

## Cr(VI) removal from synthetic textile effluent using *Tamarindus indica* bark: a kinetic and thermodynamic study

Sudesh and Varsha Goyal\*

Department of Chemistry, The IIS University, Jaipur 302 020, India

**Discharge of untreated textile effluents containing heavy metals is a serious environmental issue. Biosorption is a promising method for the removal of heavy metals. The present study analyses the biosorption of Cr(VI) from synthetic textile effluent onto tamarind bark biomass as a function of initial metal ion concentration, contact time, pH, sorbent dosage, shaking speed and temperature. The optimum pH and temperature are found to be 2 and 20°C respectively. The maximum biosorption capacity  $q_e$  is 21.001 mg/g. Freundlich isotherm model fitted well with correlation coefficient of 0.9. Kinetic study reveals that the biosorption of Cr(VI) follows a pseudosecond-order model. The biosorption of Cr(VI) is spontaneous and exothermic as shown by negative free energy change ( $\Delta G^0$ ) and negative enthalpy ( $\Delta H^0$ ). Desorption experiments with 2M NaOH, infer the reusability of the biomass up to five times with high efficiency.**

**Keywords:** Adsorption isotherm, biosorption, chromium, kinetic and thermodynamic study, *Tamarindus indica*.

THE contamination of water by toxic heavy metals is a worldwide problem. Chromium is one of the most toxic contaminants found in polluted soils and surface or groundwaters. Its application in various industries such as electroplating, tanning, pulp production, metal finishing, textile industries, etc. has resulted a negative impact on society with respect to its pollution potential. Chromium has several oxidation states ranging from Cr(II) to Cr(VI), but the trivalent and the hexavalent states are the most stable<sup>1</sup>.

Jaipur, a city located in the central part of Rajasthan, is undergoing rapid industrialization and urbanization. In last two decades, a large number of industries have come up in adjacent areas of Jaipur, viz. Sanganer, Sitapura, Vishwakarma, etc. Among these, Sanganer region is famous worldwide for its dyeing and textile industries. During the process of dyeing, a large number of mordants (colour-fixing agents) are used, of which  $K_2Cr_2O_7$  is most commonly used in large quantities. These textile units discharge tones of effluent directly, without any treatment; thus, considerable amount of dyes and heavy metals are disposed into nearby drainage system. These effluents are directly used for crops cultivation which affects the nearby agricultural land.

Cr(VI) is carcinogenic and mutagenic as well as a strong oxidizing agent which affects plant and animal tissues even in small quantities. It diffuses rapidly through the soil and aquatic environments, as well as readily passes through the skin<sup>2</sup>. The maximum permissible limit for Cr(VI) in industrial wastewater is 100  $\mu\text{g/l}$ , defined by the Environmental Protection Agency (EPA), USA.

If these metals are continuously introduced into our environment without been treated, it is dangerous for all lives on earth. There are several conventional methods used for removing heavy metals from industrial wastewater. These include: chemical precipitation, ion exchange, coagulation, solvent extraction, ultra filtration, reverse osmosis, electro dialysis, etc.<sup>2-4</sup>. Currently, chemical precipitation is the most widely used method for treatment of chromium-bearing effluents. However, a major disadvantage of this method is the undesirable production of chemical sludge in significant amounts<sup>5</sup>.

Biosorption can be a promising alternative to treat industrial effluents because of its low cost, high metal-binding capacity, high efficiency in dilute effluents and being environment-friendly<sup>6</sup>. Biosorption utilizes the ability of certain materials to accumulate heavy metal ions from aqueous solution by either metabolically mediated or physico-chemical pathways of uptake<sup>7</sup>. The basic components of plant material biomass include hemicelluloses, lignin, lipids, proteins, simple sugars, hydrocarbons, starch containing a variety of functional groups that facilitate metal complexation which helps in the sequestering of heavy metals<sup>8,9</sup>. Various agricultural waste materials such as oat biomass<sup>10</sup>, wheat bran<sup>11</sup>, coconut shells<sup>12</sup>, rubber wood saw dust<sup>13</sup>, raw rice bran<sup>14</sup>, etc. have been used for the removal of Cr(VI) ions.

The present study explores the use of *Tamarindus indica* bark (TB) as a sustainable adsorbent for chromium removal from aqueous system under different experimental conditions. In India, *T. indica* is an economically important tree which grows abundantly in the dry tracts of Rajasthan. It is a traditionally important medicinal plant. Its fruit is the chief acidulant used in the preparation of foods. A literature survey<sup>15</sup> shows that its hard pod shell has been used for the removal of Cu(II), Ni(II) and Zn(II) metal ions. However, the stem bark of these plants has not been explored for potential use as biosorbent.

Thus, the objective of the present work is to investigate and explore the possibility of utilizing TB powder as a sorbent for removing Cr(VI) from synthetic textile effluent. The effect of various experimental parameters has been studied. Adsorption isotherms, kinetic and thermodynamic study are also reported.

TB was collected from tamarind trees. The collected bark was crushed into small pieces and washed thrice using demineralized water for the removal of surface debris, particulate matter and salts. After washing, the bark pieces were dried in a hot-air oven at 70°C for two days. A domestic mixture was used to reduce the particle

\*For correspondence. (e-mail: varsha.goyal@iisuniv.ac.in)

size of the bark. The powdered (TB) biomass was sieved into 30 mesh size and preserved into a bottle.

All the chemicals used were of analytical reagent grade. In order to avoid interference with other elements in the wastewater, the experiments were conducted with aqueous solution of Cr(VI). The stock solution (1000 mg/l) was prepared by dissolving appropriate  $K_2Cr_2O_7$  in double-distilled water. All the working solutions were prepared by diluting the stock solution at different concentration (i.e. 5–50 mg/l). pH of the solution was adjusted using hydrochloric acid (1 N) and sodium hydroxide (1 N) solution.

The experiments were carried out in 250 ml Erlenmeyer flasks containing 50 ml of Cr(VI) ion solution of different concentrations (5–50 mg/l). The desired amount of a TB biomass (0.05–0.4 g/100 ml) was added to the solution and the flasks were agitated on an electrically thermostatic shaker at a speed of 120 rpm. The effect of different experimental parameters such as pH (2–10), biosorbent dose (0.05–0.4 g/100 ml), initial concentration of metal ion (5–50 mg/l), shaking speed (80–120 rpm), contact time (10–60 min) and temperature (20–70°C) was evaluated for sorption of Cr(VI) by TB biomass. At the end of the experiment, the flasks were removed from the shaker and the contents were filtered using a Whatman filter paper. The concentration of Cr(VI) ions in the solution after equilibrium was determined by a Atomic Absorption Spectrophotometer (4141-ECIL) with an air acetylene flame. The whole experimental work was conducted in triplicate for all conditions of study.

The metal uptake capacity  $q_e$  was calculated using general equation

$$q_e = \frac{(C_0 - C_e)V}{m}, \quad (1)$$

where  $q_e$  is the metal uptake (mg/g biomass),  $V$  the volume of metal containing solution in contact with the biosorbent (litres),  $C_0$  and  $C_e$  are the initial and equilibrium (residual) concentration of metal ion in the solution respectively (mg/l), and  $m$  is the amount of added biosorbent (g).

The biomass before and after adsorption was air-dried and demineralized at 60°C in an oven. The powder was analysed by FTIR (JASCO-410) using the potassium bromide pellet method in the wavenumber range 400–4000  $cm^{-1}$ .

SEM analysis was carried out using a scanning electron microscope (HITACHI, S-530) at 20.40 kV (beam accelerating voltage) to study the surface morphology of the adsorbent.

Desorption experiments were carried out with different concentrations of NaOH (0.5, 1, 1.5 and 2 M). A known quantity of chromium-loaded biomass was agitated for 6 h in a shaker. The amount of chromium desorbed from

the chromium-loaded biomass was analysed using AAS according to the standard procedure. The percentage desorption of Cr(VI) ions was calculated using the equation

$$\frac{\text{Amount of metal desorbed}}{\text{Amount of metal sorbed}} \times 100. \quad (2)$$

Parameters which influence the extent of adsorption such as pH, biosorbent dose, shaking speed, contact time, initial metal ion concentration and temperature were studied.

Biosorption of Cr(VI) by TB biomass was measured at five different initial metal ion concentrations (5, 15, 25, 35 and 50 mg/l) for a given time at an adsorbent dose of 0.02 g/100 ml. The adsorption capacity ( $q_e$ ) of the biomass increases from 2.4 to 21.005 mg/g with increasing initial metal ion concentration from 5 to 50 mg/l. It is evident from Figure 1 that the percentage removal of Cr(VI) at 5 mg/l is 96.02 while at 50 mg/l is 84.02, therefore the optimum initial metal ion concentration is taken as 50 mg/l for further experiments. The initial concentration provides an important driving force to overcome all mass transfer resistance of metal ion between the aqueous and solid phases<sup>16</sup>. The increase in metal ion concentration also enhances the interaction between metal ion and adsorbent as well as adsorption uptake of metal ( $q_e$ ). Though an increase in metal uptake is observed, the decrease in percentage biosorption could be attributed to lack of sufficient surface area to accommodate more metal available in the solution.

The percentage removal of Cr(VI) ion as a function of contact time. It can be seen that the percentage of metal removal increases with an increase in contact time. The uptake of Cr(VI) is rapid for the first 30 min and after 60 min the amount of metal ions adsorbed is almost constant. Hence, in the present study 60 min is chosen as an equilibrium time. In the initial stages of contact, a large number of vacant sites are available, and hence the uptake is faster. The slowing down of metal uptake later is

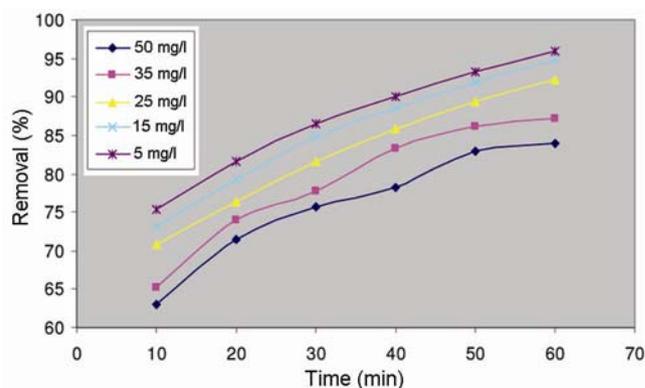


Figure 1. Effect of contact time on percentage removal of Cr(VI).

due to difficulty in occupying the remaining vacant sites. Repulsive forces between the adsorbed Cr(VI) ions and aqueous Cr(VI) also contribute in slowing down the uptake of metal at equilibrium<sup>17</sup>. Percentage adsorption increases from 70.1 to 89.32 during a contact time period from 10 to 60 min. The rapid initial adsorption is likely due to the binding of extracellular polymeric sites (ionizable), and the slower sorption results from intracellular binding<sup>18</sup>.

It is found that as the shaking speed increases from 80 to 120 rpm, the adsorption capacity also increases from 10.86 to 24.7 mg/g for Cr(VI) ion. The increase in adsorption capacity at higher shaking speed could be explained in terms of the reduction of boundary layer thickness around the adsorbent particles<sup>19</sup>. Therefore, with increasing shaking speed, the concentration on metal ions near the adsorbent surface would also increase.

The pH of the solution is one of the most important parameters influencing adsorption capacity of adsorbents. Initial pH is shown to affect the magnitude of negative charge on the surface of adsorbents and the adsorption capacities<sup>20</sup>. Adsorption experiments were carried out in the pH range 2–10, while keeping all other parameters constant. The maximum removal of Cr(VI) by TB biomass was found at pH 2 (Figure 2). This can be explained by the fact that Cr(VI) exists as oxyanions like  $\text{HCrO}_4^-$  and  $\text{Cr}_2\text{O}_7^{2-}$  predominantly at pH less than 6 (ref. 21). At low pH, the surface of the adsorbent is saturated with protons it positively charged, which increases the adsorption of negatively charged Cr oxyanions.

In order to study the effect of adsorbent dosage on Cr(VI) removal from the metal solution of 50 mg/l,

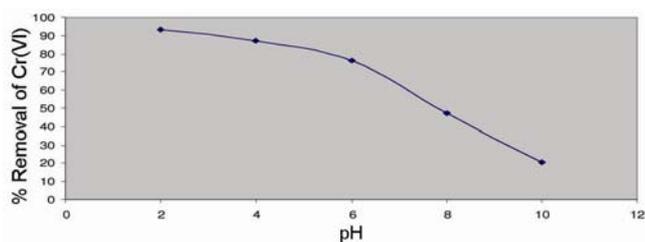


Figure 2. Effect of pH on percentage removal of Cr(VI).

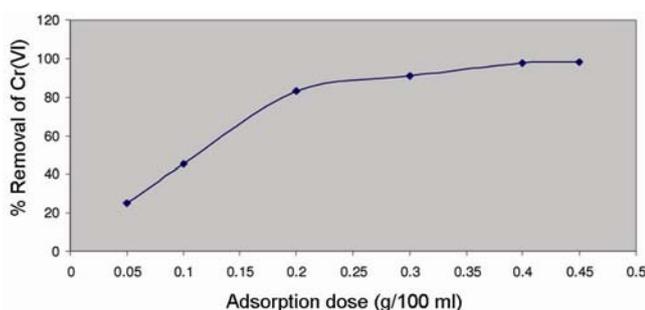


Figure 3. Effect of adsorbent dose on percentage removal of Cr(VI).

experiments were conducted by varying the adsorbent dosage (0.05, 0.1, 0.2, 0.3, 0.4 and 0.45 g/100 ml). The percentage removal values, obtained after agitation for a period of 1 h, were plotted against the quantity of biomass used. The adsorption was found to increase with increase in the biomass dose (Figure 3). It can be seen that the percentage removal increase from 24.8 to 98.28 when biomass dose increases from 0.05 to 0.45 g/100 ml. Therefore the optimum biosorbent dosage is taken as 0.45 g/100 ml for further experiments. The increase in percentage removal could be attributed to the fact that as adsorbent dosage increases, more adsorption sites are available for Cr(VI), thus enhancing the uptake<sup>22</sup>. However, on further increasing the biomass dose, the adsorbent capacity to the unit weight of biomass gets reduced, thus causing a decrease in metal uptake ( $q_e$ ) value. This may be due to complex interactions of several factors, including availability of solute, electrostatic interactions, interference between binding sites, etc.

The adsorption of metal ions at four different temperatures, viz. 293, 313, 333 and 343 K onto TB was studied for 50 mg/l initial concentration. The maximum removal is found to be 91.58% at 293 K. With further increase in temperature, the percentage removal of Cr(VI) is found to decrease (Figure 6). This shows that temperature has a negative effect on the biosorption efficiency for Cr(VI) biosorption.

In order to analyse the rate of adsorption and possible adsorption mechanism of the two ions onto biomass, pseudo-first-order<sup>23</sup>, pseudo-second-order<sup>24</sup> and intra-particle-diffusion<sup>25</sup> kinetic models were applied to adsorption data.

The linear form of pseudo-first-order is generally expressed as

$$\log(q_e - q_t) = \log q_e - (k_1 / 2.303)t \quad (3)$$

where  $q_e$  and  $q_t$  are the amount of chromium adsorbed at equilibrium ( $\text{mg g}^{-1}$ ) and time  $t$  respectively and  $k_1$  is the rate constant of adsorption. The respective values are given in Table 1.  $R^2$  values appear linear but experimental  $q_e$  values differ from the corresponding  $q_e$  calculated from the linear plots (figure not shown) showing that biosorption of metal ions does not follow pseudo-first-order kinetic model.

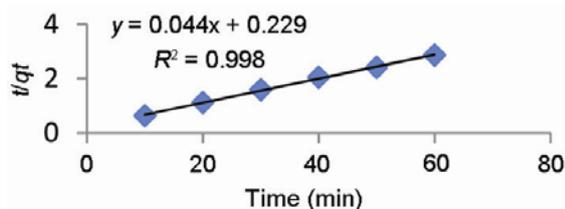
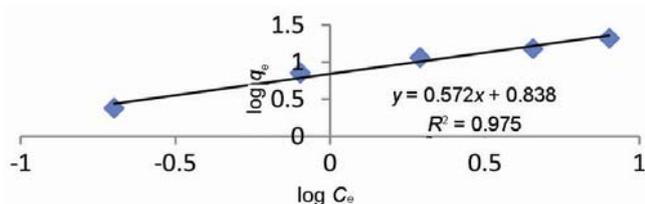
The kinetics of adsorption is also described by pseudo-second-order kinetic equation expressed as

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

where  $k_2$  is the second-order rate constant of adsorption. The plot (Figure 4) of  $t/q_t$  versus  $t$  of the above equation gives a linear relationship from which the  $q_e$  and  $k_2$  values can be determined. The rate constants and the

**Table 1.** Kinetic parameters for Cr(VI) biosorption onto *Tamarindus indica* bark (TB)

Initial metal concentration (mg/l)	$q_e$ (exp) (mg/g)	Pseudo second-order			Pseudo first-order			Intraparticle		
		$q_e$ (cal) (mg/g)	$K_2$	$R^2$	$q_e$ (cal) (mg/g)	$K_1$	$R^2$	$K_i$	$I$	$R^2$
50	21.00	21.36	0.012	0.999	11.57	0.06	0.902	1.22	12.08	0.986
35	15.24	16.55	0.011	0.999	14.87	0.08	0.963	0.85	8.92	0.988
25	11.52	12.36	0.015	0.998	11.96	0.08	0.892	0.59	6.94	0.999
15	7.10	7.59	0.026	0.998	5.95	0.07	0.913	0.35	4.36	0.999
5	2.40	2.55	0.083	0.999	2.05	0.08	0.899	0.11	1.52	0.999

**Figure 4.** Pseudo-second-order plot of Cr(VI) sorption.**Figure 5.** Freundlich Isotherm model of sorption of Cr(VI).

correlation coefficients are calculated and summarized in Table 1. The value of correlation coefficient  $R^2$  for pseudo-second-order adsorption model is relatively high ( $>0.998$ ). Also  $q_e$  (calculated) using pseudo-second-order model is equal to that obtained experimentally. These values indicate that biosorption follows the pseudo-second-order mechanism and the rate of biosorption is controlled by chemisorption.

To explain the diffusion mechanism, the kinetic results were analysed using the Weber and Morris intraparticle diffusion model. It is given as

$$q_t = k_i t^{1/2} + I, \quad (5)$$

where  $I$  is the intercept and  $k_i$  is the intraparticle diffusion rate constant. Larger the intercept, greater is the contribution of the surface sorption in the rate-controlling step. The parameters of intra-particle rate constant  $k_i$  and  $I$  are summarized in Table 1. The calculated  $k_i$  value is higher at higher concentrations, but the intraparticle diffusion is not the sole rate-limiting step, as regression of  $q_t$  versus  $t_{1/2}$  is linear (figure not shown) but not passing through the origin. This indicates the existence of some boundary layer effect.

Langmuir, Freundlich and Temkin adsorption isotherms were plotted to study the interaction between the biomass and the metal ion<sup>26</sup>.

The heterogenous adsorption capacity,  $q_e$  ( $\text{mg g}^{-1}$ ) of TB biomass for Cr(VI) was determined by following Freundlich isotherm equation<sup>27</sup>

$$\log q_e = \log k_f + \frac{1}{n} \log C_e, \quad (6)$$

where  $k_f$  and  $n$  are Freundlich constant. Plot of  $\log q_e$  versus  $\log C_e$  (Figure 5) gives a straight line with a slope of  $1/n$  and intercept of  $\log k_f$ . Table 2 gives the evaluated constants. The value  $n = 1.745$  in the range of 1–5, indicates favourable adsorption. The shape of the isotherm,  $R^2$  value (0.994) and the heterogeneity factor ( $1/n$ ) support a Freundlich isotherm model of adsorption. Thus, it is inferred that the biosorption of Cr(VI) onto TB biomass is a heterogeneous process.

In Langmuir isotherm model, maximum monolayer adsorption capacity,  $q_m$  ( $\text{mg g}^{-1}$ ) and other parameters were determined from following linearized form of equation<sup>28</sup>

$$\frac{C_e}{q_e} - \frac{1}{q_m b} + \frac{C_e}{q_m}, \quad (7)$$

where  $q_m$  ( $\text{mg g}^{-1}$ ) is the maximum uptake capacity and  $b$  is the Langmuir constant related to the energy of adsorption. The value of Langmuir parameter  $q_m$  and  $K_L$  are calculated from the slope and intercept of the linear plot of  $C_e/q_e$  versus  $C_e$  (graph not given). Values of  $q_m$ ,  $b$  and regression coefficient  $R^2$  are listed in Table 2.

The essential features of the Langmuir isotherm parameters can be used to predict the affinity between the following relation given by Hall.

$$R_L = \frac{1}{1 + bC_0}. \quad (8)$$

where  $C_0$  is the initial concentration of metal ion ( $\text{ng l}^{-1}$ ). The value of  $R_L$  was found to be 0.043 for concentration of  $50 \text{ mg l}^{-1}$  of Cr(VI) metal ion. This is in the range 0–1,

**Table 2.** Isotherm model parameters for Cr(VI) onto TB

Metal ion	Freundlich isotherm parameters			Langmuir isotherm model			Temkin isotherm model		
	$K_f$	$N$	$R^2$	$Q_m$	$b$	$R^2$	$A$	$B$	$R^2$
Cr	10.856	1.745	0.975	24.80	0.896	0.974	12.705	4.899	0.964

**Table 3.** Thermodynamic parameters for Cr(VI) biosorption onto TB

Temperature (K)	$K_D$	$\Delta G^0$ (KJ/mol)	$\Delta H^0$ (KJ/mol)	$\Delta S^0$ (J/mol K)
293	5.43	-4.124		
313	3.37	-3.164	-15.197	-37.496
333	2.52	-2.560		
343	2.22	-2.272		

which indicates near-favourable sorption. The value of  $R^2$  does not show linearity (0.957) indicating the adsorption of Cr(VI) ion does not obey the Langmuir adsorption isotherm model.

Temkin isotherm model<sup>29</sup> is given as

$$q_e = B \ln A + B \ln C_e, \quad (9)$$

where  $A$  is the equilibrium binding constant, corresponding to the maximum binding energy and constant  $B$  is related to heat of adsorption.  $A$  and  $B$  can be calculated by the slope and intercept of plots of  $q_e$  against  $\ln C_e$  (graph not given). The values of  $A$  and  $B$  (Table 2) related to heat of adsorption gave good results according to the adsorption capacity of a particular adsorbent. Heat of adsorption values are found to be more for the adsorbent which has greater adsorption capacity, indicating exothermic adsorption. Thus Temkin adsorption also fits well with these adsorption studies.

The thermodynamic parameters such as changes in free energy change  $\Delta G^0$ , enthalpy  $\Delta H^0$ , and entropy  $\Delta S^0$  were determined<sup>30</sup> from the equations

$$K_0 = \frac{C_{\text{solid}}}{C_{\text{liquid}}}, \quad (10)$$

$$\Delta G = -RT \ln K_D, \quad (11)$$

$$\Delta G = \Delta H - T\Delta S, \quad (12)$$

$$\ln K_D = -\frac{\Delta G}{RT}, \quad (13)$$

$$\ln K_D = \frac{\Delta S}{R} - \frac{\Delta H}{RT}, \quad (14)$$

where  $K_D$  is the equilibrium constant.  $C_{\text{solid}}/C_{\text{liquid}}$  can be defined as 'adsorption affinity'.  $C_{\text{solid}}$  is the concentration

of metal ion (mg) in solid adsorbent.  $C_{\text{liquid}}$  is the equilibrium metal concentration (mg l<sup>-1</sup>) in liquid phase. The enthalpy changes ( $\Delta H^0$ ) and entropy changes ( $\Delta S^0$ ) for the adsorption process are obtained from the plots of  $\ln K_D$  shows against  $1/T$  (figure not given). Table 3 shows the calculated thermodynamic data.

Negative value for  $\Delta G^0$  indicates the spontaneity of biosorption process at a given temperature. The free energy values increase positively with increase in temperature for the adsorption of Cr(VI), which shows that the spontaneity of the biosorption process reduces with increase in temperature. The negative  $\Delta H^0$  values indicate the exothermic nature of the adsorption. The negative values of  $\Delta S^0$  suggest a decrease<sup>31</sup> in the randomness at solid/solution interface during the adsorption of Cr(VI) ions onto TB.

To investigate various functional groups of unloaded TB and Cr(VI) loaded TB, FTIR study was carried out and their stretching frequencies are given in Table 4.

The characteristic N-H stretching vibration peak is observed at 3359 cm<sup>-1</sup> which shifts to 3422.59 cm<sup>-1</sup> and became broad on chromium adsorption. The significant shifts of these specific peaks suggest that chemical interactions between the metal ions and -OH, -NH groups present on the biomass surface. The disappearance of bands at 1458.6 cm<sup>-1</sup> was due to change in the nature of binding after interaction with metal ions. The peaks at 2924.39 cm<sup>-1</sup> also shifted to 2920 cm<sup>-1</sup> after chromium adsorption. The above observations indicate that the main functional groups involved in biosorption process are hydroxyl, carboxyl, amine and phosphate groups.

The SEM micrographs of biomass surface before and after Cr(VI) adsorption are shown in Figure 6a and b respectively. The porous and irregular surface structure of the adsorbent can be clearly observed in the SEM image (Figure 6a). While there is a clear demarcation in the surface morphology of biomass after treatment (Figure 6b).

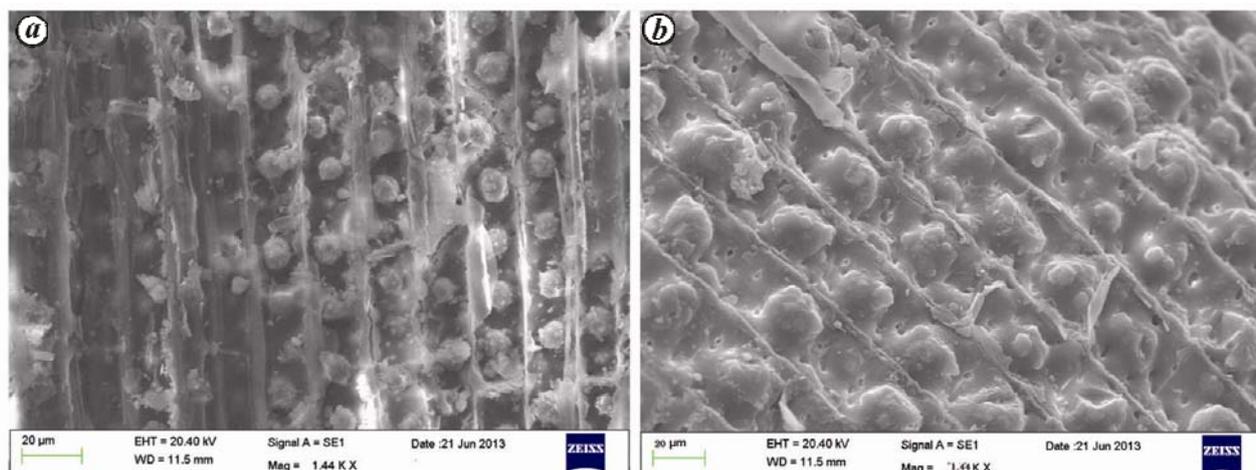
For any sorbent to be feasible, it must combine high and fast adsorption capacity with inexpensive regeneration.

**Table 4.** Results of FTIR analysis

Type of vibration	$\nu$ (cm <sup>-1</sup> ) unloaded TB	$\nu$ (cm <sup>-1</sup> ) loaded TB	Functional group	Reference
-OH, -NH (str)	3359	3422.59	Hydroxyl, amido	31
-C-H (str)	2924.2	2920	Methyl, methylene	32
-CO (str) with -NH deformation	1616.26	1620.55	Amido	31
C=O (sym. str)	1429.6	Disappearance	Carboxylic	33
-C-O (str)	1317	1316.55	Carboxylic	33
-C-N (str)	1030	1030.45	Protein	34
Phosphate	1000	779.61	Nucleic acid	34

**Table 5.** Percentage removal of metal ion after desorption

Base (NaOH) (M)	Metal in biomass before desorption (mg)	Metal in biomass after desorption (mg)	Desorption (%)
0.5	9.5	6.54	31.2
1.0	9.5	3.42	64
1.5	9.5	2.28	76
2	9.5	1.61	83

**Figure 6a, b.** SEM image before and after Cr(VI) adsorption.

In order to assess the reusability of Cr(VI)-loaded TB biomass, desorption studies were carried out. Table 5 shows the effect of strength of desorbing solution (NaOH) on the recovery of Cr(VI). The results show that as the strength of NaOH increases from 0.5 to 2 M the desorption percentage of Cr(VI) increases from 31.15 to 83. Thus a significant amount of chromium is being desorbed and after desorption the same TB biomass could be reused with equal efficiency up to five times. Also, the total cost of removal of Cr(VI) metal from TB biomass is found to be Rs 2.5/kg of biosorbent (the cost is an assessment from the process used).

The potential use of TB as a biosorbent for sequestering of Cr(VI) has been studied. This biosorbent is highly efficient, and cost-effective for the removal of Cr(VI) ions from aqueous solution. The biosorption capacity ( $q_e$ )

of Cr(VI) is 21 mg/g on TB biomass. The favourable temperature is 20°C, and optimum pH for Cr(VI) biosorption is 2. Freundlich isotherm model proved to be a good fit for the experimental data of Cr(VI) biosorption on TB biomass. Free energy change ( $\Delta G^0$ ) with negative sign reflects the feasibility and spontaneous nature of the process. FTIR spectra indicate bands corresponding to -OH, C=S, COO<sup>-</sup> and -NH<sub>2</sub> groups. Desorption of chromium-bearing biomass with 2 M NaOH resulted in metal recovery of about 83%. The chromium-loaded biomass can be desorbed and reused up to five times, thereby recycling the sorbed chromium and preventing its leaching into the environment. Also, the presence of only one metal ion is rare in textile effluents. Thus, further research is required to investigate the effects of the other toxic metal ions present on the biosorption of a certain

metal ion before applying to actual textile wastewater. Further, the chemical modification of biomass can be done and its removal capabilities can be compared.

- Bai, R. S. and Abraham, T. E., Biosorption of chromium (VI) from aqueous solution by *Rhizopus nigricans*. *Bioresour. Technol.*, 2001, **79**, 73–81.
- Yadav, S., Shukla, O. P. and Rai, U. N., Chromium pollution and bioremediation. *Environ. News Newslett Int. Soc. Environ. Bot.*, 2005, **11**, 1.
- Bulut, Y. and Baysal, Z., Removal of heavy metal Pb(II) from waste water using wheat bran. *J. Environ. Manage.*, 2006, **78**, 107–113.
- Sari, A. and Tuzen, M., Biosorption of cadmium (II) from aqueous solution by red algae (*Ceramium virgatum*): equilibrium, kinetics and thermodynamic studies. *J. Hazard Mater.*, 2008, **157**, 448–454.
- Argun, M. E., Dursun, S., Ozdemir, C. and Karatas, M., Heavy metal adsorption by modified oak sawdust: thermodynamics and kinetics. *J. Hazard Mater.*, 2007, **141**, 77–85.
- Yun, Y. S., Park, D., Park, J. M. and Volesky, B., Biosorption of trivalent chromium on the brown seaweed biomass. *Environ. Sci. Technol.*, 2001, **35**(21), 4353–4358; doi: 10.1021/es010866K.
- Cossich, E. S., Tavares, C. R. G. and Ravagnani, T. M. K., Biosorption of Cr(III) by *Sargassum* sp. *Biomass. J. Biotechnol.*, 2002, **5**(2), 133–140.
- Bailey, S. E., Olin, T. J., Bricka, R. M. and Adrain, D. D., A review of potentially low cost sorbents for heavy metals. *Water Res.*, 1999, **33**, 2469–2479.
- Hashem, A., Abdel-Halim, E. S., El-Tahlawy, K. F. and Hebash, A., Enhancement of adsorption of Co(II) and Ni(II) ions onto peanut hulls through estrification using citric acid. *Adsorp Sci. Technol.*, 2005, **23**, 367–380.
- Gardea-Torresdey, J. L. et al., Characterization of chromium (VI) binding and reduction of chromium (III) by the agricultural by-product of *Avena monida* (oat) biomass. *J. Hazard Mater B*, 2000, **80**, 175–188.
- Farajzadeh, M. A. and Monji, A. B., Adsorption characteristics of wheat bran towards heavy metal cations. *Sep. Purif. Technol.*, 2004, **38**, 197–207.
- Mohan, D., Singh, K. P. and Singh, V. K., Trivalent Cr removal from waste water using low cost activated carbon fabric cloth. *J. Hazard Mater B*, 2006, **135**, 280–295.
- Karthikeyan, T., Rajgopal, S. and Miranda, L. R., Chromium (VI) adsorption from aqueous solution by *Hevea brasiliensis* sawdust activated carbon. *J. Hazard Mater B*, 2005, **124**, 192–199.
- Oliveira, E. A., Montanher, S. F., Andrade, A. D., Nobrega, J. A. and Rollemberg, M. C., Equilibrium studies for the sorption of chromium and nickel from aqueous solutions using raw rice bran. *Process Biochem.*, 2005, **40**, 3485–3490.
- Ahalya, N., Kanamadi, R. D. and Ramachandra, T. V., Biosorption of chromium (VI) by *Tamarindus indica* pod shells. *J. Environ. Sci. Res. Intern.*, 2008, **1**(2), 77–81.
- Ang, X. W., Sethu, V. S. and Andresen, J. M., Copper(II) ion removal from aqueous solutions using biosorption technology: thermodynamic and SEM-EDX studies. *Clean Technol. Environ. Policy*, 2013, **15**, 401–407; doi: 10.1007/s10098-012-0523-0.
- Bhatnagar, A. and Minocha, A. K., Biosorption optimization of nickel removal from water using *Punica granatum* peel waste. *Colloids Surf. B*, 2010, **76**, 544–548.
- Areco, M. M. and Dos, S. A. M., Copper, zinc, cadmium and lead biosorption by *Gymnogongrus torulosus* thermodynamics and kinetics studies. *Colloid Surf. B*, 2010, **81**, 620–628.
- Hanafiah, M. A. K., Zakaria, H. and Ngah, W. S. W., Preparation, characterization and adsorption behaviour of Cu(II) ions onto alkali-treated weed (*Imperata cylindrica*) leaf powder. *Water Air Soil Pollut.*, 2009, **201**(1–4), 43–53.
- Cordero, B., Lodeiro, P., Herrero, R., Sastre, de Vicente, M. E., Biosorption of cadmium by *Fucus spiralis*. *Environ. Chem.*, 2004, **1**, 180.
- Iiesanmi, O., Albert, O. A. and Olubode, O. A., Adsorptive removal of chromium (VI) from aqueous solution using cow hooves. *J. Sci. Res. Rep.*, 2013, **2**(1), 288–303.
- Hanif, M. A., Nadeem, R., Bhatti, H. N., Ahmad, N. R. and Ansari, T. M., Ni(II) biosorption by cassia fistula (Golden Shower) biomass. *J. Hazard Mater.*, 2007, **139**, 345–355.
- Namasivayam, C. and Kanchana, N., Removal of Congo red from aqueous solutions by waste banana pith. *Pertanika*, 1993, **1**, 32–42.
- Ho, Y. S. and McKay, G., Pseudo-second order model for sorption processes. *Process Biochem.*, 1999, **34**, 451–465.
- Weber, W. J. and Morris, J. C., Kinetics of adsorption on carbon from solution. *J. Saint. Eng. Div. Am. Soc. Civ. Eng.*, 1963, **89**, 31–60.
- Bishnoi, N. R., Kumar, S. and Rani, S., Biosorption of Cr(III) from aqueous solution using algal biomass spirogyra spp. *J. Hazard Mater.*, 2007, **145**(1–2), 142–147.
- Freundlich, H. M. F., Over the adsorption in solution. *J. Phys. Chem.*, 1906, **57**, 385–471.
- Langmuir, I., The adsorption of gases on plane surfaces of glass, mica and platinum. *J. Am. Chem. Soc.*, 1918, **40**, 1361–1368.
- Chen, Z., Ma, W. and Han, M., Biosorption of nickel and copper onto treated alga (*Undaria pinnatifida*): application of isotherm and kinetic models. *J. Hazard Mater.*, 2008, **155**(1–2), 327–333.
- Senthilkumar, P., Ramalingam, S., Sathyaselvabala, V., Dinesh Kirupha, S. and Sivanesan, S., Removal of copper(II) ions from aqueous solution by adsorptions using cashew nut shell. *Desalination*, 2011, **266**(1–3), 63–71.
- Park, D., Yun, Y. S. and Park, J. M., Studies on hexavalent chromium biosorption by chemically treated biomass of *Ecklonia* sp. *Chemosphere*, 2005, **60**, 1356–1364.
- Gnanasambandam, R. and Protor, A., Determination of pectin degree of esterification by diffuse reflectance Fourier transform infrared spectroscopy. *J. Food Chem.*, 2008, **68**, 327–332.
- Mukhopadhyay, M., Role of surface properties during biosorption of copper by pretreated *Aspergillus niger* biomass. *Colloids Surf. A*, 2008, **329**, 95–99.
- Guibaud, G., Tixier, N., Bouju, A. and Baudu, M., Relation between extracellular polymers composition and its ability to complex Cd, Cu and Pb. *Chemosphere*, 2003, **52**, 1701–1710.

ACKNOWLEDGEMENTS. Sudesh thanks the Agriculture Board, Durgapura, Jaipur for permission to use the AAS. V.G. thanks Ganpat Choudhary (IIT Jodhpur) for technical assistance during FTIR and SEM analysis.

Received 25 March 2015; revised accepted 11 August 2015

doi: 10.18520/cs/v110/i3/392-398