Original Research

Biosorption of Hexavalent Chromium Using Bark of *Cassia spectabilis*

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Abstract	Article Information
Biosorption is a relatively new process that has proven very promising in the removal of heavy metal contaminants from aqueous solutions. The biosorption of Cr(VI) from aqueous solution using bark of *Cassia spectabilis* has been investigated in a batch system. The effect of various parameters such as pH, contact time, adsorbent dosage and initial concentration of Cr(VI) on the biosorption process were studied. The maximum removal of Cr(VI) was observed at pH 1.0. The Study indicated that both biosorption and bioreduction were involved in removal of Cr(VI). The sorption equilibrium exhibited a better fit to the Langmuir isotherm than Freundlich isotherm. The maximum biosorption of *Cassia spectabilis* bark to remove Cr(VI) was 12.865 mg/g. The dimensionless equilibrium parameter, R_L signifies a favorable adsorption of Cr(VI) on the adsorbent and is found to be 0.441 (0 < RL<1). Pseudo first-order and second order kinetic models were used to evaluate the mechanism of adsorption. Kinetic evaluation of the experimental data showed that the biosorption process follows pseudo- second order kinetic model.	
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INTRODUCTION

Heavy metals pollution in the aquatic system become a serious threat and of great environmental concern due to their extended persistence in the biological systems and tendency to bioaccumulate as they moved up the food chain (Paknikar *et al.,* 2003; Wang *et al.,* 2006). Their toxic effects are more pronounced in the animals at higher trophic levels (Farooq *et al.,* 2010).

Chromium is one of the heavy metals was used in electroplating, leather tanning, metal finishing and chromate manufacturing industries dated back years ago. Both trivalent and hexavalent chromium are among the constituents of effluents from these industries, specifically Cr(VI) with concentration ranging from tens to hundreds of mg/l (Barnhart 1997). It is very toxic to both plants and animals because it can easily penetrate the cell wall and exert its noxious influence in the cell itself, being also a source of various cancer diseases (Barnowski *et al.,* 1997; Gil *et al.,* 2006)

The discharge of Cr (VI) to surface water is regulated to <0.05mg/L, according to the US EPA, whereas the total chromium (containing Cr(III),Cr(VI), and other forms of chromium) is regulated to be discharged at < 2mg/L (Donghee *et al.,* 2006). To achieve these standards different physico-chemical methods have been employed to remove chromium and other toxic metal ions from aqueous solution which includes chelation extraction, chemical coagulation, chemical precipitation, evaporation, electroplating, adsorption and ion exchange processes have been used to remove chromium from wastewater

(Addagalla *et al.,* 2009). But the effectiveness of these technologies is limited to high concentration of heavy metals. They are either ineffective or expensive when heavy metals are present in the wastewater at low concentration. Hence new technologies are required that can reduce heavy metals concentration to environmentally acceptable levels at affordable costs (Rajasimann and Murugaiyan, 2010). The use of biomaterial is one of the promising techniques to treat chromium containing waste water (Donghee *et al.,* 2006). There are three major advantages of biological technologies for the removal of pollutants; first biological processes can be carried out *in situ* at the contaminated site; second, bioprocess technologies are usually environmentally benign (no secondary pollution) and third, they are cost effective (Vijayaraghavan and Yun, 2008).

METHODS AND MATERIALS
Adsorbent Preparation

Cassia spectabilis bark was obtained from mature trees in the campus of University of Mysore,. It was washed with double distilled water and then left to be air dried until easily crashed and milled. After drying the material was grounded repeatedly with domestic mixer and the finest powder is separated using a stainless steel fine sieve to use in the experiment.

Stock Chromium Solution Preparation

An aqueous solution of hexavalent chromium was prepared by dissolving 2.829 g Analytical grade potassium dichromate (K_2CrO_7) salt to obtain a stock

Yohannes Tefera and Devi Prasad

Sci. Technol. Arts Res. J., April-June 2014, 3(2): 83-87

solution of 1000mg/L. This solution was used for further preparation of experimental solutions using series of dilution according to the concentrations needed.

Batch Biosorption Experiments

Batch biosorption experiments were carried out in 250 ml Erlenmeyer flask containing 100 ml of synthetic Cr (VI) solution. Before mixing the adsorbent the pH of each solution was adjusted to the required value with analytical grade aqueous NaOH and HCl solutions. Known amount (0.3 g) of the previously prepared biosorbent was added to the solution. The mixture was shaken on a rotary shaker at a speed of 200 rpm at room temperature (25 °C) for overnight to ensure equilibrium. The suspension was filtered using Whatman® quantitative filter paper, ash less, grade42 and the concentration of Cr(VI) ions in the filtrate was analyzed spectrophotometrically by 1,5-diphenyl carbazide method at wave length of 540 nm using Systronic 169 spectrophotometer.

The influence of pH on the biosorption of Cr (VI) on biosorbent was investigated by mixing the biosorbent with metal solution (C_i = 40 mg/L) in the pH range 1-8. Due to the reduction of hexavalent chromium when contacted with organic matter at low pH, potassium permanganate have been used in acidic condition to oxidized Cr(III) into Cr(VI) in the presence of sodium azide. The amount of adsorbed chromium ions on biosorbent was calculated from the mass balance equation as follows:

$$q_e = \frac{C_i - C_e}{m} \times V$$

where $q_e$is the metal ion adsorbed (mg metal ion/ g biosorbent) at equilibrium, $V$is the volume of the solution (L) , C_i and C_e are the initial and equilibrium concentration of metal ion (mg/L) and m is the dry weight of the biosorbent (g). A control experiment was carried out at the same conditions in the absence of biosorbents.

Adsorption Isotherm

Different concentrations of chromium(VI) were prepared and 3gof the adsorbent is added to study the adsorption isotherm. The pH of the solution was adjusted to pH 1.0. The mixture was shaken till equilibrium, filtered and the filtrates were analyzed as mentioned in batch biosorption experiment.

Adsorption Kinetic

Kinetic experiments were performed at different doses of biosorbent at optimum pH (pH 1.0)for Cr(VI).In all kinetic experiments, the working volume of the solution was 100 ml in 250 ml Erlenmeyer flask and agitated on the shaker at 200 rpm at room temperature. The solution samples were collected at regular time intervals, filtered and the filtrate analyzed for the chromium ions as mentioned earlier.

RESULTS AND DISCUSSION
Effect of pH

Figure 1 shows effect of pHinthe adsorption process. As the pH level decreased from 8.0 to 1.0 the percentage removal of hexavalent chromium automatically increased to 97%. At lower pH, (pH = 1.0), dominant species of Cr (VI) is $HCrO_4^-$ while the surface of adsorbent is charged positively (Suresh *et al.* 2007). The functional groups present on adsorbent surface highly favor attachment of oxyanions of chromate to its surface. This explains and justifies the removal of chromate ions and less or no removal of positively charged ions in highly acidic conditions. An increase in pH above this point makes the

functional groups on the biomass type deprotonate and act as negative species and thus it binds with the positive metal ions. Gupta and Rastogia (2008); Kumari *et al.* (2006) reported that the amount of total Cr and Cr(VI) at low pH is approximately same. This indicates that the presence of Cr(III) in the final solution of Cr(VI) is insignificant.
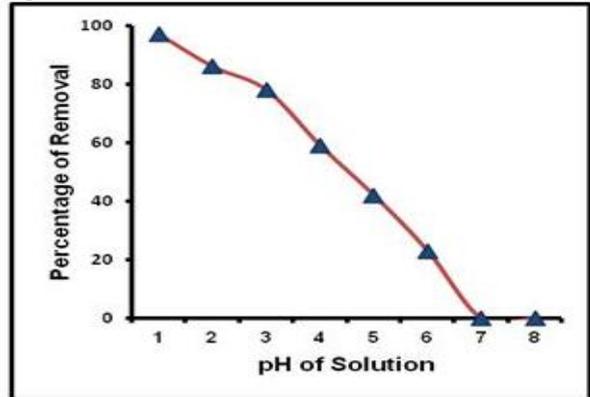

Figure 1: Effect of pH on percentage removal of chromium during biosorption Cr (VI) by *Cassia spectabilis bark* (C_i = 50 mg/L; Adsorbent Dose 3g/L; Agitation speed = 200 rpm; time = 210 minutes)

Effect of Initial Concentration

The effect of chromium ion concentration on the removal of Cr(VI) by *Cassia spectabilis bark* is shown in Figure 2. The results showed that the chromium removal of *Cassia spectabilis* bark decreased from 91% to 47% as the initial concentration increased from 20 mg/L to 50 mg/L using 1g/L adsorbent dose. But the percentage removal shows only slight change when 3g/L adsorbent dose is used. The decrease in percentage of sorption may be attributed to the fact that at very low concentrations of metal ions, the ratio of sorptive surface area to the total metal ions available is high and thus, there is a greater chance for metal removal. When metal ion concentrations increased, binding sites become more quickly saturated as the amount of biomaterials concentration remained constant (Chandra *et al.*, 2003).
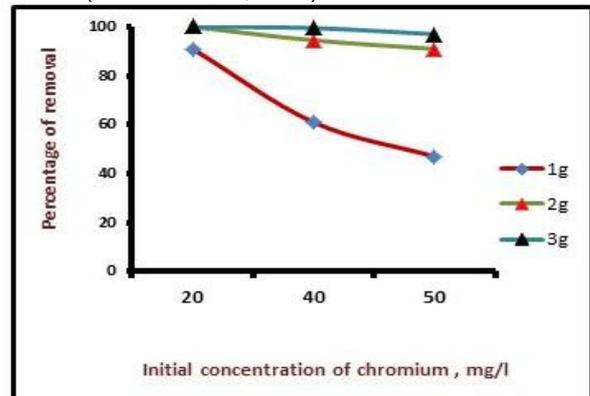

Figure 2: Effect of Initial concentration on percentage removal of chromium during biosorption Cr (VI) by *Cassia spectabilis*bark (pH = 1.0; time = 210 minutes; Agitation speed= 200 rpm ;)

Effect of Adsorbent Dose

Effect of adsorbent dosage on Cr (VI) adsorption was investigated by changing the sorbent dose from 1 to 3 g/L with 20mg/l, 40mg/l and 50mg/l initial Cr (VI) concentration as shown in figure 3. The removal efficiency of Cr(VI) increased when adsorbent dose increased from

Yohannes Tefera and Devi Prasad

Sci. Technol. Arts Res. J., April–June 2014, 3(2): 83-87

1 to 3 g/l with *Cassia spectabilis* bark and then reached with more than 90% of Cr(VI) in solution being removed. At a low adsorbent dose, e.g. 1 g/L, the available sorption sites were quite insufficient compared with the large amount of Cr (VI) ions in solution, resulting in low removal efficiency. At a higher dose, the sorption sites were sufficient and the ions will have the chance to bind to the active sites. The larger the surface area, the larger the amount of metal ion adsorbed. This appears to be due to the increase in the available binding sites in the biomass for the binding of the heavy metals (Innocent *et al.*, 2009).
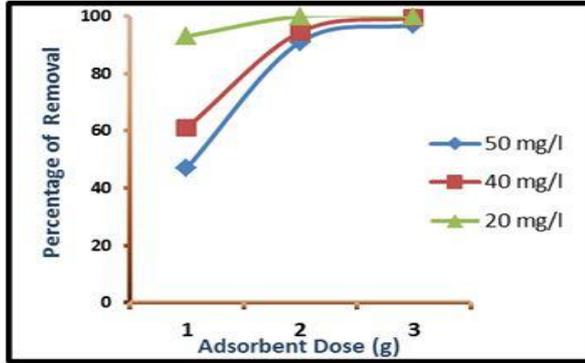

Figure 3: Effect of Adsorbent Dose on percentage removal of chromium during biosorption of Cr (VI) by *Cassia spectabilis* bark (pH = 1.0; Agitation =200 rpm; time = 210 minutes)

Adsorption Isotherms

The linearized Langmuir and Freundlich isotherm models were used to describe the equilibrium data in this study. The linear plots of two models are presented in Figure 4 and 5. The essential features of Langmuir isotherm model can be expressed in term of dimensionless constant separation or equilibrium parameter (R_L). The value of R_L indicates the type of biosorption isotherm to be linear (R_L =1), favorable (0< R_L<1), unfavourable (R_L>1) and irreversible (R_L =0). The calculated R_L values were found to be 0.609 to 0.441 for *Cassia spectabilis* bark. The value of 1/n obtained from Freundlich adsorption model was 0.133 and 0.0317 for 40 mg/L and 80 mg/L initial concentration, which lies between 0.0 and 1.0 indicating favourable biosorption (Ho and McKay, 1998). According to coefficient of determination, the Langmuir isotherm model (R^2 = 0.997) is better fitted the equilibrium data than the Freundlich adsorption model (R^2 = 0.9377) which suggested that chromium ions are adsorbed onto the surface of *Cassia spectabilis* in a monolayer pattern.
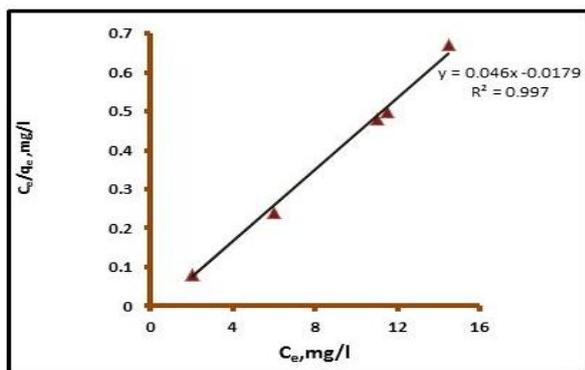

Figure 4: Langmuir isotherm for adsorption of chromium during biosorption of Cr (VI) by *Cassia spectabilis* bark (C_i = 40mg/l; Adsorbent Dose = 3g/l; Agitation speed = 200 rpm; pH =1.0)
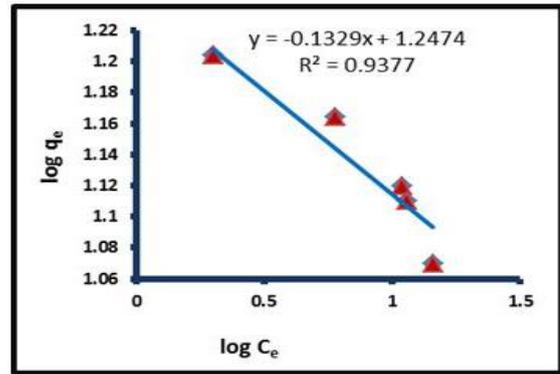

Figure 5: Freundlich isotherm for adsorption of chromium during biosorption of Cr (VI) by *Cassia spectabilis* bark (C_i = 40mg/l; Adsorbent Dose = 3g/l; Agitation speed = 200 rpm; pH =1.0)

Adsorption Kinetics

Kinetic models have been used to investigate the mechanism of sorption and potential rate controlling step which is helpful for selecting optimum operating condition for the full-scale batch process (Kalavathy *et al.*, 2005).

The kinetics of the biosorption data was analyzed using two kinetics models, pseudo-first order (Lagergren, 1898) and pseudo-second order models.

The calculated values are given in Table 1. The value of q_e estimated from pseudo first-order model gave significant difference compared to experimental value and r^2 value were found to be slight lower indicating that, the pseudo first-order model might be insufficient to interpret the mechanism of Cr(VI) biosorption (Ho *et al.*, 2001).

Experimental data were also analyzed using pseudo second-order kinetic model which can be expressed as

$$\frac{t}{q_t} = \frac{1}{K_{2,ads} \cdot q_e^2} + \frac{1}{q_e} \cdot t$$

where q_t (mg/g) is the amount of metal ion adsorbed at time "t" (min), q_e is the amount of metal ion adsorbed at equilibrium (mg/g), $K_{2,ads}$ is the constant of pseudo second-order kinetic (g mg^{1}min^{-1}). The linear plot of $\frac{t}{q_t}$ versus t at different dose of *Cassia spectabilis bark* are shown in Figures 6, 7 and 8. The values of $K_{2,ads}$ and q_e are calculated from the slope and intercept of the plot. The value of q_e was in close agreement with that of experimental value indicating that, the adsorption data were well represented by pseudo second-order kinetic model. This suggests that the rate-limiting step of the sorption system can be chemisorptions involving valances forces through sharing or exchange of electrons between adsorbent and adsorbate (Lu and Gibb, 2008).

Table 1: Parameter values calculated using the pseudo-first order and pseudo-second order kinetic models for the biosorption of Cr(VI) Cassia spectabilis bark.

Biosorbent dose (g/L)	First-order kinetic model		
	$K_{1,ads}$ (min^{-1})	q_e (mg.g^{-1})	R^2
1	0.0022	3.55	0.5879
2			

Biosorbent dose (g/L)	Second-order kinetic model		
	$K_{2,ads}$ (g.mg^1.min^{-1})	q_e (mg.g^{-1})	R^2
1	0.1324	12.865	0.998
2	0.0454	1.0067	

Yohannes Tefera and Devi Prasad

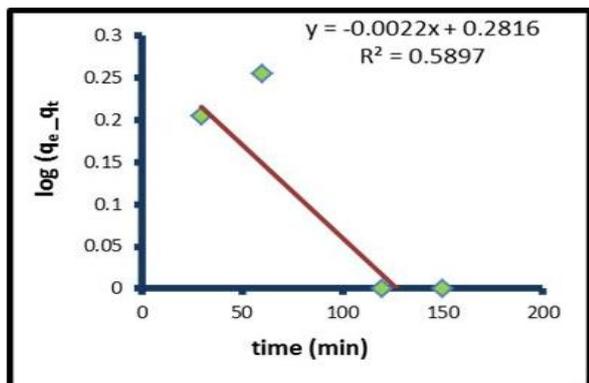Sci. Technol. Arts Res. J., April–June 2014, 3(2): 83-87

Figure 6: Pseudo first order kinetic plot for the sorption of chromium for adsorption of chromium during biosorption of Cr (VI) by *Cassia spectabilis bark* (C_i = 40mg/l; Adsorbent Dose = 1g/l; Agitation speed = 200 rpm; pH =1.0).
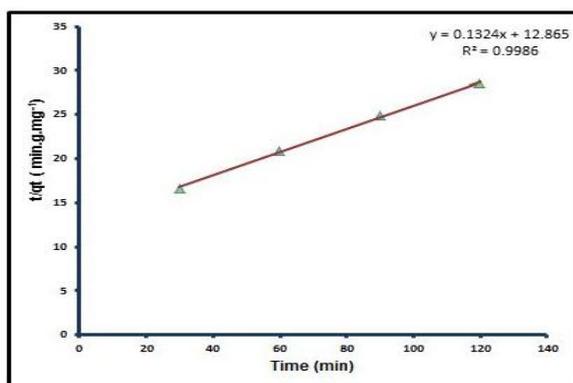

Figure 7: Pseudo second order kinetic plot for the sorption of chromium for adsorption of chromium during biosorption of Cr (VI) by *Cassia spectabilis bark* (C_i = 40mg/l; Adsorbent Dose = 1g/l; Agitation speed = 200 rpm; pH =1.0)
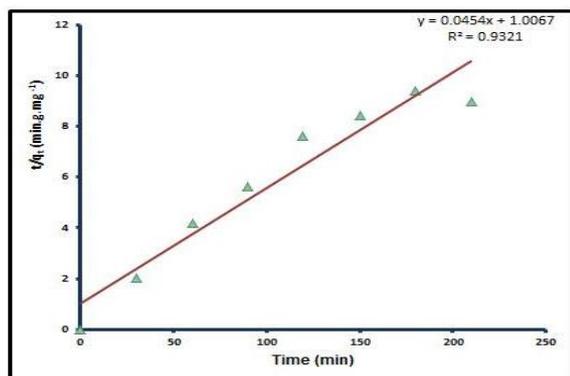

Figure 8: Pseudo second order kinetic plot for the sorption of chromium for adsorption of chromium during biosorption of Cr (VI) by *Cassia spectabilis bark* (C_i = 80mg/l; Adsorbent Dose = 3g/l; Agitation speed = 200 rpm; pH =1.0)

It is clear from the table that, coefficient of determination of pseudo-second order model was higher in comparison to pseudo first order model. This suggests

that, the pseudo second order kinetic model fitted the biosorption kinetic data of Cr(VI) on the biosorbent than pseudo-first order kinetic model. In accordance with pseudo-second order kinetic model, the rate limiting step of this sorption system cheimosorption involving valency forces through sharing or exchange of electrons between sorbent and sorbate (Mohammed and Devi Prasad, 2009). The adsorption rate increase with an increase of biosorbent dosage and decrease with an increase in initial concentration.

CONCLUSIONS

The present study shows that *Cassia spectabilis* bark adsorbs chromium (VI) from aqueous solution. It is observed that the pH is the important parameter in the biosorption process and complete removal of Cr(VI) was achieved at pH 1.0, due to biosorption coupled bioreduction processes. Among the isotherm models used Langmuir isotherm model is better fitted the equilibrium data than Freundlich adsorption model showing monolayer biosorption of chromium by *Cassia spectabilis* bark. Pseudo- second model describes the kinetic data. The adsorption rate increases with an increase of biosorbent dosage and decrease with an increase in the initial concentration of the chromium solution. This biomaterial can be obtained as waste during wood processing. Hence the usage of such material is ecofriendly, economical, easily available and technically feasible for removal of Cr(VI) from waste water.

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