Recent Research in Science and Technology 2010, 2(3): 86–91
ISSN: 2076-5061
www.recent-science.com

POLLUTION & ENVIRONMENTAL SCIENCES

BIOSORPTION OF COPPER FROM AQUEOUS SOLUTIONS USING *TRIDAX PROCUMBENS*

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Abstract

Bioremediation of heavy metal pollution remains a major challenge in environmental biotechnology. Many plants have been shown to bind heavy metals with varying degrees of specificity and affinity. This paper highlights the potential of *Tridax procumbens* for biosorbing copper metal ion in aqueous solutions. Experiments were carried out as a function of pH, biosorbent concentration, copper concentration, contact time. A removal of 91% was achieved under optimized conditions. At pH 5 the maximum adsorption capacity of Cu was observed. The mechanism of metal sorption by *Tridax procumbens* gave good fits for Freundlich and Langmuir models.

Keywords: Heavy metal, Bioremediation, Biosorption, Isotherms, *Tridax procumbens*

Introduction

Industrial effluents loaded with heavy metals are a cause of hazard to humans and other forms of life. The environment impact due to their toxicity has led to the enforcement impact due to their toxicity has led to the enforcement of stringent standards for the maximum allowable limits of their discharge into open landscapes and waterbodies. Since most of these engineering technologies have failed in effluent cleanup process. As alternatives, slowly, biological tools are being substituted in pollution abatement programs. This new technology has been loosely grouped together under the term biosorption [1]. This calls for a research effort to develop an industrially viable, cost effective and environmental compatibility technology for the removal of metal ions from wastewater. Dried leaves of *Tridax procumbens* was used here in this study for removal of copper from synthetic solution.

Heavy metals released by a number of industrial processes are major pollutants in marine, ground, industrial and even treated wastewaters. Heavy metals can be extremely toxic as they damage nerves, liver, kidney and bones and also block functional groups of vital enzymes. Copper and its compounds are widely used in metal finishing, plating, dyeing and petroleum industries. These industries produce large quantities of toxic wastewater effluents. Since copper is an essential metal in a number of enzymes for all forms of life, problem arise when it is deficient or in excess. However the carcinogenic character of copper is accepted and epidemiological evidence, such as the higher incidence of cancer among coppersmiths, suggests a primary carcinogenic role of copper [2]. According to the Environment Quality Act 1974, the permitted concentration for Copper (II) discharged in effluents was 0.05mg/L.

Recent studies have showed that heavy metals can be removed using plant materials such an palm pressed fibers and coconut husk [3] , water fern *Azolla filiculoidis* [4], peat moss [5].The most convenient means of determining metal uptake abilities is through a batch reaction process. In the present research work, *Tridax procumbens (Asteraceae*) a novel medicinal plant material was used as lowcost sorbent for subsequent removal of Cu.

Materials and Methods

Metal solutions

All the reagents were of analytical reagent grade were prepared in double distilled H_2O. An aqueous stock solution (1000mg/l) of Cu ions was prepared using copper sulphate ($CuSO_4.5H_2O$) salt. This was used as the source of Cu in the synthetic wastewater. pH of the solution was adjusted using 0.1N HCl or NaOH. Fresh dilutions were used for each study.

Copper Ion Determination

The change in Cu concentration due to adsorption was determined using Atomic absorption spectrophotometer [6]. The percentage of Cu removal due to bioadsorption was calculated as %

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Cu removal= $[(C_0-c_i)/C_o]$ x 100%, where C_i and C_o are initial and equilibrium concentration of Cu solution (mg/L) respectively.

Preparation of Biosorbent

Tridax procumbens was collected from local environment of Thanjavur, India. The collected biomaterial is washed extensively in running tap water and with deionized water to remove dirt and other particulate matter. The dried plant materials are powdered into required particle size (2mm) and stored in desiccators and used for biosorption studies.

Pretreatment of Biosorbents

The pretreatment of biosorbent is mainly carried out to increase the metal uptake efficiency. About 50g of the *Tridax procumbens* leaves are treated with 500ML of 1N formalin for 24 hrs and kept on the water bath (70°C) for half an hour. It is cooled and is neutralized with 250mL NaOH.

Biosorption studies

Batch experiments are conducted in screw cap bottles of 125mL capacity. 100ml of the solution containing predetermined concentration of the adsorbate under investigation is taken in the bottles. After the addition of known amount of adsorbent, the bottles are equilibrated for a predetermined period of time in an orbital shaker(250 rpm). At the end of the equilibration period, the solutions are separated using membrane filters and the residual adsorbate in solution is determined. The pH of the test solution is adjusted by using pH meter. All biosorption experiments were performed in triplicate and mean values reported.

Effect of Biosorbent dose

The influence of biosorbent dose on metal adsorption is investigated by performing experiments taking 10mg/l of Cu solutions and equilibrating with varying amount of biosorbent (0.4g to3g) after adjusting the pH, for 30 minutes at room temperature and at agitation speed of 250rpm. After equilibration time the solutions are separated using filters and the supernatant is analysed for residual Cu concentration to establish the extent of removal in each case.

Effect of pH

Adsorption of metal ions by biomass was studied at pH values 1to 8. A fixed biomass of 3g was added to 10mg/l of heavy metal solution containing Cu. To avoid shifts in pH due to biomass addition, the pH was adjusted with 0.1N HCl or 1N NaOH after the solution had been in contact with the adsorbent.

Effect of contact time

To determine the optimal incubation time, a fixed adsorbent concentration of 3g of biomass was added to 10 mg/l of heavy metal solution containing Cu samples were taken at 15 to 120min and analyzed for removal.

Effect of initial metal ion concentration

To evaluate the effect of initial metal ion concentration on adsorption behavior of Cu, by biomass, aliquots from 10mg to 50 mg/l copper sulphate solution was added to fixed biomass weight of 3g. The pH was adjusted to 5 with 0.1N HCl and 1N NaOH, and samples were mixed well by shaking. For sorption isotherm experiments, flasks were agitated on a rotary shaker (250 rpm) until no additional metal was removed (75 min). The samples were filtered through filters. Triplicate samples were analyzed by atomic absorption spectrophotometry. Samples also were taken from experimental controls, which contained no biomass.

Adsorption isotherm

The sorption of copper by *Tridax procumben*s was carried out different initial copper ion concentrations ranging from 10 to 50mg/L at optimum pH 5 at 250 rpm while maintaining the adsorbent dosage at 1g. Langmuir and Freundlich models were applied to the adsorption isotherm and different constants were generated.

Results and Discussion

Effect of pH

pH is an important parameter for adsorption of metal ions from aqueous solution because it affects the solubility of the metal ions, concentration of counter ions on the functional groups of the adsorbent and the degree of ionization of the adsorbate during reaction. Biomass has active sites capable of binding metal ions thus it is regarded as a complex ion exchanger similar to a commercial resin. Such bond formation could be accompanied by displacement of protons and is dependent in part on the extent of protonation which is determined by the pH [7].

To examine the effect of pH on the Cu removal efficiency, the pH was varied from 1.0 to 8.0. As shown in the figure 1 the uptake of free ionic Cu depends on pH, where optimal metal removal efficiency occurs at pH 5 and then declining at higher pH. In contrast optimum pH value was found to be 5.5 in studies on a batch system using *Tectonia grandis* [8].

The decrease in adsorption with increase of pH may be due to the increase in electrostatic force of attraction between the sorbate ions and sorbent. At lower pH range due to the high electrostatic force of attraction the percentage of Cu removal is high. At very lower pH value the surface of sorbent would also be surrounded by the hydronium ions which enhance copper ions interaction with the binding sites of biosorbent by greater attractive forces. A sharp decrease in adsorption above the pH 5.0 may be due to the occupation of anionic species which retards the approach of such ions further towards sorbent surface [9].

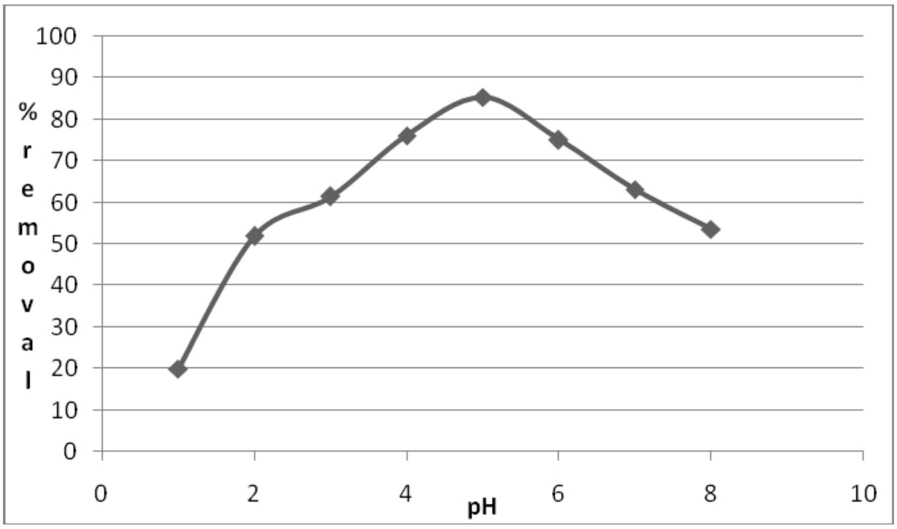

Fig.1. Effect of pH on the percentage removal of copper

Effect of biosorbent dose

The concentration of both the metal ions and the biosorbent is a significant factor to be considered for effective biosorption. It determines the sorbent/sorbate equilibrium of the system. Biosorption of copper with varying biosorbent concentration is shown in the figure 2. Copper uptake rose with increase in biosorbent concentration from 10% at 0.4g biomass to 80% at 3g biomass. This appears to be due to the increase in the available binding sites in the biomass for the complexation of copper. However, the copper uptake decreased gradually when the biosorbent concentration exceeded 3g. In contrast the optimum dose was found to be 2.5g in studies on biosorption of Cr (III) from aqueous solutions using *Tridax procumbens*[10].

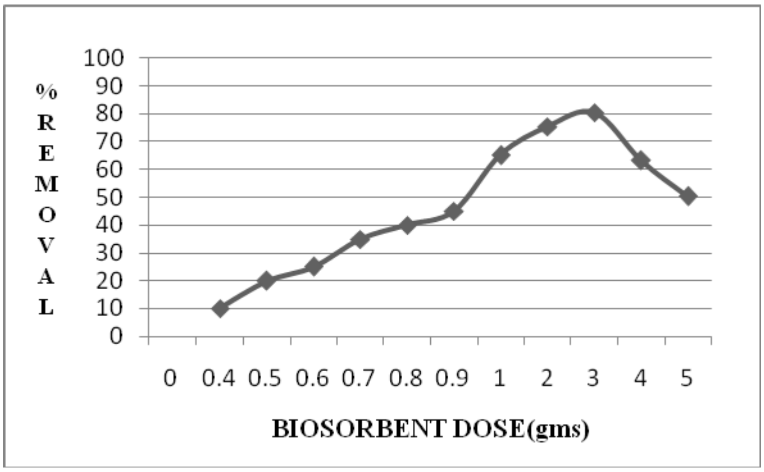

Fig.2. Effect of amount of biosorbent on the percentage removal of copper

Effect of contact time

Shaking time was varied from 15 to 120 min. As can be seen in figure 3, the percentage removal of ion increased with the time of shaking. A sharp increase was observed at around the time of 45 min and attained an optimum at the time of 75 min (90.1% removal). Hence the contact time 75 minutes was set for all other experiments. This result is important, as equilibrium time is one of the important parameters for an economical wastewater treatment system .In contrast 98.5% removal was achieved at 150 min in studies on biosorption of Cr (III) from aqueous solutions using indigenous materials [11].

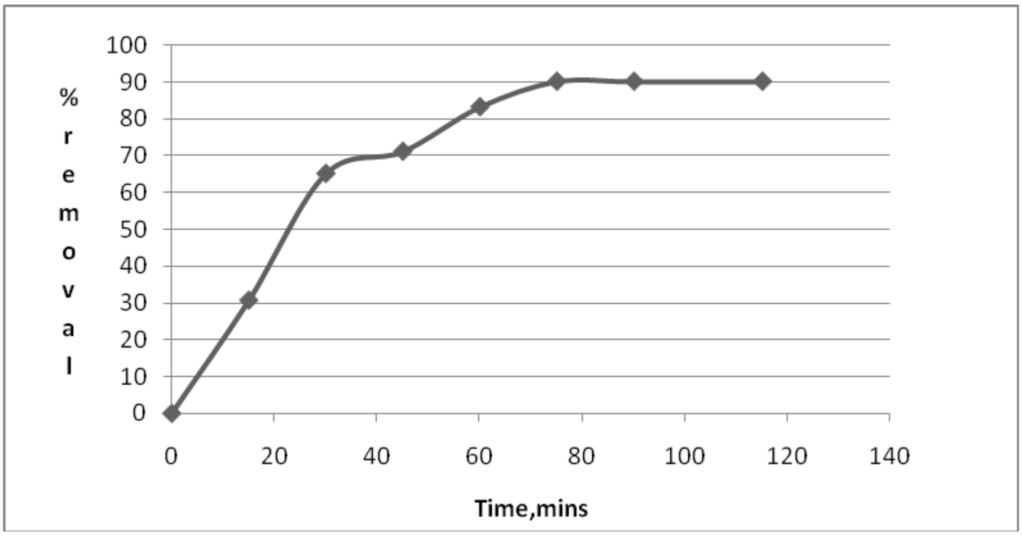

Fig.3. Effect of contact time on the percentage removal of copper ions

Effect of initial metal ion concentration

Biosorption experiments with biomass were conducted for solutions containing (10 to 50 mg/l) of Cu solution. As shown in figure 4, at lower concentrations of Cu solution (10mg/l), percentage of removal was maximum (91%) but at higher concentrations the percentage of removal is low (59.1%). At low concentrations, all metal ions present in the solution would interact with the binding sites and thus facilitated 100% adsorption. At higher concentrations more Cu ions are left unabsorbed in solution due to the saturation of binding sites. This appears to be due to the increase in the number of ions competing for the available binding sites in the biomass [12]. The same mechanism of removal was observed in biosorption of heavy metal (chromium) using biomass[13].

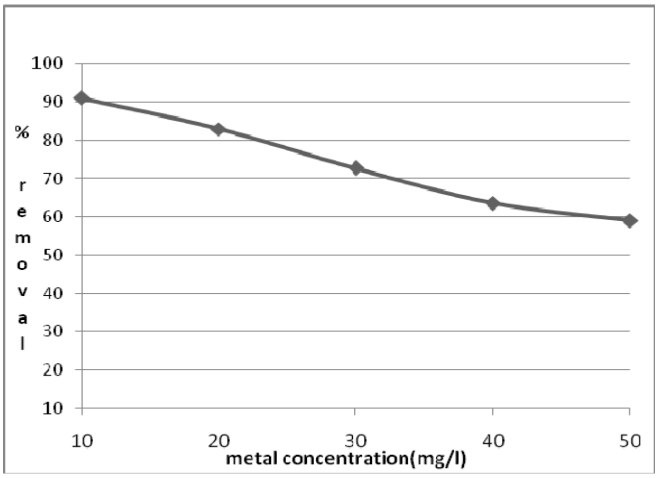

Fig.4. Effect of initial metal ion concentration on removal of copper ions

Isotherm modeling

Analysis of the isotherm data is important in order to develop an equation which accurately represents the results of the column and which could be used for column design purposes. Adsorption isotherm also describes how solutes interact with adsorbent and so is critical in optimizing the use of adsorbent. The copper uptake capacity of *Tridax procumbens* was evaluated using the Langmuir [14] and Freundlich [15] equation. The Langmuir equation equation which is valid for monolayer sorption onto a surface with a finite number of identical sites which are homogenously distributed over the adsorbent surface is given by the equation:

$$C_a = C_0S/k+S$$

where C_0 and k are constants determined experimentally by plotting 1/Ca against 1/S. The linear plot gives an intercept experimentally by plotting1/C_a against 1/S. The linear plot gives an intercept equal to 1/C_0 and a slope equal to k/co.C_a is the amount of solute adsorbed per unit amount of adsorbent (g/g), k is the equilibrium constant and S is the Solute concentration in liquid phase.

On the other hand, the Freundlich equation is an empirical equation based onadsorption on a heterogenous surface is given by Equation $C_a=kS^n$, where C_a is the amount of solute adsorbed and S is the solute concentration in the liquid phase. The results obtained from varying initial metal concentration study were modeled with varies isotherm equations discussed in the proceeding paragraphs. Fitted curves of each model with the experimental data are illustrated in figures 5 and 6.

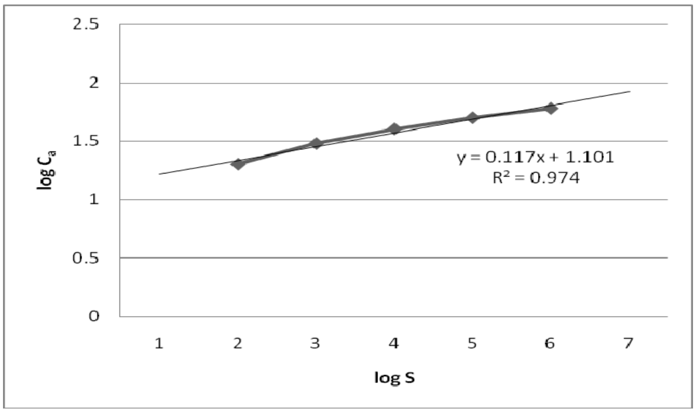

Fig.5. Freundlich isotherm plot of Cu adsorption on *Tridax procumbens*

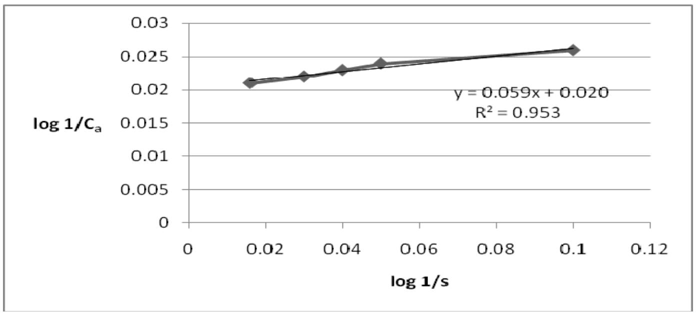

Fig.6. Langmuir isotherm plot of Cu adsorption on *Tridax procumbens*

Fitted isotherm parameters

Freundlich isotherm			Langmuir isotherm		
k_f	n	R^2	C_a	k	R^2
0.33	0.11	0.97	55.5	1.11	0.95

Linear plots of log s versus log C_a showed that that the Freundlich isotherm was also representative for the Cu adsorption by the adsorbent tested. K_f and n were calculated from the slopes of the Freundlich plots and were found to be 0.33 and 0.117 respectively. As indicated from the tables, the coefficients of determination (R^2) of both models were more or less greater than 0.9 indicating that both models were adequately describing the experimental data of metal biosorption experiments. Similar results were obtained by Hany Hussein *et al*. (2004) for his studies of biosorption of heavy metals from waste water using *Pseudomonos* sp [16].

Conclusion

A suitable indigenous plant material has been identified as an effective biosorbent to remove copper ions from aqueous solution. The biosorption of copper was found to be time dependent and optimum time for the uptake was 75min. Furthermore, the equilibrium data of adsorption are in good agreement with the models of Freundlich and Langmuir. On the whole dried leaves of *Tridax procumbens* can remove 91% copper from synthetic metal solution at pH 5.0 with continuous stirring at 250 rpm. This adsorbent can be a good choice for adsorption of not only copper ions but also other heavy metal ions in wastewater stream.

Acknowledgements

The authors are grateful to the authorities of PRIST University for the facilities. They are thankful to Dr. S. Ravikumar, Dean, Faculty of Biotechnology, PRIST University for the encouragement and technical assistance all through the study.

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