



Removal of hexavalent chromium from contaminated water by adsorption using mango leaves (*Mangifera indica*)

Rumpa Saha^{a,b,*}, Bidyut Saha^{b,*}

^aK.G. Engineering College, Bishnupur, Bankura, WB, India

^bBioremediation Laboratory, Department of Chemistry, The University of Burdwan, Golapbag, Pin 713104, Burdwan, WB, India

Emails: rumu.chem@gmail.com (R. Saha); b_saha31@rediffmail.com (B. Saha)

Received 18 March 2013; Accepted 22 April 2013

ABSTRACT

The objective of this study is to assess the uptake of hexavalent chromium Cr(VI) from aqueous solutions onto mango leave dust. Batch adsorption procedure is utilized to test the ability of leave dust as an adsorbent for Cr(VI) (reduction coupled adsorption). The contribution of various parameters on sorption, such as contact time, sorbate concentration, pH of the medium, and temperature, was estimated, and maximum uptake of Cr(VI) from contaminated water was 250.23 mg g⁻¹ at pH 2.0 and temperature 40°C. Cr(VI) uptake from contaminated water followed the pseudo-first-order rate expression. ΔG^0 , ΔH^0 , and ΔS^0 have also been evaluated, and it has been concluded that the sorption was feasible, spontaneous, and endothermic in nature. The process follows well Langmuir isotherm. The nature of the possible adsorbent and metal ion interactions was examined by the Fourier transform infra-red (FTIR) technique. FTIR spectroscopy revealed the involvement of –OH, C=O, C–O groups on the cell surfaces in chromium binding. This study indicated that mango leaves can be used as an effective and environmentally friendly biosorbent for the treatment of Cr(VI) containing aqueous solutions.

Keywords: Cr(VI); Mango leave dust; Biosorption; Sorption isotherm; Sorption kinetics; Thermodynamic parameters

1. Introduction

Chromate is used or generated by a large number of industrial processes. These are chrome plating, wood preservation, leather tanning, cooling with water, pulp producing, film and photography, petroleum refining, pigments, catalysis, metal finishing, brass, electrical and electronic equipments [1,2]. Chromates are used as strong oxidizing agents in organic

chemistry [3–6]. In addition to the anthropogenic sources, Cr(VI) comes into the environment in natural way [2,7]. In this case, the origin of Cr(VI) in water may be associated with the weathering of pyroxene (augite), followed by the oxidation of trivalent chromium by manganese oxides. Among the above processes, wood preservation, leather tanning, and chrome plating are main sources of toxicity. The contamination of aquatic environment by toxic metals, such as Cr(VI), is of great concern due to its trends to accumulate on vital organs of human and animals causing several

*Corresponding author.

health problems [1,2]. Cr(VI) compounds are more toxic than trivalent chromium due to their high water solubility and mobility. Acute exposure to Cr(VI) causes nausea, diarrhea, liver and kidney damage, dermatitis, internal hemorrhage, and respiratory problems. Inhalation may cause acute toxicity, irritation, and ulceration of the nasal septum and respiratory sensitization [2,4]. Several treatment technologies have been developed to remove Cr(VI) from water and wastewater. These are reduction followed by chemical precipitation [8], ion exchange [9,10], membrane separation [11], electrocoagulation [12], solvent extraction [13], reverse osmosis [14], dialysis/electrodialysis [15], and adsorption/filtration [16]. Sodium sulfite, ferrous sulfate, metallic iron, ascorbic acid, sucrose solutions are used to reduce Cr(VI) and lime is added to form Cr(OH)₃ precipitate in reduction followed by chemical precipitation. Disadvantages are generation of sludge, the presence of other ions, affected by low pH, ineffective in low Cr(VI) ion concentration. Membranes may consist of dry solids, gels, or immobilized liquids in membrane separation process. This is just the reverse of classical membrane process osmosis. Cellulose acetate and permasep are mainly used as membranes. Reverse osmosis is a pressure driven membrane process. Water can pass through the membrane, while the heavy metal is retained. Disadvantages are high price equipments, expensive monitoring system, high-energy requirement, and sludge generation. A reversible interchange of ions between the solid and liquid phases occurs in ion-exchange process. Insoluble substance (resin) captures ion from an electrolytic solution and releases other ions of like charge in chemically equivalent amount without any structural change of the resin. Disadvantages are high-operating cost, incomplete Cr(VI) removal. Electrodialysis is an electro-driven membrane process in which ions are transported through ion permeable membranes from one compartment to another under the influence of an electrical potential gradient. Disadvantages are high capital and operating cost, requirement of highly trained human resources, fouling and scaling of membranes. Anion and cation exchangers are used as solvents in solvent extraction depending on the oxidation states of the chromium present in the solution. Anion exchangers such as high-molecular-weight amines have been used for the extraction of Cr(VI) from effluent. Disadvantages are loss of solvent, release of chromium(VI) containing waste solution.

Bioremediation is a group of technique, using living or dead organisms in order to degrade or transform contaminants into their less toxic forms. These techniques are of low cost and environment friendly [17]. There is a wide variety of techniques that have

been developed in the past years. These are natural attenuation, bioaugmentation, biostimulation, bioleaching, biofilters, biopiling, biosorption, bioventing, composting, phytoremediation, landfarming, and rhizoremediation [18].

Heavy metal ion uptake into the cellular structure is followed by sorption onto biomolecule binding sites. This uptake is independent of biological metabolism and is known as "biosorption" or "passive uptake". Metal uptake can also involve active metabolic passage across the cell membrane into the cell. This is termed as active uptake. The combination of active and passive model is called "bioaccumulation". Metal uptake by dead cells takes place only by the passive mode.

Biosorption is an efficient and economical process used for the removal of heavy metals from industrial waste water [1,18–23]. There are several advantages of biosorption by nonliving biomass [24]. These are (i) growth-independent, nonliving biomass is not subject to toxicity limitation of cells. No requirement of costly nutrients required for the growth of cells in feed solutions. For this reason, the problem of disposal of surplus nutrients or metabolic products is not present. (ii) Biomaterial can be obtained chiefly or free of cost from various sources. (iii) The process is not monitored by the physiological constraint of living microbial cells. (iv) A wider range of operating conditions, such as pH, temperature, and metal concentration, is possible due to nonliving nature of biomaterial. (v) Recovery of adsorbed metal is possible. Biological materials like coconut shell, banana pith, beech leaves, orange peel, waste tea, water hyacinth, moss, algae, chitin, bagasse, tree fern, soya cake, olive cake, almond shells, cactus leaves, fly larva, cypress, chinchona, pine leaves, and many others, and in many cases, their carbonized products have been widely used [16]. These biomaterials are involved for the removal of lead, cadmium, mercury, zinc, copper, chromium, nickel, aluminum, and arsenic. Sometimes these biomaterials are chemically modified to enhance their activity [16]. Our group has used chattim tree saw dust [19] and mosambi peel [22] for hexavalent chromium removal. We have chosen mango leave dust for the removal of Cr(VI) from waste water because mango leave dust is cheap/no cost, easily available and biodegradable.

Leaves of different trees are very versatile natured chemical species as these contain a variety of organic and inorganic compounds. Cellulose, hemicellulose, pectins, and lignin present in the cell wall are the most important sorption sites. Leaves have chlorophyll, carotene, anthocyanin, and tannin which contribute to metal biosorption. The important feature of these compounds is that they contain hydroxyl,

carboxylic, carbonyl, amino and nitro groups that are important sites for metal sorption.

2. Experimental

2.1. Materials and methods

2.1.1. Preparation of biomaterials

Mango leave dust was used as a biosorbent for the removal of Cr(VI) from contaminated water. The leave dust was first washed thoroughly with deionized water. The soluble colored components of leave dust were then removed by washing repeatedly with hot deionized water (70°C). The leave dust was then dried at 70°C for 24 h. The dried leave dust then crushed and sieved through 100 meshes and stored in polythene bottles.

2.1.2. Chemical reagents

All the primary chemicals used were of analytical grade. Potassium dichromate, potassium permanganate, caustic soda, hydrochloric acid solution, and other necessary chemicals were purchased from E. Merck India Limited, Mumbai, India. The stock solution containing 1,000 ppm of Cr(VI) was prepared by dissolving 1.4134 g quantity of AR grade $K_2Cr_2O_7$ in 500 ml of de-ionized, double-distilled water.

2.1.3. Chromium analysis

A colorimetric method [25] was used to measure the concentrations of the different chromium species present in water. The pink-colored complex, formed from 1,5-diphenyl carbazide and Cr(VI) in acidic solutions was spectrophotometrically analyzed at 540 nm (UV-2450, Shimadzu). To estimate the total chromium concentration, the Cr(III) was first converted to Cr(VI) at high temperature (130–140°C) by the addition of excess $KMnO_4$ prior to the 1,5-diphenyl carbazide reaction.

2.1.4. Batch experiments for Cr(VI) removal

Batch mode of operation was used in order to measure the progress of adsorption. Batch sorption studies were carried out at desired pH value, contact time, temperature, and sorbate concentration. Different amount of biosorbent was taken in a 250-ml stopper conical flask and took 50 ml of test solution. Different initial concentration of Cr(VI) solution was prepared by proper dilution from stock 1,000 ppm Cr(VI)

standard. pH of the solution was adjusted by adding HCl or M NaOH solution as required. Contents in the flask were shaken at 125 rpm. The time needed to reach equilibrium condition was estimated by drawing samples at regular interval of time till the attainment of equilibrium. Then, centrifuge was carried out at 15,000 rpm to separate content of flask from biosorbent. Solution was analyzed for remaining chromium concentration. Biosorbent reduces Cr(VI) to trivalent chromium and then adsorbs trivalent chromium according to its capacity [18]. So, after separation of biosorbent from solution, solution contains trivalent and Cr(VI). Solution is then oxidized quantitatively with potassium permanganate and amount of chromium is known from calibration curve.

Chromium adsorbed by biosorbent (mg/g) = {chromium present in solution before adsorption (mg) — chromium present in solution after adsorption (mg)} / Amount of biosorbent (g).

2.1.5. Fourier transform infra-red (FTIR) spectra

The leave dust sample (~5 mg) was finely ground with ~1,000 mg of KBr (spectroscopic grade) in a mortar pressed into 10-mm-diameter disks under 10 ton/m² of pressure and high vacuum for 10 min. FTIR spectra were obtained on a JASCO FTIR-3500 spectrometer. The analysis conditions used were 16 scans at a resolution of 4 cm⁻¹ measured between 500 and 4,000 cm⁻¹.

2.1.6. Scanning electron microscopy (SEM)

The samples mounted directly onto metal studs were analyzed in a JEOL JSM-5900 LV microscope to obtain information regarding surface morphology. The secondary electron images of the material depict approximate sizes in the range of a few microns.

3. Result and discussion

3.1. Effect of pH

Experiments were performed on 50 ml solution containing 200 mg L⁻¹ Cr(VI) with 1 g of mango leave dust at 30°C and different hydrogen ion concentration to study the effect of solution pH. pH was adjusted from 1 to 10 by addition HCl or NaOH as required. Fig. 1 clearly indicates that the adsorption characteristics are highly pH-dependent and maximum adsorption occurs at pH 2. Cr(VI) can exist in several stable forms [26] as CrO_4^{2-} , $HCrO_4^-$, and $Cr_2O_7^{2-}$. Chromium ion concentration and solution pH determine the relative abundance of a particular species. Better

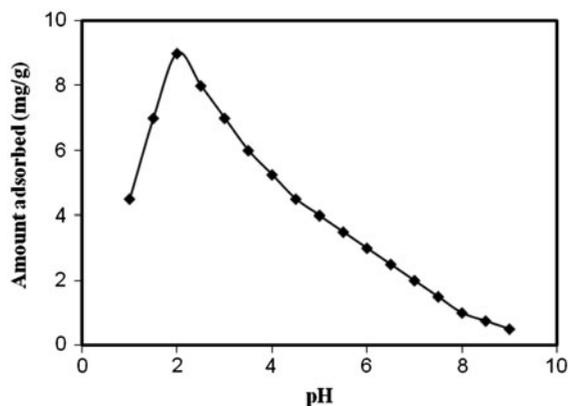


Fig. 1. Effect of pH on the adsorption by mango leave dust. Condition pH=1–9, $[\text{Cr(VI)}]_T=200 \text{ mg dm}^{-3}$, temperature 30°C , particle size $<180 \mu\text{m}$, $[\text{biosorbent}]_T=20,000 \text{ mg dm}^{-3}=20 \text{ gm dm}^{-3}$.

adsorption capacity at low pH (optimum pH 2) is because of easy protonation of the leave dust at this pH, and thus, the biosorbent attracts negatively charged chromium species easily [1].

3.2. Effect of biosorbent

Effect of biosorbent (mango leave dust) concentrations to sorption was studied using 50 ml 200 mg L^{-1} (hexavalent chromium concentration) at pH 2 at different biosorbent doses $5\text{--}50 \text{ g L}^{-1}$ (Fig. 2). It was observed that quantitative removal of the Cr(VI) ion was attained for natural adsorbent dosages of at least 20 g L^{-1} . Chromium removal remained almost same for higher biosorbent dosages. Chromium ion adsorption increases with biosorbent doses due to increase in biosorbent surface areas. Number of adsorption sites

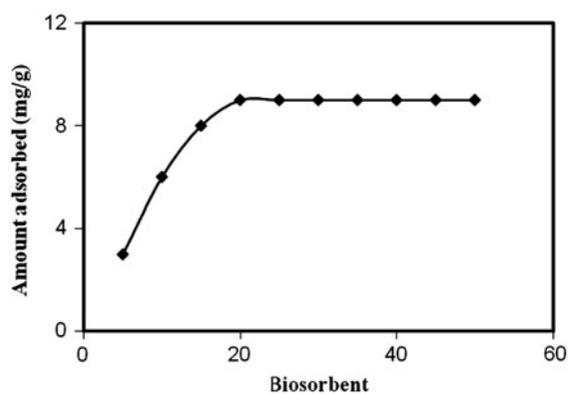


Fig. 2. Effect of biosorbent dose on the adsorption by mango leave dust. Condition pH=2, $[\text{Cr(VI)}]_T=200 \text{ mg dm}^{-3}$, temperature 30°C , particle size $<180 \mu\text{m}$, $[\text{biosorbent}]_T=(5\text{--}50) \text{ gm dm}^{-3}$.

available for chromium adsorption is directly proportional to biosorbent surface area.

3.3. Effect of initial metal ion concentration and contact time

Effect of initial metal ion concentration and contact time on sorption was estimated using 50 ml 200 mg L^{-1} , 250 and 300 mg L^{-1} concentrations and contact time 20–200 min with an interval of 20 min at pH 2 and 1 g of biosorbent (Fig. 3). The extent of chromium adsorption increased rapidly in the initial stages but became slow in the later stages till the equilibrium is reached. Equilibrium time for chromium adsorption on mango leave dust at various adsorbate concentrations was found to be 120 min. It proved that equilibrium time was independent of initial adsorbate concentration.

3.4. Effect of temperature

Experiments were carried out at different temperatures 30 , 35 , and 40°C (Fig. 4). The amount of adsorption increases with the increase in temperature indicating endothermic nature of the adsorption. This is due to diffusion of adsorbate to porous adsorbent [27]. It can be also concluded that the generation of adsorption sites in adsorbent is due to breaking of some internal bonds of adsorbent [27].

3.5. Adsorption kinetics

In order to predict adsorption kinetic models of Cr(VI), first-order reversible, pseudo-first-order, and pseudo-second order kinetic models were tested to the

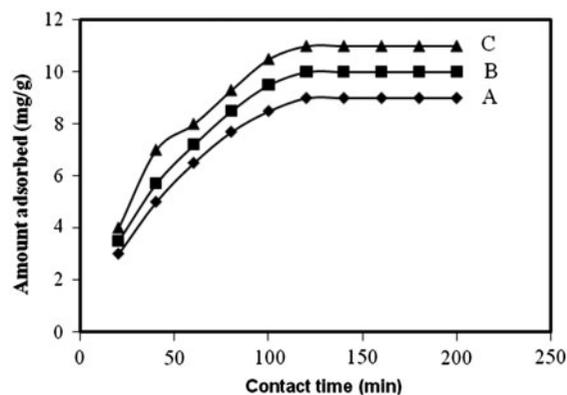


Fig. 3. Effect of contact time and Cr(VI) concentration on adsorption. pH=2.0, temperature 30°C , particle size $<180 \mu\text{m}$, $[\text{Cr(VI)}]_T=200 \text{ mg dm}^{-3}$ (C), 250 mg dm^{-3} (B), 300 mg dm^{-3} (A), $[\text{biosorbent}]_T=20 \text{ gm dm}^{-3}$.

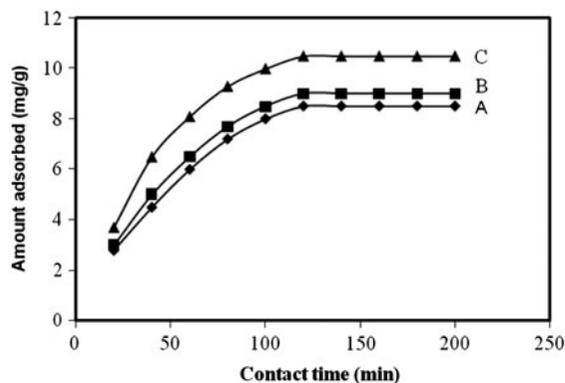


Fig. 4. Effect of temperature on the sorption by mango leave dust. $[\text{Cr(VI)}]_T = 200 \text{ mg dm}^{-3}$, $\text{pH} = 2$, $[\text{biosorbent}]_T = 20 \text{ gm dm}^{-3}$, temperature 25°C (A), 30°C (B), 35°C (C), particle size $< 180 \mu\text{m}$.

data. The effect of the initial Cr(VI) concentrations and temperatures was investigated to find the best kinetic model. The straight-line plots of $-\ln(1 - U_{(t)})$ vs. t (min) were tested for reversible first-order kinetic model. For the pseudo-first-order model, the straight-line plots of $\log(q_e - q_t)$ against time were analyzed. For pseudo-second-order t/q_t was plotted against t (time). Good correlation coefficients were obtained for the pseudo-first-order kinetic model, which showed that the chromium uptake process followed the pseudo-first-order rate expression, so only the pseudo-first-order plots are presented in Fig. 5.

3.6. Adsorption isotherm

Adsorption equilibrium measurements with different adsorption isotherms are conducted to determine the maximum adsorption capacity. The Langmuir and

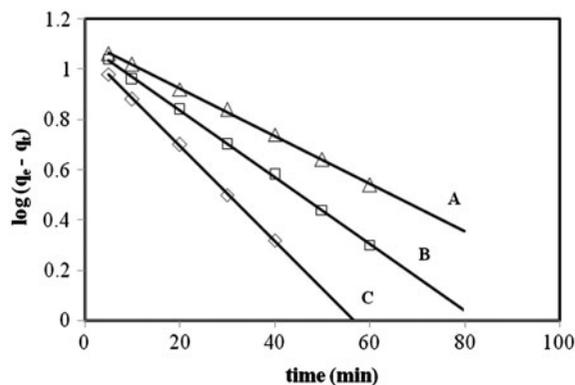


Fig. 5. Pseudo-first-order plots for Cr(VI) removal using mango leave dust at 25°C (A), 30°C (B), and 35°C (C). Conditions: Particle size $< 180 \mu\text{m}$; $\text{pH} = 2.0$; agitation rate 125 rpm , mango leave dust $= 5 \text{ gm dm}^{-3}$.

Freundlich equations are generally use to describe adsorption equilibrium for waste water treatment. Langmuir adsorption isotherm is based on monolayer coverage of the adsorbate on the surface of adsorbent. The linear forms [1] of the Langmuir isotherm are represented by the Eq (1).

$$C_e/q_e = 1/Q_{\max}b + C_e/Q_{\max} \quad (1)$$

where C_e is the equilibrium concentration of the adsorbate, q_e is the amount of the adsorbed adsorbate at equilibrium, Q_{\max} and b are the Langmuir's constants related to the capacity and energy of the adsorption, respectively. The linearity of the plots C_e/q_e vs. C_e (Fig. 6) suggested the suitability of Langmuir isotherm for the present system. The value of Q_{\max} and b were calculated from the slope and intercept of the plot.

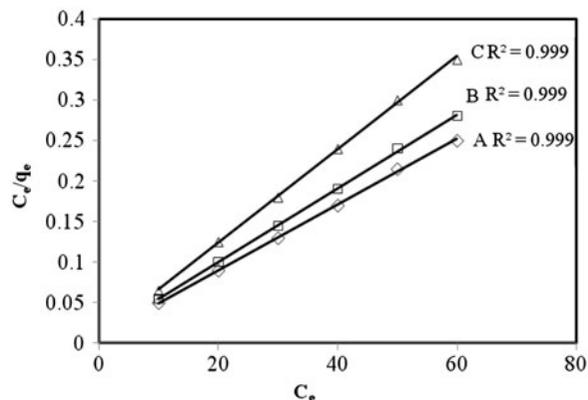


Fig. 6. Langmuir isotherm plots for Cr(VI) removal using mango leave dust. $\text{pH} = 2$, $[\text{biosorbent}]_T = 250 \text{ mg dm}^{-3}$, temperature 25°C (A), 30°C (B), 35°C (C), particle size $< 180 \mu\text{m}$.

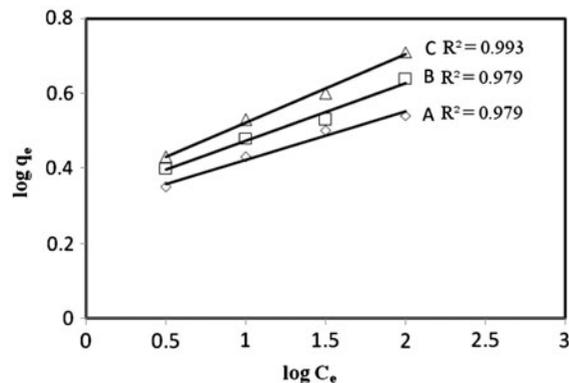


Fig. 7. Freundlich isotherm plots for Cr(VI) removal using mango leave dust. Conditions: particle size $< 180 \mu\text{m}$; $\text{pH} = 2.0$; temperature 25°C (A), 30°C (B) and 35°C . $[\text{Cr(VI)}]_T = 200, 250, 275, 225, \text{ and } 300 \text{ mg dm}^{-3}$.

Table 1
Values of Langmuir and Freundlich sorption constants for the sorption of Cr(VI) on mango leave dust at different temperatures

Temperature (°C)	Langmuir constants		Freundlich constants	
	Q_{\max} (mg g ⁻¹)	b (L mg ⁻¹)	n	K_F
40	250.23	0.31	5.49	2.186
35	227.53	0.27	6.49	2.09
30	178.12	0.62	7.81	1.97

Table 2
Thermodynamic parameters for the adsorption of Cr(VI) on mango leave dust

$-\Delta G^0$ (kJ mol ⁻¹)			ΔH^0 (kJ mol ⁻¹)	ΔS^0 (JK ⁻¹ mol ⁻¹)
(30°C)	(35°C)	(40°C)		
7.15	9.27	10.72	97.10	344.28

In 1906, the Freundlich isotherm (Fig. 7) was first proposed. The isotherm is based on multilayer adsorption with interaction between adsorbed molecules [1]. The Freundlich equation is represented linearly as

$$\log q_e = \log K_F + 1/n \log C_e \quad (2)$$

Values of Langmuir and Freundlich sorption constants for the sorption of Cr(VI) on mango leave dust at different temperatures are given on Table 1.

The values of K_F and n is obtained (Table 2) from the slope and intercept of a plot of $\log q_e$ vs. $\log C_e$. The value of r^2 (Figs. 6 and 7) was higher for Langmuir isotherm than for the Freundlich isotherm, this means the Langmuir isotherm represented the adsorption process very well [28]. High Q_{\max} value for mango leave dust compared with other leave dusts (Table 3) is observed.

3.7. Thermodynamic parameters:

Dependence of adsorption on temperature has also been justified on the basis of thermodynamic parameters. These are standard free energy change (ΔG^0), standard enthalpy change (ΔH^0), and standard entropy change (ΔS^0) of adsorption. The values are calculated from the Eqs. (3)–(5) [27].

$$K_c = C_{Ae}/C_e \quad (3)$$

where K_c is the equilibrium constant, and C_{Ae} and C_e (both in mg L⁻¹) are the equilibrium concentrations for solute on the sorbent and in solution respectively.

Table 3
Sorption capacities of different leaves

Leave dust	Sorption capacity ((mg/g) (a) or (m mole/g) (c)) or removal efficiency (%) (b)	Refs.
Mangrove leaves	11.377(a)	[29]
Neem leaf powder	87 (b)	[30]
Oak leaf	48.7(b)	[31]
London plane leaves	83.33 (a)	[22]
Yerba mate leaves	11.77 (a)	[32]
<i>Ficus religiosa</i> leaves	26.25 (a)	[33]
Mango leaves	250.23 (a)	This study

The K_c values are used in Eqs. (4) and (5) to determine the ΔG^0 , ΔH^0 and ΔS^0 .

$$\Delta G^0 = -RT \ln K_c \quad (4)$$

where ΔG^0 (kJ mol⁻¹) is the free energy of adsorption, T is the absolute temperature, and R is the universal gas constant.

The K_c may be expressed in terms of the ΔH^0 (kJ mol⁻¹) and ΔS^0 (J K⁻¹mol⁻¹) as a function of temperature.

$$\ln K_c = -(\Delta H^0/RT - \Delta S^0/R) \quad (5)$$

Standard free energy change of adsorption (ΔG^0), the heat of adsorption (ΔH^0) and standard entropy changes (ΔS^0) during the removal process are calculated using Eqs. (3)–(5). The temperature range used was from 30 to 40°C. ΔH^0 and ΔS^0 are obtained from the slope and intercept of a plot of $\ln K_c$ against $1/T$ (Fig. 8). The values of the parameters thus calculated

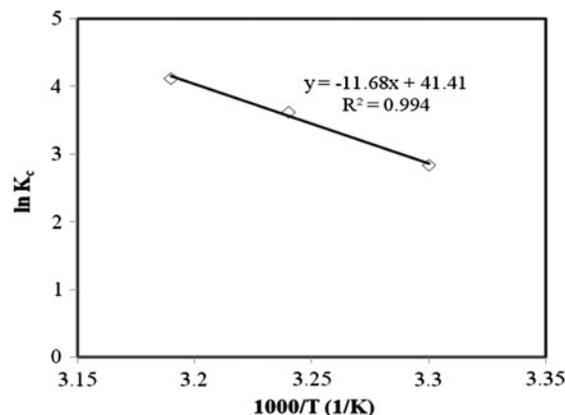


Fig. 8. A plot of $\ln K_c$ against $1/T$ for Cr(VI) adsorption by mango leave dust.

are recorded in Table 2. Negative values of ΔG^0 indicate the spontaneous nature of the adsorption process. The value of ΔG^0 becomes more negative with increasing temperature. This shows that an increase in temperature favors the removal process. The positive value of ΔH^0 indicates that the sorption process is endothermic in nature, and the positive value of ΔS^0 suggests the probability of favorable adsorption.

3.8. FTIR analysis

FTIR spectra of raw and chromium loaded biosorbent (mango dust) were obtained using KBr disk containing ~ 5 mg of each of finely ground raw and loaded leaf dusts with $\sim 1,000$ mg of KBr to prepare transparent disks. The spectra are shown in Fig. 9. Fig. 9(A) displays a good number of frequencies indicating the complex nature of the mango leaf dust. The salient features are: strong and broad band

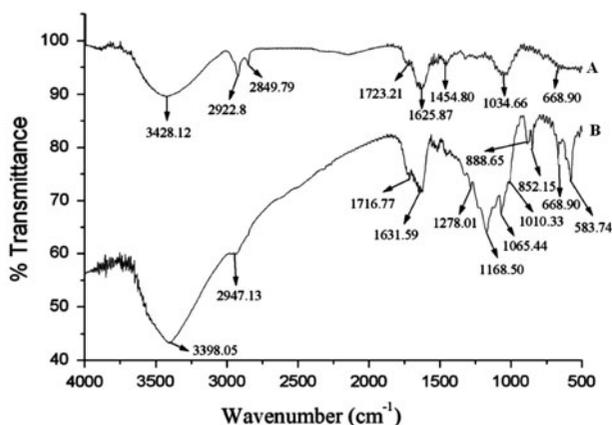


Fig. 9. FTIR spectrum of pure (A) and Cr(VI) loaded (B) mango leaf dust.

centered at $3,428\text{ cm}^{-1}$ characteristic of $-\text{OH}$ and $-\text{NH}$ stretches arising from the surface hydroxyl and amine groups; weak and broad band centered at $2,922\text{ cm}^{-1}$ assignable to the aliphatic $\text{C}-\text{H}$ group; the band at $1,723\text{ cm}^{-1}$ arising from $\text{C}=\text{O}$ group of carboxylic acid or ester; the peak at $1,625\text{ cm}^{-1}$ may presumably be due to stretching frequency of $\text{C}=\text{O}$ group of amide. Distinct peak at $1,454\text{ cm}^{-1}$ may correspond to symmetric bending of $-\text{CH}_3$ group present in the raw mango leaf dust. The multiple numbers of peaks around $1,034\text{ cm}^{-1}$ may correspond to $\text{C}-\text{O}$ group present with different kinds of environment in the polysaccharide units. Fig 9(B) shows distinct shift of the bands as well as change of intensity at $3,398$, $2,947$, $1,716$, $1,631$, $1,278$, $1,168$, $1,065\text{ cm}^{-1}$, which is strongly suggestive of the fact that the otherwise free $-\text{OH}$, $\text{C}=\text{O}$, $\text{C}-\text{O}$ groups in unloaded leaf dust are now bound to some kind of covalent bonding after chromium biosorption [19,22].

3.9. SEM analysis

The morphological characteristics of dried and Cr (VI) loaded leaf dust were evaluated similar to catla catla scales [18] using a scanning electron microscope (SEM). Samples of dried and Cr(VI) loaded leaf dust were all gold plated and an electron acceleration voltage of 20 kV was applied for SEM observation. Fig. 10 shows the SEM micrographs of the dried and Cr(VI) loaded leaf dust samples at $1,000$ times magnification. The image Fig. 10(a) shows the dried leaf dust particle is mostly irregular in shape and has a porous surface. It can be seen from Fig. 10(b), that the blurred image showing the surface of Cr(VI) loaded particles was covered by oily-like materials and it is almost non-porous.

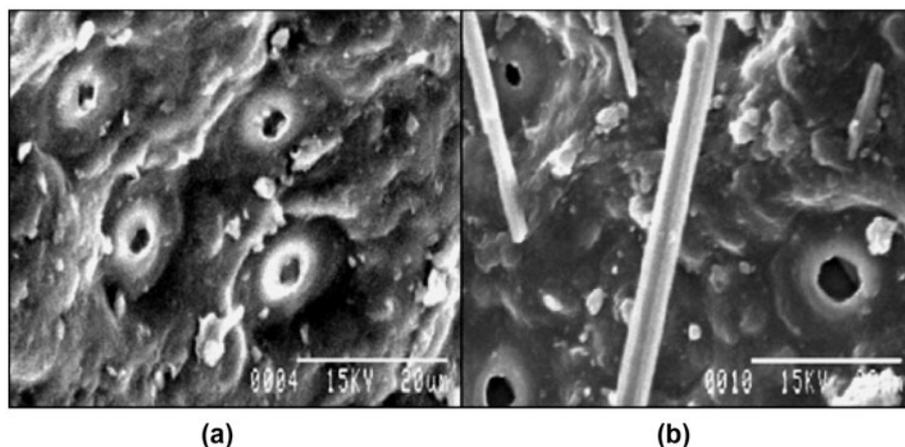


Fig. 10. SEM picture of pure (a) and chromium loaded (b) mango leaf dust.

4. Conclusion

Mango leave dust was found to be an effective bio-sorbent for the removal of Cr(VI) from contaminated water. The optimum pH for maximum removal of Cr(VI) was 2. Percentage removal (91% at 30°C at [Cr(VI)] = 200 mg dm⁻³) of Cr(VI) decreased with increase in concentration but increases with increase in temperature. The removal of Cr(VI) was rapid in initial stages and became slower afterwards. Thermodynamic studies confirmed that process was spontaneous and endothermic. The fitness of the adsorption data into Langmuir isotherm confirmed the monolayer adsorption of Cr(VI) on Mango leave dust.

Nomenclature

C_e	— equilibrium concentration of solute in bulk solution (mg L ⁻¹)
C_0	— initial adsorbate concentration put in contact with the adsorbent (mg L ⁻¹)
q	— amount adsorbed of the metallic ion by the adsorbent (mg g ⁻¹)
dq	— differential of q
q_e	— amount of the adsorbate adsorbed at the equilibrium (mg g ⁻¹)
Q_{max}	— the maximum adsorption capacity of the adsorbent (mg g ⁻¹)
b	— Langmuir's constant
C_{Ae}	— equilibrium concentration of solute on the sorbent (mg L ⁻¹)
K_F	— the Freundlich constant related with adsorption capacity (mg g ⁻¹ (mg L ⁻¹) ^{-1/n})
n	— dimensionless exponents of Freundlich equation
K_c	— equilibrium constant
q_t	— amount of adsorbate adsorbed at time t (mg g ⁻¹)
t	— time of contact
V	— volume of adsorbate put in contact with the adsorbent (L)
R	— universal gas constant
ΔG^0	— change in standard free energy (kJ mol ⁻¹)
ΔH^0	— change in standard enthalpy (kJ mol ⁻¹)
ΔS^0	— change in standard entropy (JK ⁻¹ mol ⁻¹)
T	— absolute temperature (K)

Acknowledgement

The authors are thankful to the CSIR, New Delhi, India, for financial support in form of a project and fellowship.

References

- [1] B. Saha, C. Orvig, Biosorbents for hexavalent chromium elimination from industrial and municipal effluents, *Coord. Chem. Rev.* 254 (2010) 2959–2972.
- [2] R. Saha, R. Nandi, B. Saha, Sources and toxicity of hexavalent chromium, *J. Coord. Chem.* 64 (2011) 1782–1806.
- [3] M. Islam, B. Saha, A.K. Das, Kinetics and mechanism of picolinic acid promoted chromic acid oxidation of maleic acid in aqueous micellar media, *J. Mol. Catal.: A Chem.* 266 (2007) 21–30.
- [4] R. Saha, A. Ghosh, B. Saha, Micellar catalysis on 1, 10-phenanthroline promoted hexavalent chromium oxidation of ethanol, *J. Coord. Chem.* 64 (2011) 3729–3739.
- [5] K.M. Chowdhury, J. Mandal, B. Saha, Micellar catalysis of chromium(VI) oxidation of ethane-1,2-diol in the presence and absence of 2,2'-bipyridine in aqueous acid media, *J. Coord. Chem.* 62 (2009) 1871–1878.
- [6] R. Saha, S.K. Ghosh, A. Ghosh, I. Saha, K. Mukherjee, A. Basu, B. Saha, Choice of a suitable hetero-aromatic nitrogen base as promoter for chromic acid oxidation of dl-mandelic acid in aqueous media at room temperature, *Res. Chem. Intermed.* 39 (2013) 631–643.
- [7] D.E. Kimbrough, Y. Cohen, A.M. Winer, L. Creelman, C.A. Mabuni, A critical assessment of chromium in the environment, *Crit. Rev. Environ. Sci. Technol.* 29 (1999) 1–46.
- [8] D. Park, Y.S. Yun, J.Y. Kim, J.M. Park, How to study Cr(VI) biosorption: Use of fermentation waste for detoxifying Cr(VI) in aqueous solution, *Chem. Eng. J.* 136 (2008) 173–179.
- [9] S. Rengaraj, K.H. Yon, S.H. Moon, Removal of chromium from water and wastewater by ion exchange resins, *J. Hazard. Mater.* 87 (2001) 273–287.
- [10] D. Petruzzelli, R. Passino, G. Tiravanti, Ion exchange process for chromium removal and recovery from tannery wastes, *Ind. Eng. Chem. Res.* 34 (1995) 2612–2617.
- [11] C.A. Kozłowski, W. Walkosiak, Removal of chromium(VI) from aqueous solutions by polymer inclusion membranes, *Water. Res.* 36 (2002) 4870–4876.
- [12] F. Akbal, S. Camci, Comparison of electrocoagulation and chemical coagulation for heavy metal removal, *Chem. Eng. Technol.* 33 (2010) 1655–1664.
- [13] E. Salazar, M.I. Ortiz, A.M. Urriaga, Equilibrium and kinetics of chromium(VI) extraction with Aliquat 336, *Ind. Eng. Chem. Res.* 31 (1992) 1516–1522.
- [14] H. Ozaki, K. Sharma, W. Saktaywin, Performance of an ultra-low-pressure reverse osmosis membrane (ULPROM) for separating heavy metal: Effects of interference parameters, *Desalination* 144 (2002) 287–294.
- [15] T. Mohammadi, A. Moheb, M. Sadrzadeh, A. Razmi, Modeling of metal ion removal from wastewater by electrodialysis, *Sep. Purif. Technol.* 41 (2005) 73–82.
- [16] S. Babel, T.A. Kurniawan, Low-cost adsorbents for heavy metals uptake from contaminated water: a review, *J. Hazard. Mater.* B97 (2003) 219–243.
- [17] M.X. Loukidou, T.D. Karapantsios, A.I. Zouboulis, K.A. Malis, Diffusion kinetic study of chromium(VI) biosorption by *aeromonas caviae*, *Ind. Eng. Chem. Res.* 43 (2004) 1748–1755.
- [18] K. Parvathi, R. Nagendran, Biosorption of chromium from effluent generated in chrome-electroplating unit using *saccharomyces cerevisiae*, *Sep. Sci. Technol.* 42 (2007) 625–638.
- [19] R. Saha, I. Saha, R. Nandi, A. Ghosh, A. Basu, S.K. Ghosh, B. Saha, Application of chattim tree (*Devil tree*, *Alstonia scholaris*) saw dust as a biosorbent for removal of hexavalent chromium from aqueous solution, *Can. J. Chem. Eng.* 91 (2013) 814–821.
- [20] M. Kobya, Removal of Cr(VI) from aqueous solutions by adsorption onto hazelnut shell activated carbon: Kinetic and equilibrium studies, *Bioresour. Technol.* 91 (2004) 317–321.
- [21] P. Suksabye, P. Thiravetyan, W. Nakbanpote, S. Chayabutra, Chromium removal from electroplating wastewater by coir pith, *J. Hazard. Mater.* 141 (2007) 637–644.
- [22] R. Saha, K. Mukherjee, I. Saha, A. Ghosh, S.K. Ghosh, B. Saha, Removal of hexavalent chromium from water by adsorption using mosambi peel (*Citrus limetta*), *Res. Chem. Intermed.* 39 (2013) 2245–2257.

- [23] V. Sarin, K.K. Pant, Removal of chromium from industrial waste by using eucalyptus bark, *Bioresour. Technol.* 97 (2006) 15–20.
- [24] Y. Khamhaty, K. Mody, S. Basha, B. Jha, Kinetics, equilibrium and thermodynamic studies on biosorption of hexavalent chromium by dead fungal biomass of marine *Aspergillus niger*, *Chem. Eng. J.* 145 (2009) 489–495.
- [25] G. Limousin, J.P. Gaudet, L. Charlet, S. Szenknect, V. Barthes, M. Krimissa, Sorption isotherms: A review on physical bases, modeling and measurement, *Appl. Geochem.* 22 (2007) 249–275.
- [26] D. Mohan, K.P. Singh, V.K. Singh, Removal of hexavalent chromium from aqueous solution using low-cost activated carbons derived from agricultural waste materials and activated carbon fabric cloth, *Ind. Eng. Chem. Res.* 44 (2005) 1027–1042.
- [27] K.K. Singh, R. Rastogi, S.H. Hasan, Removal of Cr(VI) from wastewater using rice bran, *J. Colloid Interf. Sci.* 290 (2005) 61–68.
- [28] K. Srividya, K. Mohanty, Biosorption of hexavalent chromium from aqueous solutions by *Catla catla* scales: Equilibrium and kinetics studies, *Chem. Eng. J.* 155 (2009) 666–673.
- [29] R. Elangovan, L. Philip, K. Chandraraj, Biosorption of chromium species by aquatic weeds: Kinetics and mechanism studies, *Hazard. Mater.* 152 (2008) 100–112.
- [30] A. Sharma, K.G. Bhattacharyya, Adsorption of chromium (VI) on *Azadirachta Indica* (Neem) leaf powder, *Adsorption* 10 (2004) 327–338.
- [31] D. Park, S.R. Lim, Y.S. Yun, J.M. Park, Reliable evidences that the removal mechanism of hexavalent chromium by natural biomaterials is adsorption-coupled reduction, *Chemosphere* 70 (2007) 298–305.
- [32] G.J. Copello, R.E. Garibotti, F. Varela, M.V. Tuttolomondo, L.E. Diaz, Exhausted yerba mate leaves (*Ilex paraguariensis*) as biosorbent for the removal of metals from aqueous solutions, *J. Braz. Chem. Soc.* 22 (2011) 790–795.
- [33] S. Qaiser, A.R. Saleemi, M.M. Ahmad, Heavy metal uptake by agro based waste materials, *Electron. J. Biotechnol.* 10 (2007) 409–416.