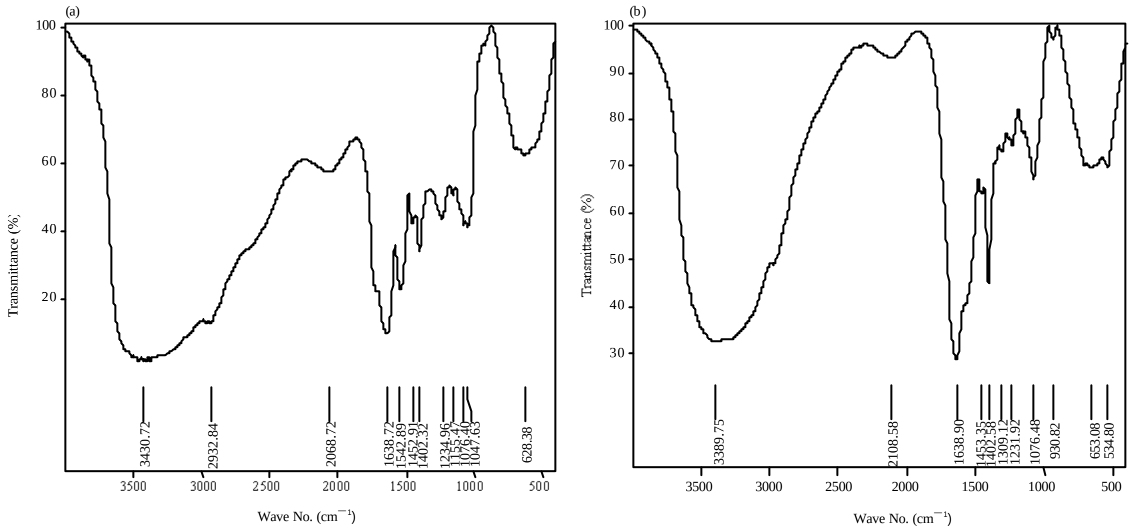

Fig. 6(a-b): (a) FTIR spectra of untreated biosorbent and (b) FTIR spectra of treated biosorbent

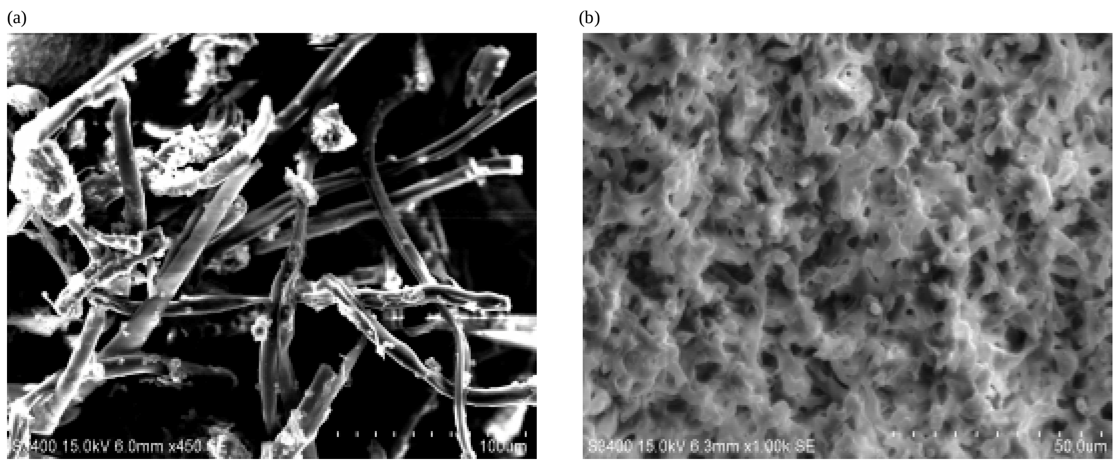

Fig. 7(a-b): (a) SEM Micrograph of untreated biosorbent and (b) SEM Micrograph of treated biosorbent

was explained due to the electrostatic binding to positively charged groups such as amines of the Cassia fistula cell wall components (Gupta and Keegan, 1998; Bajpai *et al.*, 2004; Fourest *et al.*, 1994; Sharma and Foster, 1993). The optimum incubation time was observed at 24 h analogous to earlier reports on *Aspergillus versicolor* (Das *et al.*, 2007) and *Rhizopus oligosporus* (Ozsoy, 2010).

The increase in temperature improved the Cr (VI) biosorption rate and decreased the contact time required for complete Cr (VI) removal (Khambhaty *et al.*, 2009). Reports have suggested that if the interaction between metal ions and microbial cell wall is endothermic, higher temperature would enhance binding, whereas the exothermic interaction would prefer binding at lower temperature. Similar reports of Bai and Abraham (2001) showed a decline in Cr (VI) sorption capacity at 50°C by *Rhizopus nigricans*. Srivastava and Thakur (2006) also observed that 30°C was the optimum temperature for the bioaccumulation of chromium by *Aspergillus* sp. The rate of biosorption decreased with increasing concentration of metal ions in the solution (Ahalya *et al.*, 2005). At lower concentration, the adsorption sites utilized the available metal more rapidly but during higher concentrations, the metal ions need to diffuse to the biomass surface by intraparticle diffusion (Horsfall and Spiff, 2004). At higher metal concentration, the percentage of metal removed decreases due to diminishing loading capacity of biomass. Reports shows that this is due to the adhesion of more ions to the biosorbent and the establishment of equilibrium between the ions bound to the sorbent and those remaining unadsorbed in the solution. In the present investigation, almost 82% reduction in Cr (VI) ions was observed when biomass dosage was increased. Similar reports available on this aspect also supports the results of the study where increase in biomass concentration enhanced the amount of Cr (VI) biosorption (Bai and Abraham, 2001; Tewari *et al.*, 2005).

The band around 3,430 cm^{-1} is indicative of the existence of the -OH groups. The band at 2,932 cm^{-1} is representative of -CH stretching where as bands at 1638 confirms the presence of N–H stretching. The band at 1,542 cm^{-1} could be attributed to Amide I and II (mostly N-H bending). The band around 1,402 and 1,155 cm^{-1} signifies the presence of $-SO_2$-N and SO_2, respectively whereas band at 1,047 cm^{-1} indicates the presence of P-O alkyl (phosphorous compounds) (Khambhaty *et al.*, 2009; Williams and Fleming, 1991). Similar reports were also suggested by Mungasavalli *et al.* (2007) who have also experimented by analyzing the presence of various functional groups on the cell wall which facilitates the binding of Cr (VI) ions. Similar results reported on this aspect where evident that a morphological change occurs during the binding of Cr (VI) ions (Khambhaty *et al.*, 2009).

CONCLUSION

The ability of *A. terreus* to adsorb Cr (VI) was studied with reference to various parameters that affect the experimental process. It was observed that pH, incubation time, temperature, initial metal ion concentration and initial biomass concentration highly affected the biosorption efficiency of the sorbent. The maximum uptake of Cr (VI) ions occurred at pH 1. The increase in the initial amount of biosorbent increases the percentage of biosorption while increase in the initial metal concentration tends to decrease the percent removal of the metal ions. Further, the biosorbent was characterized by FTIR spectral analyses which determined the binding states of functional groups of both treated and untreated fungal biomass, whereas in SEM analyses the morphological changes of the biosorbents were observed. The study demonstrated that *A. terreus* has the potency to remove hexavalent chromium from aqueous solution which shows a promising technology for the removal of heavy metals from industrial wastewaters. Further desorption studies can be carried out as the final approach for the management of heavy metals loaded biomass as an environmental friendly approach of disposal.

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REFERENCES

Ahalya, N., R.D. Kanamadi and T.V. Ramachandra, 2005. Biosorption of chromium (VI) from aqueous solutions by the husk of Bengal gram (*Cicer arientium*). Elect. J. Biotechnol., 8: 258-264.

Aksu, Z., T. Kutsal, S. Gun, N. Haciosmanoglu and M. Gholminejad, 1991. Investigation of biosorption of Cu(II), Ni(II) and Cr(VI) ions to activated sludge bacteria. Environ. Technol., 12: 915-921.

Bai, R.S. and T.E. Abraham, 2001. Biosorption of Cr(VI) from aqueous solution by *Rhizopus nigricans*. Bioresour. Technol., 79: 73-81.

Bajpai, P., V. Shaman, K.G. Ealer and A.K. Gupta, 2004. Adsorption of Cr (III) and Cr (VI) from aqueous solution by *Bacillus cereus* biomass. Electron. J. Biotechnol., 7: 399-403.

Bajpai, A.K. and L. Rai, 2010. Removal of chromium ions from aqueous solution by biosorption on to ternary biopolymeric microspheres. Indian J. Chem. Technol., 17: 17-27.

Baral, A. and R.D. Engelken, 2005. Chromium-based regulations and greening in metal finishing industries in the USA. Environ. Sci. Policy, 5: 121-133.

Barnhart, J., 1997. Occurrences, uses and properties of chromium. Regul. Toxicol. Pharmacol., 26: S3-S7.

Cabatingan, L.K., R.C. Agapay, J.L.L. Rakels, M. Ottens and L.A. M. van der Wielen, 2001. Potential of biosorption for the recovery of chromate in Industrial wastewaters. Ind. Eng. Chem. Res., 40: 2302-2309.

Clesceri, L.S., A.E. Greenberg and A.D. Eaton, 1998. Standard Methods for the Examination of Water and Wastewater. 20th Edn., American Public Health Association, Washington, DC., USA., pp: 366-368.

Costa, M., 2003. Potential hazards of hexavalent chromate in our drinking water. Toxicol. Applied Pharmacol., 188: 1-5.

Das, S.K., A.R. Das and A.K. Guha, 2007. A study on the adsorption mechanism of mercury on Aspergillus versicolor biomass. Environ. Sci. Technol., 41: 8281-8287.

Donmez , G.C., Z. Aksu, A. Ozturk and T. Kutsal, 1999. A comparative study on heavy metal biosorption characteristic of some algae. Process Biochem., 34: 885-892.

Fourest, E., C. Canal and J.C. Roux, 1994. Improvement of heavy metal biosorption by mycelial dead biomasses (*Rhizopus arrhizus, Muchor miehei* and *Pencillium chrysogenum*): pH control and cationic activation. FEMS Microbiol. Rev., 14: 325-332.

Gardea-Torresdey, J.L., K.J. Tiemann, V. Armendariz, L. Bess-Oberto and R.R. Chianelli *et al.*, 2000. Characterization of Cr (VI) binding and reduction to Cr (III) by the agricultural byproducts *Avena monida* (oat) biomass. J. Hazard Mater., 80: 175-188.

Goyal, N., S.C. Jain and U.C. Banerjee, 2003. Comparative studies on the microbial adsorption of heavy metals. Adv. Environ. Res., 7: 311-319.

Gupta, G. and B. Keegan, 1998. Bioaccumulation and biosorption of lead by poultry litter microorganisms. Poult. Sci., 77: 400-404.

Gupta, V.K., A.K. Shrivastava and N. Jain, 2001. Biosorption of chromium (VI) from aqueous solutions by green algae *Spirogyra* species. Water Res., 35: 4079-4085.

Horsfall, M. and A.I. Spiff, 2004. Effect of metal ion concentration on the biosorption of Pb^{2+} and Cd^{2+} by *Caladium bicolor* (wild cocoyam). Afr. J. Biotechnol., 4: 191-196.

Khambhaty, Y., K. Mody, S. Basha and B. Jha, 2009. Biosorption of Cr (VI) onto marine *Aspergillus niger*: Experimental studies and pseudo-second order kinetics. World J. Microbiol. Biotechnol., 25: 1413-1421.

Mungasavalli, D.P., T. Viraraghavan and Y.C. Jin, 2007. Biosorption of chromium from aqueous solutions by pretreated aspergillus niger: Batch and column studies. Colloids Surf. A: Physicochem. Eng. Aspects, 301: 214-223.

Nourbakhsh, M.N., S. Kilicarslan, S. Ilhan and H. Ozdag, 2002. Biosorption of Cr^{6+}, Pb^{2+} and Cu^{2+} ions in industrial waste water on *Bacillus* sp. Chem. Eng. J., 85: 351-355.

Ozsoy, H.D., 2010. Biosorptive removal of Hg (II) ions by *Rhizopus oligosporus* produced from corn-processing wastewater. Afr. J. Biotechnol., 9: 8783-8790.

Pagnelli, F., M.P. Petrangeli, L. Toro, M. Trifoni and F. Veglio, 2000. Biosorption of metal ions on *Arthrobacter* sp: Biomass characterization and biosorption modeling. Environ. Sci. Technol., 34: 2773-2778.

Park, D., Y.S. Yun, J.H. Jo and J.M. Park, 2005. Mechanism of hexavalent chromium removal by dead fungal biomass of *Aspergillus niger*. Water Res., 39: 533-540.

Rudolf, E. and M. Cervinka, 2005. The role of biomembranes in chromium-(III)-induced toxicity *in vitro*. Altern. Lab. Anim., 33: 249-259.

Sag, Y. and T. Kutsal, 2000. Determination of the biosorption activation energies of heavy metal ions on *Zoogloea ramigera* and *Rhizopus arrhizus*. Process Biochem., 35: 801-807.

Sharma, P. and J.M. Foster, 1993. Biosorption studies of Cr (III) and Cr (VI) by leaf, stem and root phytomass of *Quercus ilux* L (holly oak). Bioresur. Technol., 28: 227-232.

Srivastava, S. and I.S. Thakur, 2006. Isolation and process parameter optimization of *Aspergillus* sp. for removal of chromium from tannery effluent. Bioresour. Technol., 97: 1167-1173.

Tewari, N., P. Vasudevan and B.K. Guha, 2005. Study on biosorption of Cr (VI) by *Mucor hiemalis*. Biochem. Eng. J., 23: 185-192.

Williams, D.H. and I. Fleming, 1991. Spectroscopic Methods in Organic Chemistry. McGraw-Hill Book Company Ltd., New Delhi, India, pp: 40-76.

Xu, H., J.H. Tay, S.K. Foo, S.F. Yang and Y. Liu, 2004. Removal of dissolved copper(II) and zinc(II) by aerobic granular sludge. Water Sci. Technol., 50: 155-160.

Yun, Y.S., D. Park, J.M. Park and B. Volesky, 2001. Biosorption of trivalent chromium on the brown seaweed biomass. Environ. Sci. Technol., 35: 4353-4358.

Zouboulis, A.I., K.A. Matis and I.C. Hancock, 1997. Biosorption of metals from dilute aqueous solutions. Sep. Purif. Rev., 26: 255-295.