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ORIGINAL PAPER

Removal of hexavalent chromium from aqueous solutions using barks of *Acacia albida* and leaves of *Euclea schimperi*

G. Gebrehawaria · A. Hussen · V. M. Rao

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Abstract Removal of hexavalent chromium ions [Cr(VI)] from aqueous solutions by adsorbents prepared from barks of *Acacia albida* of Fabaceae family and leaves of *Euclea schimperi* of Ebenaceae family has been studied by batch adsorption technique. Double-beam UV–visible spectrophotometer was used to monitor the concentration of Cr(VI). The influence of contact time, initial chromium ion concentration, pH and adsorbent dose on the efficiency of adsorption process was studied. Among the studied parameters, pH was found to be the most influential. At the optimum pH (pH 2), 98.47 and 97.39 % removal of Cr(VI) was achieved using the adsorbents prepared from barks of *A. albida* and leaves of *E. schimperi*, respectively. After determining the optimal conditions for maximum adsorption, the applicability of the biosorbents was tested on real samples. The results indicate that these adsorbents can be employed as low-cost alternatives to commercial adsorbents for the removal of Cr(VI) from effluents. Adsorption isotherms and kinetic parameters were also studied. The results showed that the adsorption of Cr(VI) by these adsorbents follow Langmuir adsorption isotherm. The kinetics of the adsorption process follows the pseudo-second-order kinetic model.

Keywords Heavy metals · Isotherms · Kinetics · Natural adsorbents

Introduction

Waste streams such as industrial effluents may contain heavy metals such as Cu, Zn, Ni, Pb, Cd and Cr and are often encountered in various chemical industries. Among these heavy metals, pollution by chromium is of considerable concern as the metal is used in many sectors such as electroplating, metal corrosion resistance, leather tanning, metal finishing, chromate preparation, cement, dyeing, wood preservatives, paint and pigments, textile dyeing and steel fabrication industries (Hadjmohammadi et al. 2011). Most tanneries adopt chromium tanning process using chromium sulfate because of its processing speed, low cost, light color of leather, greater stability, good mechanical resistance, an extraordinary dyeing suitability and a better hydrothermic resistance of the resulting leather in comparison with hides treated with vegetable substances (Venkateswarlu et al. 2007; Belay 2010). In the chromium tanning process, the leather takes up only 60–80 % of the applied chromium, and the rest is usually discharged into the sewage system causing serious environmental hazard. Chromium ions in liquid tanning waste occur mainly in trivalent form, which gets further oxidized to hexavalent chromium form, due to the presence of organics (Sarin and Pant 2006). The latter form is of particular concern due to its greater toxicity (Venkateswarlu et al. 2007).

The maximum levels permitted in wastewater are 5.00 mg/l for trivalent chromium and 0.05 mg/l for hexavalent chromium. With this limit, it is essential for industries to treat their effluents to reduce the chromium to acceptable levels. Nowadays due to more stringent environmental regulations, most of the mineral processing plants, metal-finishing industries, are facing problems in disposing of wastewater produced in huge quantities, laden with Cr (Sarin and Pant 2006). Chromium (VI) is a cancer-

G. Gebrehawaria
Department of Chemistry, College of Natural and Computational Sciences, Aksum University, P.O. Box 1010, Aksum, Ethiopia

A. Hussen (✉) · V. M. Rao
Department of Chemistry, School of Graduate Studies, Dilla University, P.O. Box 419, Dilla, Ethiopia
e-mail: ahmed.hussen29@yahoo.com

causing agent and can pose health risks such as liver damage, dermatitis gastrointestinal ulcers, epigastric pain, nausea, vomiting, severe diarrhea and corrosion of skin. It may cause carcinoma of respiratory tract and lungs (Venkateswarlu et al. 2007). It also poses a significant threat to aquatic life (Singha and Das 2010). Removal of chromium (VI) from industrial effluents is not only essential because of its toxicity to humans but also because it affects soil fertility due to its ability to inactivate enzymes and precipitating proteins of soil microbial organisms (Gebrekidan et al. 2009).

There are various methods to remove heavy metals from aqueous solutions including chemical precipitation, coagulation, solvent extraction, electrolysis, membrane separation, ion-exchange and adsorption. Most of these methods suffer from high capital and regeneration costs of the materials. Therefore, there is currently a need for new, innovative and cost-effective methods for the removal of toxic substances from wastewaters. Biosorption is an effective and versatile method and can be easily adapted as a low-cost alternative to remove heavy metals from large amount of industrial wastewater (Oboh et al. 2009). This process includes the selective transfer of solute components in the fluid phase onto the surface as well as to the bulk of solid adsorbent materials (Singha and Das 2010). The major advantages of biosorption technology are its effectiveness in reducing the concentration of heavy metal ions to very low levels, low cost, minimization of chemical and/or biological sludge regeneration and the possibility of metal recovery (Owlad et al. 2008).

Many researchers have studied various biosorbents which are relatively inexpensive and are at the same time endowed with reasonable adsorption capacity (Kumar and Kirthika 2009), including agricultural materials such as untreated coffee husks (Oliveira et al. 2008), eucalyptus bark (Sarin and Pant 2006), sawdust and charcoal from sugarcane bagasses (Dhungana and Yadav 2009), tamarind fruit shell and hull (Popuri et al. 2007; Verma et al. 2006), treated sawdust (Baral et al. 2006), potato peel waste (Devi Prasad and Mohammed 2009), wheat bran (Nameni et al. 2008), turkish brown coal (Arsalan and Pehlivan 2007), neem sawdust and mango sawdust (Vinodhini and Das 2010), activated neem leaves (Babu and Gupta 2008), agricultural waste (Bansal et al. 2009; Hasan et al. 2008), oil palm fiber (Isa et al. 2008), helianthus annuus (sunflower) stem waste (Jain et al. 2009), walnut, hazelnut and almond shell (Pehlivan and Altun 2008). The barks of Grar (*Acacia albida*) of Fabaceae family and leaves of Dedeho (*Euclea schimperi*) of Ebenaceae family are types of plants that grow in most parts of Ethiopia and are used mainly as fire wood. These plants have not yet been used for any biosorption process. Thus, in this study, adsorbents prepared from the barks of *A. albida* and leaves of *E. schimperi* have been used for Cr(VI) removal from aqueous solution. This study was carried out at Dilla University, Ethiopia, during the academic year of 2011–2012.

Materials and methods

Chemicals

Potassium dichromate (Assay 99.8 %, Riedel-de Haen, Germany), diphenylcarbazide (Assay >99.5 %, Riedel-de Haen, Germany) and all the other chemicals were analytical grade purchased from Sigma-Aldrich and Riedel-de Haen, Germany; 1,000 mg/l of standard stock solution of Cr(VI) was prepared from potassium dichromate by taking 2.828 g $K_2Cr_2O_7$ which is equivalent to 1.0 g of Cr(VI) and transferred to 1,000 ml volumetric flask, dissolved and diluted to volume with distilled water. Other concentrations were prepared by dilution from the stock solution. A calibration curve was done by preparing a series of standard solutions of Cr(VI) from the stock solution. Six different solutions having concentrations 0.1, 0.2, 0.6, 1.0, 1.2 and 1.4 mg/l of Cr(VI) were used for the calibration graph.

Preparation of adsorbent and characterization

The collected barks of *A. albida* and leaves of *E. schimperi* were cut into small pieces and dried in sun light for about 2 days. Then, it was pounded manually and sieved using 710-µm sieve particle size analyzer. Then, these were preserved in air tight plastic bottles. Approximately 5 mg of the adsorbent was transferred into mortar, and a small amount of paraffin was added and then mixed using pestle to form into a mull. KBr pellet was used to analyze the mull sample in the range of 4,000–400 cm^{-1}. Infrared spectra of raw and metal-ion-loaded biosorbents were obtained using a Fourier transform infrared spectrophotometer (Shimadzu, IR Prestige-21).

Batch adsorption experiments

Batch experiments were carried out using a series of 250.0-ml conical flasks to investigate the effects of contact time, initial metal ion concentrations, pH and adsorbent dosage on the adsorption of the metal ions from aqueous solutions. Known amounts of adsorbents were added to the solution. The mixture was stirred gently using a magnetic stirrer at room temperature. The suspensions were filtered using Whatman filter paper No. 541, and the concentrations of the metal ions in the filtrate were analyzed using UV–visible double-beam spectrophotometer (Shimadzu, UV-1700). Chromium (VI) ions were analyzed after the formation of a colored complex with diphenylcarbazide. The absorbance of this colored complex was measured at 540 nm. All the measurements were done after standing for 5–10 min to allow for full color development against the reagent blank. The concentration of the analyte was determined from the calibration curve of the standards.

The effects of various parameters on percentage of adsorption was observed by varying contact time, t (10, 20, 30, 60, 90 and 120 min), initial concentration of chromium (VI) ions, C_o (5, 7.5, 10, 12.5, 15 and 20 mg/l), pH of solution (2, 3, 5, 7, 9 and 11) and adsorbent dosage, W (0.5, 1.0, 1.5, 2.0, 2.5 and 3 g/100 ml). The Cr(VI) removal (%) at any instant of time was determined by the Eq. (1):

$$\text{Chromium removal } (\%) = \frac{C_o - C_t}{C_o} \times 100 \tag{1}$$

where C_o and C_t are the concentrations of Cr(VI) ions initially and at a given instant of time, respectively. All experiments were carried out in triplicate measurements. Adsorption isotherm studies were carried out with different initial Cr(VI) concentrations ranging from 5 to 20 mg/l while maintaining the adsorbent dosage at 2 g.

Application to real samples

Samples of effluents were randomly collected for Cr(VI) removal from Sheba tannery, Wukro eastern Tigray, Ethiopia, from primary sedimentation pond, chromium pond and treated pond using plastic bottles. The analyses of real samples were carried out in two steps. The first one is direct analyses to determine concentration of Cr(VI) in the wastewater. The second part of the analysis was carried out by treating the wastewater with the adsorbent prepared from bark of *A. albida* to remove the pollutant using the optimized parameters. For this particular analysis, 100 ml of the wastewater was transferred into 250-ml conical flask containing 0.5 g adsorbent. pH was adjusted to 2.0 using 1 N H_2SO_4 and 1 N NaOH, and the solution was stirred for 10 min using magnetic stirrer. Finally, the solution was filtered and analyzed as described under batch adsorption experiments.

Results and discussion

Characterization of the adsorbents

The pattern of adsorption of metals by the plant materials is attributed to the active groups and bonds present on them. Plant cell walls, mainly consisting of polysaccharides, proteins and lipids, offer many functional groups such as carboxyl, carbonyl, hydroxyl, amino, aromatic nitro, silicate, sulfonate, etc., which can be involved in metal binding (Singha and Das 2010). The infrared spectra of raw and metal-ion-loaded biosorbents were taken to determine the functional groups which were responsible for the adsorption process. The infrared spectra of adsorbent prepared from barks of *A. albida* before and after loaded with Cr(VI) ions are indicated in Fig. 1.

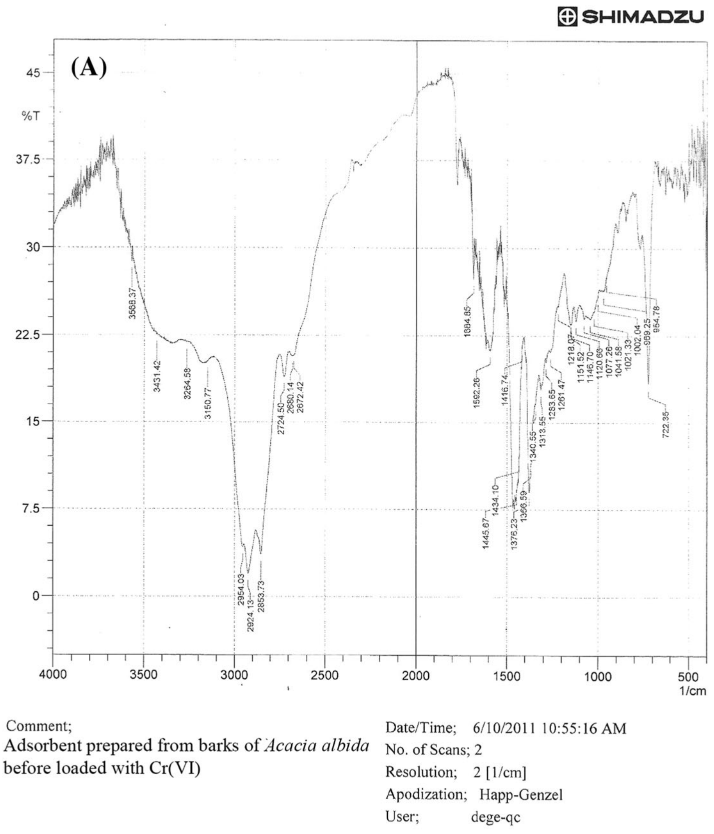
The Fig. 1 displays a number of absorption peaks, indicating the complex nature of adsorbent prepared from barks of *A. albida*. The FT-IR spectroscopic analysis indicated broad band's at 3,431, 3,264, 3,150 cm^{-1}, representing –OH and –NH stretching. The bands observed at about 2,924, 2,954 and 2,853 cm^{-1} could be assigned to the aliphatic C–H groups. The bands around 2,724, 2,680 and 2,672 cm^{-1} corresponds to O–H stretching vibrations of chelating agents with intramolecular hydrogen bonds. The band around 1,684 cm^{-1} corresponds to stretching vibration of –C=O of amide. The band at 1,592 cm^{-1} corresponds to carboxylate anion (C–O) stretching and the band at 722 cm^{-1} corresponds to C–Cl stretching vibrations. Symmetrical bending of CH_3 is observed at 1,445 and 1,434 cm^{-1}. The peaks 1,376 and 1,366 cm^{-1} indicate the stretching vibrations of the aliphatic and aromatic C–NO_2, respectively. The peaks observed at 1,283 and 1,261 are due to aromatic C–N stretching vibrations, and weak absorption bands from 1,151 to 1,021 are due to aliphatic C–N stretching vibrations (Dudley 1995).

The FT-IR spectrum of metal-loaded *A. albida* (Fig. 1) was used to investigate the changes in vibration frequencies in the functional groups of the adsorbents due to Cr(VI) adsorption. The intensity of the bands were decreased after loaded with Cr(VI). Some bands totally disappeared in the FT-IR spectrum of adsorbent after loaded with Cr(VI) compared to that before loaded with Cr(VI). For instance, the bands (3,431, 3,264, 3,150 and 1,684 cm^{-1}) corresponding to –OH, –NH and –C=O (amide) stretching disappeared from the FT-IR spectrum of adsorbent after loaded with Cr(VI) (Dudley 1995). This is due to the chemical reaction that took place between Cr(VI) and the polar functional groups such as –OH, –NH and –C=O (amide). In addition, most of the bands were shifted to new positions with reduced intensity and a new band (3,329.19 cm^{-1}) is also formed indicating that a new bond is formed between the polar functional groups of the adsorbent and the adsorbate.

Solution stability and calibration curve

The absorbance readings of the Cr(VI) solution at different times of 5, 20, 40 and 60 min are 0.2335, 0.2332, 0.2327

Fig. 1 FT-IR spectrum of adsorbent prepared from barks of *Acacia albida* before (**a**) and after (**b**) loaded with Cr(VI)



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Adsorbent prepared from barks of *Acacia albida* before loaded with Cr(VI)

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Resolution; 2 [1/cm]
Apodization; Happ-Genzel
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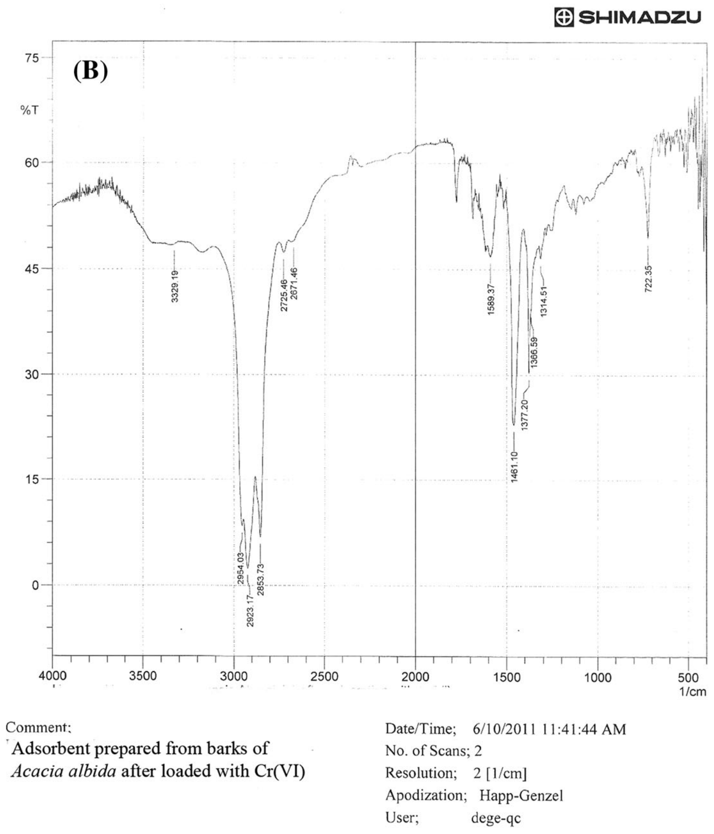

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Adsorbent prepared from barks of *Acacia albida* after loaded with Cr(VI)

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User; dege-qc

Table 1 Effect of contact time on percentage removal of Cr(VI) using adsorbent prepared from bark of *Acacia albida* and leaves of *Euclea schimperi*

Time (min)	*Acacia albida*		*Euclea schimperi*	
	C_f (mg/l)[a]	% Removal, (SD, $n = 3$)	C_f (mg/l)[a]	% Removal, (SD, $n = 3$)
10	0.7811	92.16 (0.010)	0.3008	96.99 (0.006)
20	0.7723	92.25 (0.005)	0.2559	97.43 (0.010)
30	0.7473	92.50 (0.006)	0.2530	97.47 (0.010)
60	0.5999	94.00 (0.010)	0.1876	98.12 (0.015)
90	0.5613	94.36 (0.006)	0.1764	98.24 (0.005)
120	0.4365	95.63 (0.006)	0.1668	98.34 (0.006)

[a] Final concentration remaining in the filtrate

Table 2 Effect of initial Cr(VI) ions concentration on the percentage removal of Cr(VI) using adsorbent prepared from bark of *Acacia albida* and leaves of *Euclea schimperi*

Initial conc. of Cr(VI) (mg/l)	*Acacia albida*		*Euclea schimperi*	
	C_f (mg/l)[a]	% Removal, (SD, $n = 3$)	C_f (mg/l)[a]	% Removal, (SD, $n = 3$)
5.0	0.2939	94.11 (0.010)	0.2469	95.05 (0.017)
7.5	0.4362	94.18 (0.006)	0.4332	94.22 (0.021)
10.0	0.6436	93.56 (0.012)	0.6082	93.92 (0.010)
12.5	0.9536	92.37 (0.010)	0.8006	93.59 (0.006)
15.0	1.0597	92.93 (0.006)	1.0616	92.92 (0.006)
20.0	1.2532	93.73 (0.006)	1.2145	93.92 (0.006)

[a] Final concentration remaining in the filtrate

and 0.2320, respectively. These readings indicate that the solutions of colored complex of Cr(VI)-diphenylcarbazide are stable up to 60 min. The absorbance of calibration standard solutions measured at 540 nm showed an excellent positive correlation. The correlation coefficient observed for Cr(VI) was 0.999.

Optimization of factors affecting chromium adsorption

The parameter such as contact time, initial Cr(VI) concentration, pH and adsorbent dosage which affect the removal of Cr(VI) ions were optimized by varying each at a time while keeping the remaining parameters constant. The results are presented below:

Effect of contact time

In this experiment, all of the parameters except contact time, including initial chromium concentration (10 mg/l), natural pH (5.6) and adsorbent dose (2 g/100 ml), were kept constant. The effect of contact time on chromium adsorption efficiency is shown in Table 1. There is a general increase in the biosorption efficiency with time. The equilibrium uptake of Cr(VI) was about 94 % for the adsorbent prepared from bark of *A. albida* and 98 % for leaves of *E. schimperi*. There was no significant change in equilibrium concentration after 60 min up to 120 min which means after 60 min, the adsorption phase reached equilibrium. Therefore, 60 min was selected as equilibrium time for both adsorbents and used in subsequent optimization. The results showed that the adsorbent prepared from *E. schimperi* is acting fast in adsorption. However, the filtration of the adsorbent from *E. schimperi* is taking longer time because of its sticky nature which is in contrast to *A. albida* (Fibrous in nature). In general, both adsorbents in the present study are found to be more effective than the adsorbents prepared from wheat bran which was reported to have 87.6 % adsorption of Cr(VI) attaining equilibrium at 60 min (Nameni et al. 2008).

Effect of initial chromium concentration

The experiments were conducted by keeping the contact time at 60 min, natural pH of 5.6 and 2 g of adsorbent dose (2 g/100 ml) at room temperature. As can be seen in the Table 2 comparable adsorption capacity has been observed for both the adsorbents. Percentage removal of Cr(VI) ions decreased with the increase in initial Cr(VI) ions concentration. The decrease in percentage adsorption with an increase in initial metal ions concentration may be attributed to lack of sufficient surface area to accommodate more metal ions available in the solution (Abdullah and Prasad 2009). These observations can be explained by the fact that at very low concentrations of metal ions, the ratio of active surface area to the total metal ions available is high, and thus, there is a greater chance for metal ions removal. Therefore, at low initial metal ion concentrations, the removal capacity is higher. When metal ion concentrations are increased, binding sites become more quickly saturated as the amount of biomass concentration remains constant. Thus, an initial Cr(VI) concentration of 7.5 mg/l was selected for the next optimization processes. Similar results

Table 3 Effect of pH on the percentage removal of Cr(VI) using the adsorbent prepared from barks of *Acacia albida* and leaves of *Euclea schimperi*

pH	*Acacia albida*		*Euclea schimperi*	
	C_f (mg/l)[a]	% Removal, (SD, $n = 3$)	C_f (mg/l)[a]	% Removal, (SD, $n = 3$)
2	0.1151	98.47 (0.015)	0.1958	97.39 (0.015)
3	0.1183	98.42 (0.025)	0.2877	96.16 (0.015)
5	0.1880	97.49 (0.015)	0.3205	95.73 (0.010)
7	0.6360	91.53 (0.006)	0.4824	93.57 (0.010)
9	3.4250	54.36 (0.098)	1.0026	86.63 (0.010)
11	6.4280	14.27 (0.107)	1.3558	81.92 (0.015)

[a] Final concentration remaining in the filtrate

Table 4 Effect of adsorbent dosage on the percentage removal of Cr(VI) ions using the adsorbent prepared from the barks of *Acacia albida* and leaves of *Euclea schimperi* at an optimum pH of 2

Adsorbent dosage (g)	*Acacia albida*		*Euclea schimperi*	
	C_f (mg/l)[a]	% Removal, (SD, $n = 3$)	C_f (mg/l)[a]	% Removal, (SD, $n = 3$)
0.5	0.0484	99.51 (0.015)	0.1243	98.76 (0.021)
1.0	0.0393	99.61 (0.012)	0.1109	98.89 (0.017)
1.5	0.0374	99.63 (0.015)	0.0576	99.42 (0.029)
2.0	0.0364	99.63 (0.006)	0.0543	99.46 (0.015)
2.5	0.0257	99.75 (0.025)	0.0242	99.76 (0.015)
3.0	0.0038	99.96 (0.012)	0.0304	99.69 (0.042)

[a] Final concentration remaining in the filtrate

were reported on the uptake of Cr(VI) from aqueous solutions by the adsorbent prepared from root bark of Indian Sarsaparilla (Sekhar et al. 2003) and wheat bran (Nameni et al. 2008).

Effect of pH

It was found that biosorption capacity of Cr(VI) ions was maximum at pH of 2 and significantly decreased with increase in pH values up to 11 (Table 3). At pH of 2, the uptake percentage value was found to be 98.47 % for *A. albida* and 97.39 % for *E. schimperi*. From this observation, it is clear that the efficiency of adsorption is very high at low pH. The reason for this is explained as follows:

Chromium(VI) may be present in aqueous solutions mainly as chromate, dichromate, hydrogen chromate, chromic acid and hydrogen dichromate. Chromate ion (CrO_4^{2-}) is predominant at $pH > 7$, while hydrogen chromate ($HCrO_4^-$) is predominant at $pH < 6$ (Cotton and Wilkinson 1980; Greenwood and Earnshaw 1984; Swietlik 1998; Darko et al. 2011). In aqueous solution, hydrolysis of $Cr_2O_7^{2-}$ takes place, $Cr_2O_7^{2-} + H_2O \leftrightarrows 2HCrO_4^-$, to form $HCrO_4^-$. Thus, although $Cr_2O_7^{2-}$ of $K_2Cr_2O_7$ was the source of Cr(VI) in the synthetic solution used in this study, at pH less than 6.0, the predominant form of Cr(VI) in aqueous solution is $HCrO_4^-$ (Isa et al. 2008). Therefore, the $HCrO_4^-$ form is inferred as the predominant species of Cr(VI) preferentially adsorbed by the adsorbents at pH 2.0. At low pH, the surface of the biosorbent is positively charged due to protonation with H^+, and this promotes the binding of the negatively charged $HCrO_4^-$ ions. Thus, the uptake of Cr(VI) ions increases markedly with decreasing pH. At high pH, the adsorbent undergoes deprotonation which leads to decrease in electrostatic force of attraction between the adsorbent and adsorbate ions (Abdullah and Prasad 2009). The decrease in adsorption at high pH values is also due to the competitiveness of the oxyanion of Cr(VI) and OH^- ions in the bulk solution which retards the approach of such ions further toward the adsorbent surface. Similar observations were made on the uptake of Cr(VI) from aqueous solutions by adsorbent prepared from oil palm fiber at pH 1.50–2.00 (Isa et al. 2008); neem sawdust, mango sawdust, wheat shell, sugarcane bagasse and orange peel at pH 2 (Vinodhini and Das 2009); mango and neem sawdust at pH 2 (Vinodhini and Das 2010).

Therefore, the pH of 2 was selected as optimum pH for the removal of Cr(VI) using the adsorbents prepared from both the bark of *A. albida* and leaves of *E. schimperi*. At the pH of 2, the efficiency for the removal of Cr(VI) from aqueous solutions was more for *A. albida* than that of *E. schimperi*. The same has been confirmed statistically by applying *t* test at 95 % confidence level.

Apart from handling problem attributed to the sticky nature of *E. schimperi*, it has high ability to retain its efficiency at high pH. That means its performance will not deteriorate to the same extent as that of *A. albida*. As can be seen from Table 3 (at pH 9 and 11), removal efficiency by *A. albida* significantly decreased by 50–85 %. On the other hand, removal efficiency of *E. schimperi* decreased only by 15–20 % at the same pH (9 and 11). This indicates that the adsorbent prepared from leaves of *E. schimperi* can even be employed at high pH. This unique aspect of the adsorbent is probably due to less deprotonation compared to that of *A. albida*.

Effect of adsorbent dosage

At this stage, the experiments were done by keeping the other parameters fixed at their optimized values that is 60 min of contact time, 7.5 mg/l of initial Cr(VI) concentration and pH of 2. As shown in Table 4, chromium removal efficiency was high even at low adsorbent dosage. This implies the biosorbents are so active in removing

Table 5 Comparison of Cr(VI) removal at natural pH (5.6) and optimum pH (2)

Contact time			Adsorbent dosage				Initial Cr(VI) concentration			
Time (min)	% Removal at natural pH	% Removal at optimum pH	Dosage (g)	% Removal at natural pH	Dosage (g)	% Removal at optimum pH	Concentration (mg/l)	% Removal at natural pH	Concentration (mg/l)	% Removal at optimum pH
10	92.16 (0.010)	99.69 (0.012)	1	83.88 (0.020)	0.5	99.51 (0.015)	5.0	94.11 (0.010)	25	99.39 (0.006)
20	92.25 (0.005)	99.69 (0.006)	2	90.74 (0.012)	1.0	99.61 (0.012)	7.5	94.18 (0.006)	50	99.38 (0.000)
30	92.50 (0.006)	99.66 (0.006)	3	95.00 (0.015)	1.5	99.63 (0.015)	10.0	93.56 (0.012)	75	96.28 (0.015)
60	94.00 (0.010)	99.69 (0.026)	4	94.95 (0.015)	2.0	99.63 (0.006)	12.5	92.37 (0.010)	100	91.92 (0.010)
90	94.36 (0.006)	99.68 (0.015)	5	95.05 (0.012)	2.5	99.75 (0.025)	15.0	92.93 (0.006)	125	93.27 (0.015)
120	95.05 (0.006)	99.71 (0.006)	6	95.21 (0.012)	3.0	99.96 (0.012)	20.0	93.73 (0.006)	150	92.01 (0.000)

metal ions efficiently even with smaller dose when the pH was adjusted to its optimum value (pH 2). As adsorbent dosage increased, there is an increasing trend for the percent removal of Cr(VI) for both the adsorbents. An increase in biomass dosage generally increases the amount of biosorbed metal ions due to an increase in surface area of the biosorbent, which consequently increases the number of binding sites (Abdullah and Prasad 2009). When the active sites which are responsible for adsorption process are increased, it would be more probable for $HCrO_4^-$ and $Cr_2O_7^-$ ions to be adsorbed on adsorption sites and thus adsorption efficiency increases (Nameni et al. 2008). However, since 98–99 % removal was already achieved with very low adsorbent dosage of 0.5 g (Table 4), further addition of the adsorbent did not cause that much change in the biosorption efficiency. This may be due to overlapping of adsorption sites as a result of overcrowding of adsorbent particles (Kumar and Kirthika 2009). Therefore, an adsorbent dosage of 0.5 g was selected as optimal adsorbent dose for real sample treatment. Similar observations were made on the uptake of Cr(VI) from aqueous solutions by adsorbents prepared from pine needles powder (Hadjmohammadi et al. 2011) and volcanic ash soil (Babel and Opiso 2007).

The data generated for optimization of the four factors (Tables 1, 2, 3 and 4) were tested using ANOVA single factor. The result indicates that there is significant difference in the Cr(VI) removal efficiency at 95 % confidence level for each factor.

Comparison of Cr(VI) removal at natural and optimum pH with respect to contact time, adsorbent dosage and initial Cr(VI) concentration

The percentage removal of Cr(VI) ions was studied by adjusting the pH to the optimal value and without adjusting the pH (natural pH 5.6). The same experimental conditions (10 mg/l Cr(VI), 2 g adsorbent per 100 ml solution) were applied in both the cases except pH. As shown in Table 5, by adjusting the initial pH to 2 which is optimum value, the percentage removal was highly increased. Almost 100 % removal efficiency was achieved within 10 min of contact time when the optimum pH was used. In contrast, only 95 % removal efficiency was observed after 120 min at natural pH. This implies pH is the most important parameter in the removal of Cr(VI) ions from aqueous solution using *A. albida*.

For the adsorption process at its natural pH (5.6), the experiment was conducted using an initial Cr(VI) concentration of 7.5 mg/l and a contact time of 60 min by varying the adsorbent dosage from 1 to 6 g. On the other hand for the optimum pH, the experiment was carried out at an initial Cr(VI) concentration of 10 mg/l and a contact time of 10 min by varying adsorbent dosage from 0.5 to 3 g. Regardless of relatively higher initial concentration, shorter contact time and small adsorbent dosage, which are supposed to have a negative impact on the extent of Cr(VI) removal, the percentage removal was higher at optimum pH. For instance, when the percentage removal is compared at 1, 2 and 3 g of adsorbent dosage, which are common in both experiments, the removal is higher when pH was adjusted to optimum value than at natural pH (Table 5). It is interesting to note that more than tenfold adsorbent dosage is required (6 g to get 95.21 % removal) at natural pH to reach at equivalent removal efficiency of 0.5 g (99.51 %) of the same adsorbent employed at optimum pH. This indicates remarkable role played by pH on the adsorption efficiency of the adsorbent prepared from barks of *A. albida*.

Another experiment was conducted at natural pH using 2 g of adsorbent and 60 min of contact time, while for the optimum pH, the same experiment was carried out using 0.5 g of the adsorbent and 10 min of contact time. In this experiment, Cr(VI) concentration was varied from 5–20 to 25–150 mg/l for natural and optimum pH, respectively. Generally percentage removal is favored at longer contact times, lower initial concentrations and at relatively higher adsorbent dosage. But contrary to this general expectation, the percentage of adsorption was higher in the case of optimum pH (where there is high initial concentration) than it is at natural pH (where there is low initial concentration) (Table 5). This can be attributed to the role of pH which has pronounced effect compared to other parameters.

Real sample analysis

Samples collected from primary sedimentation pond, chromium pond and treated pond have been treated with an adsorbent prepared from the bark of *A. albida* and analyzed for Cr(VI) removal using the optimized conditions. As expected, higher concentration of Cr(VI) was present in the samples collected from the primary sedimentation pond and chromium pond compared to the samples collected from the treated pond (Table 6). This implies that the conventional wastewater treatment such as precipitation and biological techniques performed by the factory has positive effect in reducing the concentration of Cr(VI) from the effluent. However, the treatment being carried out at the factory did not bring Cr(VI) concentration below maximum permissible concentration (0.05 mg/l).

The effluent samples containing Cr(VI) in different concentrations were now treated with the adsorbent prepared form the bark of *A. albida* under optimized experimental conditions. The percentage of Cr(VI) removed from these samples are shown in Table 6. In the case of samples from primary pond, it was reduced from 2.3699 to 0.1513 mg/l after applying 0.5 g of this adsorbent and 10 min contact time at pH 2. Similarly, for the samples collected from chromium and treated ponds, the concentration of Cr(VI) was reduced from 2.2802 to 0.3308 mg/l and 0.7633 to 0.1981 mg/l, respectively. Thus, it is shown that this adsorbent can be effectively used as an alternative to the conventional effluent treatment methods which are costly and less effective (Owlad et al. 2008). The lower percentage removal in the case of real effluent samples is due to higher affinity of adsorbents to other pollutants because of complex nature of the effluents. For example, the percent removal of Cr(VI) obtained from treated pond is relatively smaller than the other two (Table 6). This is because the pond was full of various colored chemicals and fillers that come from the tanning process and interferes with the adsorption process. In order to reduce the Cr(VI) concentration below the maximum permissible limit, usage of higher adsorbent dosage or tandem treatment or consecutive treatment of effluents can be used as a solution.

Table 6 Treatment of tannery effluents contaminated by Cr(VI)

Site of sampling	Average initial conc. of Cr(VI) (mg/l), $n = 3$	Average concentration left after treatment, $n = 3$	% Removal, (SD, $n = 3$)
Primary sedimentation pond	2.3699	0.1513	93.62 (0.270)
Chromium pond	2.2802	0.3308	85.49 (1.021)
Final treated pond	0.7633	0.1981	74.05 (0.270)

Adsorption isotherms

Adsorption isotherms were studied by fixing adsorbent dosage at 2 g and varying adsorbate concentration. The Langmuir and Freundlich adsorption models were applied for the experimental data at room temperature (Gupta and Babu 2006; Saradhi et al. 2010; Dhungana and Yadav 2009).

The Langmuir parameters $q_{\max}$ and K_L were calculated from the intercepts and slopes of the linear plots of $\frac{1}{q_e}$ versus $\frac{1}{C_e}$ based on Eq. (2), where $q_{\max}$ and K_L (l/mg) are the Langmuir constants related to maximum sorption capacity (mg/g) and energy of adsorption (l/mg), respectively.

$$\frac{1}{q_e} = \frac{1}{q_{\max}} + \frac{1}{K_L q_{\max}} \cdot \frac{1}{C_e} \tag{2}$$

The separation factor (R_L) values for the adsorption of Cr(VI) by adsorbent prepared from barks of *A. albida* and leaves of *E. schimperi* were calculated based on Eq. (3).

$$R_L = \frac{1}{1 + K_L C_i} \tag{3}$$

The separation factor values obtained in the study are varied between 0.41 and 0.14 in the case of *A. albida* and 0.27–0.085 for *E. schimperi* when the initial chromium concentration was varied from 5 to 20 mg/l by increment of 5 mg/l. All these results are between 0 and 1 which implies favorable adsorption. Higher R_L values at lower ion concentrations showed that adsorption is more favorable at lower concentration. Similar results were obtained using pine needles powder as a biosorbent for Cr(VI) removal from aqueous solution (Hadjmohammadi et al. 2011).

Similarly Freundlich parameters (n, K_f) were calculated from slopes and intercepts of the linear plot of log q_e versus log C_e based on the Eq. (4), where $1/n$ is adsorption intensity and K_f is related to biosorption capacity.

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \tag{4}$$

In both the Eqs. 2 and 4, q_e and C_e are the amount adsorbed per amount of adsorbent (mg/g) and equilibrium concentration (mg/l), respectively.

The results indicate that there is linear relationship between the amounts (mg) of Cr(VI) ions adsorbed per unit mass (g) of the biosorbents against the concentration of Cr(VI) ions remaining in the solution (mg/l). The values of regression coefficients obtained from these models were used as the fitting criteria to find out these isotherms. It was observed that the experimental data fit well to Langmuir and Freundlich adsorption isotherms indicating both monolayer homogeneous and heterogenous surface conditions. The maximum adsorption capacities, energies of adsorption and values of regression coefficients are also shown in Table 7.

The values of $\frac{1}{n}$ obtained from Freundlich model were 0.8673 for barks of *A. albida* and 0.8174 for leaves of *E. schimperi* which lie between 0.0 and 1.0 indicating favorable biosorption (Abdullah and Prasad 2009). From the values of correlation coefficients (R^2) given in the Table 7, the equilibrium data is better fitted to the Langmuir isotherm model than the Freundlich adsorption model for both the adsorbents.

Table 7 Langmuir and Freundlich parameters for Cr(VI) biosorption using the adsorbents prepared from barks of *Acacia albida* and leaves of *Euclea schimperi*

Biosorbents	Langmuir parameters			Freundlich parameters		
	$q_{\max}$ (mg/g)	K_L (l/mg)	R^2	$1/n$	K_f	R^2
Barks of *Acacia albida*	2.9833	0.2941	0.9867	0.8673	0.6849	0.9713
Leaves of *Euclea schimperi*	3.9463	0.5402	0.9862	0.8174	1.4365	0.9825

Adsorption kinetics

The kinetic parameters for the adsorption process were studied from variation in contact time and analyzed using two simple kinetic models: the pseudo-first-order and pseudo-second-order models (Vinodhini and Das 2010). The following pseudo-first-order rate expression of Lagergren was used to calculate the kinetic parameters [Eq. (5)].

$$\log (q_e - q_t) = \log q_e - 0.4342 k_1 t \tag{5}$$

Straight line was obtained by plotting log ($q_e - q_t$) versus t. The slope and intercept of this plot were used to obtain the pseudo-first-order rate constant k_1 and equilibrium adsorption capacity q_e, respectively. The calculated q_e, k_1 and correlation coefficient R^2 values are summarized in the Table 8.

The pseudo-second-order kinetic parameters were calculated from the linear plot of t/q_t versus t in Eq. (6).

$$\frac{t}{q_t} = \frac{1}{k_2 (q_e)^2} + \frac{t}{q_e} \tag{6}$$

The values of pseudo-second-order rate constant k_2 and equilibrium adsorption capacity q_e were calculated from the intercept and slope of the plot, respectively. The calculated q_e, k_2 and correlation coefficient R^2 values are also presented in Table 8.

From the results in Table 8, it can be concluded that pseudo-second-order rate equation provides the best correlation coefficient (R^2) and also there is better agreement between the calculated q_e and the experimental q_e values which suggests that the chemisorption is the rate-determining step in the adsorption of Cr(VI) ions in the case of

Table 8 Regression parameters of the kinetic models for the removal of Cr(VI) using the adsorbent prepared from barks of *Acacia albida*

Kinetic model	
$q_{e,\ \mathrm{experimental}}$	0.4782
Pseudo-first-order	
k_1	0.0140
q_e	0.0214
R^2	0.9622
Pseudo-second-order	
k_2	2.4582
q_e	0.4792
R^2	0.9999

Table 9 Comparison of adsorption capacity of different adsorbents for the Cr(VI) removal

Adsorbent	Solute	$q_{\max}$ (mg/g)	C_o (mg/l)	Reference
Potato peel waste	Cr(VI)	8.012	20–120	Abdullah and Prasad 2009
Isarog ash soil	Cr(VI)	0.864	5–25	Babel and Opiso 2007
Mandalagan ash soil	Cr(VI)	0.171	5–25	Babel and Opiso 2007
Neem leaves	Cr(VI)	10.40	20–200	Gupta and Babu 2006
Wheat bran	Cr(VI)	0.942	2.5–25	Nameni et al. 2008
Orange peel	Cr(VI)	19.80	10–150	Vinodhini and Das 2010
Aspergillus niger	Cr(VI)	6.970	25–100	Munir et al. 2010
Euclea schimperi	Cr(VI)	3.9463	5–20	Present study
Acacia albida	Cr(VI)	2.983	5–20	Present study

adsorbent prepared from bark of *A. albida* (Kumar and Kirthika 2009; Rozaini et al. 2010).

Comparison of adsorption capacity of the current adsorbents with other adsorbents

Direct comparison of the performance of these adsorbents with other adsorbent materials might be difficult, owing to the different experimental conditions under which they were applied. Nevertheless, the performance can at least be compared based on their maximum adsorption capacity ($q_{\max}$). Accordingly, the present adsorbents have been compared with adsorbents reported in the literature as shown in Table 9.

The $q_{\max}$ values depend on the initial concentration of the metal ions. If the initial metal ion concentration increases, the $q_{\max}$ value will also increase proportionally (Table 9). In the present study when the initial concentration of Cr(VI) was varied from 5 to 20 mg/l, its $q_{\max}$ value is 2.983 mg/g. This value is very much higher than the $q_{\max}$ obtained for Isarog and Mandalagan ash soil (Babel and Opiso 2007), which are in the comparable initial Cr(VI) concentration ranges. Similarly, in this study, when the analysis was further performed by varying initial Cr(VI) ion concentration ranging from 25 to 150 mg/l, the value of $q_{\max}$ was 22.573 mg/g. This $q_{\max}$ is much higher than the $q_{\max}$ of orange peel and Neem leaves (19.80 and 10.40, respectively) having comparable ranges of initial Cr(VI) concentration. Thus, in general, the performance of the adsorbents in the present study is better than that of similar adsorbents reported in literature.

Conclusion

The differences in the FT-IR spectra of adsorbent before and after the adsorption process indicate that chemical reactions took place between Cr(VI) and the functional groups of the adsorbents.

Effects of different parameters such as contact time, pH, amount of adsorbents and initial Cr(VI) concentration were investigated for the removal of Cr(VI) ions using these adsorbents. Among these parameters, pH was found to be the most important parameter that influences the adsorption process. In general, the investigation revealed that almost complete removal of Cr(VI) (>99 %) was obtained using both adsorbents at optimized conditions. The performance of these adsorbents in the removal of Cr(VI) from aqueous solutions is found to be better than the similar biosorbents reported in the literature.

Based on the values of separation factor (R_L) and heterogeneity factor, the experimental data fit well to Langmuir and Freundlich adsorption isotherm models indicating both monolayer homogeneous and heterogeneous surface conditions. From the values of correlation coefficients (R^2), the equilibrium data are better fitted to the Langmuir isotherm model than the Freundlich adsorption model for both the adsorbents.

The pseudo-second-order kinetics was found to explain the kinetics of adsorption more effectively based on the agreement of calculated and experimental adsorption capacities and correlation coefficients, suggesting that chemisorption is the rate-determining step in the adsorption process.

In conclusion, it may be stated that the biosorbents prepared from bark of *A. albida* and leaves of *E. schimperi* are found to be very effective for Cr(VI) removal from industrial effluents, thus providing a cost-effective, viable substitute for the commercially available adsorbents generally used in the industry.

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References

Abdullah MA, Prasad AGD (2009) Kinetic and equilibrium studies for the biosorption of Cr(VI) from aqueous solutions by potato peel waste. Int J Chem Eng Res 1(2):51–62

Arsalan G, Pehlivan E (2007) Batch removal of chromium(VI) from aqueous solution by Turkish brown coals. Biosour Technol 98:2836–2845

Babel S, Opiso EM (2007) Removal of chromium from synthetic waste water by sorption into volcanic ash soil. Int J Environ Sci Technol 4(1):99–107

Babu BV, Gupta S (2008) Adsorption of Cr(VI) using activated neem leaves: kinetic studies. Adsorption 14:85–92

Bansal M, Garg U, Singh D, Garg VK (2009) Removal of Cr(VI) from aqueous solutions using pre-consumer processing agriculture waste: a case study of rice husk. J Hazard Mater 162:320

Baral SS, Das SN, Rath P (2006) Hexavalent chromium removal from aqueous solution by adsorption on treated sawdust. Biochem Eng J 31:216–222

Belay AA (2010) Impacts of chromium from tannery effluent and evaluation of alternative treatment options. J Environ Prot 1:53–58

Cotton FA, Wilkinson G (1980) Chromium. In: Advanced inorganic chemistry: a comprehensive text, 4th edn. Wiley, New York, p 719–736

Darko HA, Tatjana DA, Ruzica SN, Milovan MP, Srdjan DB, Aleksandar LB, Milica MR (2011) Leaching of chromium from chromium contaminated soil: a speciation study and geochemical modeling. J Serb Chem Soc 76:1–20

Devi Prasad AG, Mohammed AA (2009) Biosorption potential of potato peel waste for the removal of nickel from aqueous solutions: equilibrium and kinetic studies. Int J Chem Eng Res 1(2):77–87

Dhungana TP, Yadav PN (2009) Determination of chromium in tannery effluent and study of adsorption of Cr(VI) on sawdust and charcoal from sugarcane bagasse. J Nepal Chem Soc 23:93–101

Dudley HW (1995) Spectroscopy methods in organic chemistry, 5th edn. The McGraw-Hill Companies, London, pp 32–38

Gebrekidan A, Gebresellasie G, Mulugeta A (2009) Environmental impacts of Sheba tannery (Ethiopia) effluents on the surrounding water bodies. Bull Chem Soc Ethiop 23(2):269–274

Greenwood NN, Earnshaw A (1984) Chemistry of the elements. Pergamon Press, Oxford, pp 1187–1200

Gupta S, Babu BV (2006) Adsorption of Cr(VI) by a low-cost adsorbent prepared from neem leaves. Proc Natl Conf Environ Conserv 1–3:175–180

Hadjmohammadi MR, Salary M, Biparva P (2011) Removal of Cr(VI) from aqueous solution using pine needles powder as a biosorbent. J Appl Sci Environ Sanit 6(1):1–13

Hasan SH, Singh KK, Prakash O, Talat M, Ho YS (2008) Removal of Cr(VI) from aqueous solutions using agricultural waste 'maize bran'. J Hazard Mater 152:356–365

Isa MH, Ibrahim N, Aziz HA, Adlan MN, Sabiani NHM, Zinatizadeh AAL (2008) Removal of chromium (VI) from aqueous solution using treated oil palm fibre. J Hazard Mater 152:662–668

Jain M, Garg VK, Kadirvelu K (2009) Chromium(VI) removal from aqueous system using *Helianthus Annus* (sunflower) stem waste. J Hazard Mater 162:365–372

Kumar PS, Kirthika K (2009) Equilibrium and kinetic study of adsorption of nickel from aqueous solution onto bael tree leaf powder. J Eng Sci Technol 4(4):351–363

Munir K, Yusuf M, Noreen Z, Hameed A, Hafeez FY, Faryal R (2010) Isotherm studies for determination of removal capacity of bi-metal (Ni and Cr) ions by *Aspergillus niger*. Pak J Bot 42(1):593–604

Nameni M, Moghadam MRA, Arami M (2008) Adsorption of hexavalent chromium from aqueous solutions by wheat bran. Int J Environ Sci Technol 5(2):161–168

Oboh I, Laluyor E, Audu T (2009) Biosorption of heavy metal ions from aqueous solutions using a biomaterial. Leonardo J Sci 14:58–65

Oliveira WE, Franca AS, Oliveira LS, Rocha SD (2008) Untreated coffee husks as biosorbents for the removal of heavy metals from aqueous solutions. J Hazard Mater 152:1073–1081

Owlad M, Aroua MK, Daud WAW, Baroutian S (2008) Removal of hexavalent chromium-contaminated water and wastewater. Water Air Soil Pollut. doi:10.1007/s11270-008-9893-7

Pehlivan E, Altun T (2008) Biosorption of chromium(VI) ion from aqueous solution using walnut, hazelnut and almond shells. J Hazard Mater 155:378–384

Popuri SR, Jammala A, Reddy KVNS, Abburi K (2007) Biosorption of hexavalent chromium using tamarind (*Tamarindus indica*) fruit shell: a comparative study. Electron J Biotechnol 10:358–367

Rozaini AC, Jain CW, Tan KW, Tan LS, Azraa A, Tong KS (2010) Optimization of nickel and copper ions removal by modified mangrove barks. Int J Chem Eng Appl 1(1):84–89

Saradhi BV, Rao SRK, Kumar YP, Vijetha P, Venkata Rao K, Kalyani G (2010) Applicability of Freundlich and Langmuir theory for biosorption of chromium from aqueous solution using test of sea urchin. Int J Chem Eng Res 2(2):139–148

Sarin V, Pant KK (2006) Removal of chromium from industrial waste by using eucalyptus bark. Bioresour Technol 97:15–20

Sekhar KC, Kamala CT, Chary NS, Anjaneyulu Y (2003) Removal of heavy metals using a plant biomass with reference to environmental control. Int J Miner Process 68:37–45

Singha B, Das S (2010) Cr(VI) adsorption: mechanistic approach for biosorption from aqueous solutions. Bioscan 2(special issue):509–514

Swietlik R (1998) Speciation analysis of chromium in waters. Pol J Environ Stud 7(5):257–266

Venkateswarlu P, Ratnam MV, Rao DS, Rao MV (2007) Removal of chromium from an aqueous solution using *Azadirachta indica* (neem) leaf powder as an adsorbent. Int J Phys Sci 2(8):188–195

Verma A, Chakraborty S, Basu JK (2006) Adsorption study of hexavalent chromium using tamarind hull-based adsorbents. Sep Purif Technol 50:336–341

Vinodhini V, Das N (2009) Biowaste materials as sorbents to remove chromium (VI) from aqueous environment- a comparative study. ARPN J Agr Biol Sci 4(6):19–23

Vinodhini V, Das N (2010) Relevant approach to assess the performance of sawdust as adsorbent of chromium(VI) ions from aqueous solutions. Int J Environ Sci Technol 7(1):85–92