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Efficacy of mangrove leaf powder for bioremediation of chromium (VI) from aqueous solutions: kinetic and thermodynamic evaluation

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Abstract Biosorption of heavy metals by bio-materials has been posited as a potential alternative to the existing physicochemical technologies for detoxification and recovery of toxic and valuable metals from wastewaters. In this context, the role of mangrove leaf powder (MLP) as biosorbent for chromium removal was investigated. In the present study, the effect of process parameters such as particle size, solution pH, initial concentration of Cr(VI) ion and adsorbent dose on chromium removal by MLP was investigated. The maximum sorption was observed at particle size 0.5 mm and pH 2.0. The adsorption data follow the pseudo second-order kinetics model. The isotherms denote that Langmuir model is the best fitted than Freundlich model. The maximum adsorption capacity (Q^0) of 60.24 mg/g of Cr(VI) at 30 min on MLP was determined using the Langmuir model. The adsorption isotherm model indicates that the chromium is adsorbing as monolayer on the surface of MLP with heterogeneous energetic distribution of active sites. Various thermodynamic parameters, such as Gibb's free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) have been calculated. The thermodynamic data revealed that the adsorption of chromium ions onto MLP is endothermic in nature and a spontaneous process. The results of the present study suggest that MLP is an effective bioremediation measure for removal of high concentration of Cr(VI) in waste waters.

Introduction

Heavy metal release to the environment has been increasing continuously as a result of industrial activities and technological development, posing a significant threat to the environment, public and soil health (Cerbasi and Yetis 2001). Among the heavy metals released into environment, chromium is an important pollutant. Chromium is a redox active element, with oxidation states from −2 to +6, but only the +3 and +6 states are prevalent in the aqueous environment. Cr(III) and Cr(VI) are environmentally stable oxidation states and exhibit different types of toxicity mechanism on biota. Chromium is released into the environment by a large number of industries such as mining, iron sheet cleaning, chrome plating, leather tanning and wood preservation (Krishna and Philip 2005). These industries contain Cr(III) and Cr(VI) at a concentration ranging from 10 to 100 mg/L (Park et al. 2005). Long-term release of such wastewater may result in the accumulation of heavy metals in soil exerting a selection pressure on soil micro-biota.

Cr(VI) is a highly soluble and toxic chromate anion, and is a suspected carcinogen and mutagen (Costa 2003). The conventional methods for removing Cr(VI) ions from wastewater are based on the combination of different physical and chemical reduction processes (Kurniawan et al. 2006). However, such processes are becoming undesirable due to the use of expensive and toxic chemicals.

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Further these methods are also inefficient in the removal of Cr(VI), particularly with wastewater containing with a low Cr concentration and also associated with the production of secondary effluents (Baral and Engelken 2002).

Prakasham et al. (1999) and Kadimpati et al. (2013) suggested that the removal of heavy metals by adsorption on various biomass surfaces is the best alternative to the physico and chemical methods. In recent years, many researchers used the various bio-materials such as tea factory waste (Cay et al. 2004; Malkoc and Nuhoglu 2005, 2006), sawdust (Acar and Malkoc 2004; Yu et al. 2003), soya cake (Daneshvar et al. 2002), sugar cane bagasse (Gupta and Ali 2004), green algae (Gupta et al. 2001; Malkoc and Nuhoglu 2003), distillery sludge (Selvaraj et al. 2003) for removal of heavy metals from waste waters. Most of the low-cost sorbents have the limitation of poor sorptive capacity, and thereby, for the same degree of treatment it generates more solid waste (pollutant laden sorbent after treatment) leading to disposal problems. Therefore, there is a need to explore low cost, economically viable and effective sorbent, having high pollutant sorption capacity (Ho et al. 2005).

Andaman and Nicobar (A & N) archipelago is one of the mega-biodiversity hotspots of India. The archipelago consists of 572 islands, located in the Bay of Bengal, lying between 6°45′–13°45′N and 92°12′–93°57′E in the Indo-Burmese microplate junction. The islands are spread over a distance of 1,120 km with a coast line of 1,962 km. The close proximity of these groups of islands to the equator and the irregular and deeply indented coast line, creeks, bays and estuaries facilitate the rich and diverse mangrove forests. Rozaini et al. (2010) reported that mangrove bark has a potent adsorbent for Ni(II) and Cu(II) ions from aqueous solutions. The current study was aimed to determine the capability of mangrove leaves from A & N islands as a potent adsorbent to remove the chromium (VI) from aqueous solutions.

Materials and methods

Collection and processing of adsorbent

In the present study mangrove leaf powder (MLP) (biomass) was used as adsorbent for chromium removal. The sorbent material, mangrove leaves (*Avicennia marina*) was collected from mangrove plants located in the Minnie Bay area, Port Blair, A & N islands, India. The collected leaves were shade dried and then powdered in a pulverizer. The dirt and color components were removed by washing with distilled water until a colorless solution of MLP was obtained. Processed MLP was shade dried and sieved to obtain the desired particle size (1.4–0.25 and <0.25 mm).

Sorption studies

The vibrant behavior of adsorption was explored based on the effect of particle size (1.4–0.25 and <0.25 mm), effect of pH (2–8), metal ion concentration (100–600 mg/L), amount of biomass (2–10 g/L) and temperature (10–40 °C). Experiments were conducted in a batch system in 250-mL Erlenmeyer flasks containing 100 mL of the adsorption solution (with desired concentration and pH) and anticipated MLP concentration. The initial pH adjustments were carried out using the 1 N HCl and 1 N NaOH. The flasks were agitated on a rotary shaker at 70 rpm, the samples were taken to determine the residual Cr(VI) concentration in the solution at predetermined time intervals. The sorbent material was separated from the solution by filtration through Whatman No. 1 filter paper and the metal concentration was determined in the filtrate. The amount of metal adsorbed was determined by calculating the difference between the initial Cr(VI) concentration and remnant in filtrate.

Analytical method

The Cr(VI) loading on sorbents was computed based on mass balance through the loss of metal from aqueous solution. Cr(VI) concentration in aqueous phase was estimated by diphenyl carbazide method (APHA 1985). Cr(VI) reacts with diphenyl carbazid, which forms a red–violet colored complex. The absorbance of the colored complex was measured in a double beam UV-visible spectrophotometer at 540 nm wavelength (Lambda 25, Perkin Elmer).

Kinetic modeling

Adsorption kinetics play a vital role in the scale-up studies of waste water treatment process design. These designs give a chance to pick the optimum operational conditions of heavy metals and sorbent to facilitate the effective adsorption process at large-scale processes.

It was assumed that the adsorption of chromium from liquid to MLP was a reversible reaction with an equilibrium state being established between two phases. To correlate the rates of reaction a simple first-order, pseudo first-order and pseudo second-order models were used (Hamadia et al. 2001).

The first-order rate constants were calculated using the following equations:

$$\ln[1 - U(t)] = -k_{r}'t \tag{1}$$

where $U(t)$ fractional attainment of equilibrium, k_{r}' overall rate constant, t time

$$U(t) = \frac{X_A}{X_{A_e}} \tag{2}$$

X_A the fractional conversion of adsorbate, X_{A_e} the fractional conversion of adsorbate at equilibrium

$$k_r' = k_1 \left(1 + \frac{1}{K_c} \right) = k_1 + k_2 \qquad (3)$$

K_c equilibrium constant was calculated based on the following equation:

$$K_c = \frac{C_{B_e}}{C_{A_e}} \qquad (4)$$

C_{B_e} and C_{A_e} are the concentrations for chromium on the sorbent and solution at equilibrium.

The pseudo first-order rate constants were determined using the following equation:

$$\log (q_e - q) = \log(q_e) - \frac{k_1'}{2.303} t \qquad (5)$$

where q_e amount of solute adsorbed per unit weight of adsorbent (mg/g) at equilibrium, q amount of solute adsorbed per unit weight of adsorbent (mg/g) at time t, k_1' adsorption constant calculated from the slope of plot between the time and $\log (q_e - q)$.

The following equation was used to determine the pseudo second-order constant:

$$\frac{t}{q} = \frac{1}{k_2' q_e^2} + \frac{1}{q_e} t \qquad (6)$$

where k_2' second-order rate constant.

The initial sorption rate (h) (mg/g/min) was calculated using the following equation

$$h = k_2' q_e^2. \qquad (7)$$

The rate constants were obtained from the kinetic plots of Eqs. (1), (5) and (6) correspondingly.

Adsorption isotherm

An adsorption isotherm was used to characterize the interactions of sorbent molecule with the adsorbent material. The adsorption model assumes that the species are adsorbed at a fixed number of well-defined sites, each of which is capable of holding only one molecule. These sites are also assumed to be energetically equivalent and distant from each other so that there are no interactions between molecules adsorbed on adjacent sites. Adsorption equilibrium is called as adsorption isotherm and is obtained by plotting solute (adsorbate) concentration in the solid phase as a function of solute concentration in liquid phase at a given temperature.

To describe the adsorption equilibrium between chromium and MLP, Langmuir and Freundlich equations were used. The empirical Freundlich equation is as follows:

$$q_e = K_f (C_e)^{1/n} \qquad (8)$$

C_e equilibrium concentration (mg/L), K_f equilibrium constant for adsorption capacity, n equilibrium constant for adsorption intensity.

To calculate the K_f and n the Eq. (8) was linearized. The logarithmic form of Eq. (8) is follows as

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e. \qquad (9)$$

The linear form of Langmuir isotherm model is

$$\frac{C_e}{q_e} = \frac{1}{Q^0 b} + \frac{C_e}{Q^0} \qquad (10)$$

b constant related to the energy or net enthalpy of adsorption (1/mg), Q^0 constant related to adsorption capacity (mg/g) at equilibrium.

Langmuir constants were obtained from the slope and intercept of linear plot of C_e/q_e versus C_e.

Equilibrium parameter or separation factor (R_L) is a dimensionless constant which is an essential characteristic of Langmuir isotherm. R_L value indicates the type of isotherm. The R_L was determined using the following equation:

$$R_L = \frac{1}{1 + bC_0} \qquad (11)$$

where b Langmuir constant obtained from the Eq. (10), C_0 the initial metal ion concentration (mg/L), R_L values between 0 and 1 indicate favorable adsorption.

Estimation of thermodynamic parameters

Using the following equations thermodynamic parameters such as change in free energy ($\Delta G°$), enthalpy ($\Delta H°$) and entropy ($\Delta S°$) were determined (Romero-Gonzalez et al. 2006).

$$\Delta G° = -RT \ln K_c \qquad (12)$$

where R gas constant ($R = 8.314$ J/mol/K), T temperature in Kelvin, K_c equilibrium constant

$$K_c = \frac{q_e}{C_e} \qquad (13)$$

where as

$$\Delta G° = \Delta H° - T \Delta S° \qquad (14)$$

Substituting the Eq. (14) in Eq. (12) and rearranging, yields the following equation:

$$\ln K_c = \left(\frac{\Delta H°}{R} \right) \frac{1}{T} + \frac{\Delta S°}{R}. \qquad (15)$$

Using the Khan and Singh plots ($\ln q_e/C_e$ versus q_e) the K_c was calculated. The enthalpy and entropy were obtained

from the slope and intercept of ln K_c versus $1/T$ (Van-Hoff plot) (Romero-Gonzalez et al. 2006).

Desorption and regeneration studies

Elution of adsorbed metal ions from biosorbents and reusability of MLP consecutive adsorption–desorption cycles were repeated five times using the same MLP. Desorption experiments were conducted in 0.1 N HCl and 0.1 N NaOH solutions. The MLP loaded with Cr(VI) ions was placed in the desorption medium, and the mixture was agitated on a rotary shaker at 70 rpm for a period of 30 min. The MLP was removed by filtration and Cr(VI) concentration was determined in the filtrate. After each cycle of adsorption–desorption, the MLP was washed with distilled water and conditioned for adsorption in the subsequent cycle. The percent desorption was calculated based on the amount of Cr(VI) adsorbed on the MLP (at equilibrium stage) and the amount of metal ion concentration in the desorption medium.

Results and discussion

Effect of particle size on Cr(VI) removal

Adsorption of Cr(VI) on MLP increased with decreased particle size 1.4–0.5 mm, then decreased proportionately with further reduction in particle size reduced (Fig. 1). The amount of Cr(VI) adsorption increased from 13.07 to 18.95 mg/g at pH 3 with decreased particle size from 1.4 to 0.5 mm. The increased adsorption with decreased particle size is attributed to the fact that smaller particle size has more surface area than the larger particles. However, fine particles (<0.5 mm) form an agglomerate in the solution and decrease the overall surface area which results in lesser uptake of metals (Hamadia et al. 2001). Hamadia et al. (2001) also observed a decrease in Cr(VI) adsorption as the average particle size was increased from 0.38 to 0.9 mm, which in agreement with the current results.

Effect of pH on chromium removal

pH of the solution is of greater importance in heavy metal sorption (Hamadia et al. 2001). This is because H$^+$ or OH$^-$ ions influence the ionization capacity of the metal ion present in it (Kumar and Chakraborty 2009). To investigate the effect of pH on the chromium removal using MLP, studies were conducted at pH range of 2–8 and 100 mg/L chromium solution with 4 g/L biomass. It was observed that the adsorption was the highest (23.75 mg/g) at pH 2 and decreased with the increasing pH. Increasing the

solution pH from 2 to 8, resulted in a decrease in the adsorption of Cr(VI) from 23.75 to 9.02 mg/g (Fig. 2). By changing the solution pH from 3 to 2 the adsorption efficiency was increased from 84 to 95 %. It is evident from the data represented in Fig. 2 that the chromium sorption is influenced by pH of the solution.

The surface of any biological materials contains several diverse active sites. The metal adsorption depends on these active sites as well as on the nature of metal ions in the solution. The higher chromium sorption by this material at lower pH may be attributed to the fact that the large number of hydrogen ions can easily co-ordinate with the –NH$_2$ and C=O groups present on the biomass surface. Cr(VI) is an anionic species, and as the biomass surface is positively charged, increasing electrostatic attraction between negatively charged sorbate and adsorbent might have resulted in the increased adsorption of metal ions. With increase in pH the adsorbent surface became more negatively charged which enhances the repulsions of sorbent ions (Malkoc and Nuhoglu 2007).

Effect of chromium ion concentration on biosorption of Cr(VI)

The biomass potential of chromium removal was further evaluated by studying the chromium ion concentration range of 100–600 mg/L using 4 g/L MLP at pH 2 (Fig. 3). The adsorption capacity of MLP was increased up to the sorbent concentration 400 mg/L. Further a decreased adsorption was noticed with increasing metal concentration. The uptake capacity of MLP increased from 22.99 to 43.43 mg/L by increasing Cr(VI) concentration from 100 to 400 mg/L. However, the present adsorption decreased from 91.97 to 43.43 % with increase in the sorbent
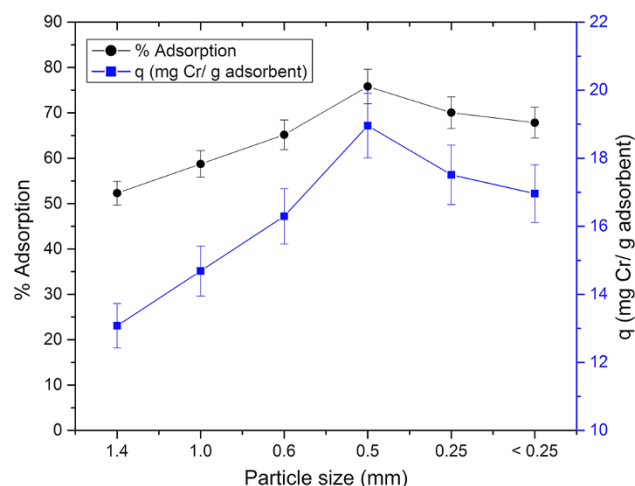

Fig. 1 Effect of particle size of mangrove leaf powder on Cr(VI) adsorption at Cr(VI) ion concentration 100 mg/L, pH 3 and adsorbent dose of 4 g/L
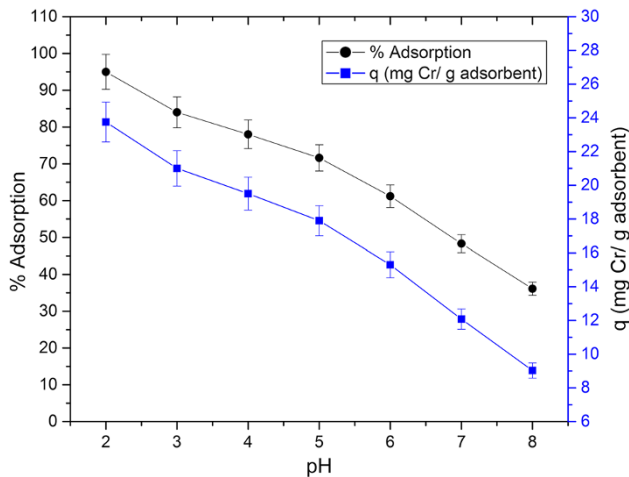
Fig. 2 Effect of pH on chromium sorption onto mangrove leaf powder at Cr(VI) concentration of 100 mg/L, adsorbent dose of 4 g/L and particle size = 0.5

concentration to 400 mg/L. The decreased adsorption at higher concentration may be due to the saturation of binding sites and increase in repulsion forces on sorbent ions (Malkoc and Nuhoglu 2007).

While increasing the Cr ion concentration from 100 to 300 mg/L for 4 g/L of MLP recorded an increase in the adsorption capacity. At 400 mg/L Cr(VI) on the same quantity of MLP, the Cr ions covered all available binding surface of MLP that leads to saturation, which creates non-availability of cations on sorbent that leads to repulsion of Cr(VI) anions from further addition at 400 mg/L which decreases the adsorption capacity. The adsorption isotherms (Freundlich and Langmuir isotherms) also reveal that Cr(VI) adsorbs as a monolayer on the surface of MLP.
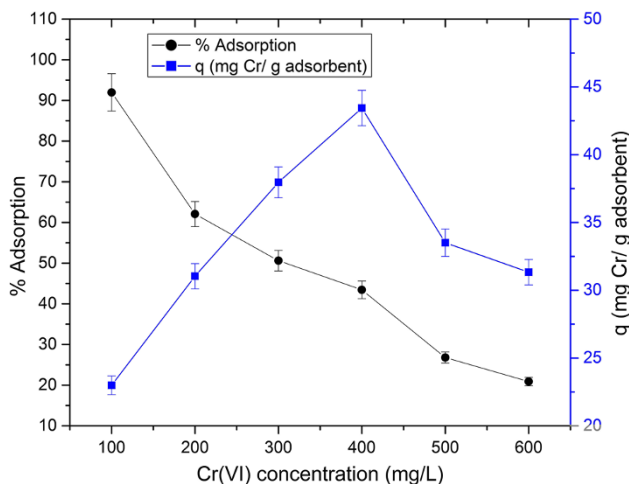
Effect of biomass variation on chromium removal

Another important parameter that affects the biosorption process is the amount of adsorbent used (Malkoc and Nuhoglu 2007). From the data of Fig. 4, it is evident that the percent Cr(VI) removal was increased from 27.35 to 92.15 % with an increasing MLP concentration from 2 to 10 g/L. With the increasing MLP concentration, the uptake capacity of metal ions decreased from 54.71 to 36.85 mg/g. This is attributed to the fact that due to higher amounts of MLP increase the surface area made available more adsorption sites resulting in higher removal of Cr(VI).

Adsorption kinetics

In the present study for a batch reaction, the adsorption dynamics were determined using the Eqs. (1), (5)–(7). Table 1 depicts the comparison of various constants obtained with the correlation coefficients. Good fits were observed for all particle sizes. The smallest correlation coefficient (0.8308) was observed with the 1.4 mm particle size of MLP at second order. Except particle size of 1.4 mm, the remaining particles' sorption reaction can be approximated with the second-order kinetics model. It can be observed that the initial sorption rate (h) is higher at particle size at 0.5 mm than others. The change in rate constants depending on the particle size shows that particle size is a rate-limiting step for surface adsorption of Cr(VI) by MLP.

Adsorption isotherms

The linearized form of Freundlich and Langmuir adsorption isotherms of Cr(VI) by MLP was obtained at the temperatures of 10, 25 and 40 °C. Figures 5 and 6 show the linearized Freundlich and Langmuir adsorption isotherms. The
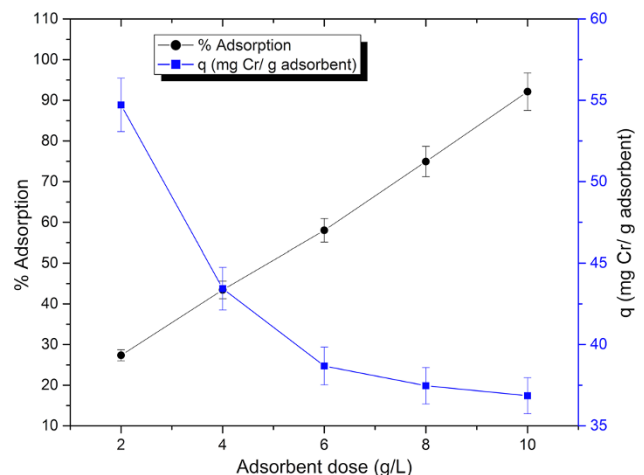

Fig. 3 Effect of initial Cr(VI) concentration on sorption onto mangrove leaf powder (pH 2, adsorbent dose = 4 g/L, particle size = 0.5)


Fig. 4 Effect of adsorbent dose on sorption of Cr(VI) onto mangrove leaf powder (pH 2, particle size = 0.5, Cr(VI) = 400 mg/L)
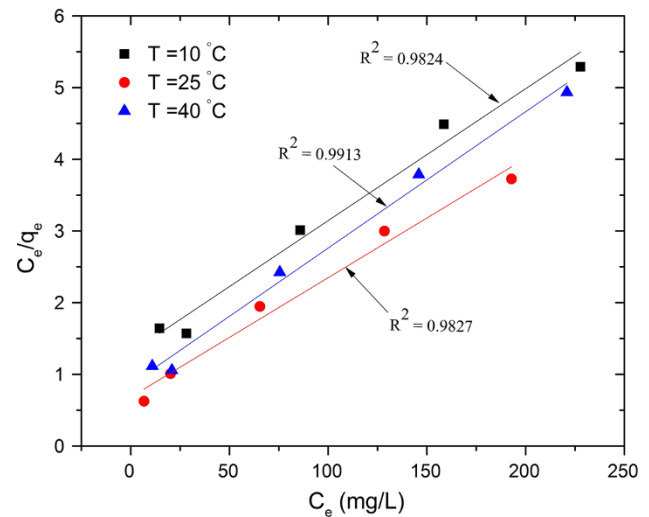
Table 1 The first-order, pseudo first-order and pseudo second-order rate constants for mangrove leaf powder at different particle sizes

	Particle size (mm)				
	1.4	1.0	0.6	0.5	0.25
First-order kinetics					
k_r' (1/min)	0.1190	0.0875	0.1545	0.1233	0.1372
K_c	1.1366	1.4502	1.9856	24.0466	8.0160
k_1 (1/min)	0.0633	0.0517	0.1027	0.1183	0.1219
k_2 (1/min)	0.0556	0.0357	0.0517	0.0049	0.0152
R^2	0.9600	0.9335	0.9017	0.9655	0.9321
Pseudo first-order kinetics					
k_1' (1/min)	0.1119	0.0875	0.1545	0.1234	0.1372
R^2	0.9600	0.9334	0.9017	0.9655	0.9321
Pseudo second-order kinetics					
k_2' (g/mg min)	0.0299	0.0556	0.0623	0.0871	0.0691
h (mg/g min)	0.0084	0.0195	0.0275	0.0802	0.0546
R^2	0.8308	0.9641	0.9499	0.9738	0.9471
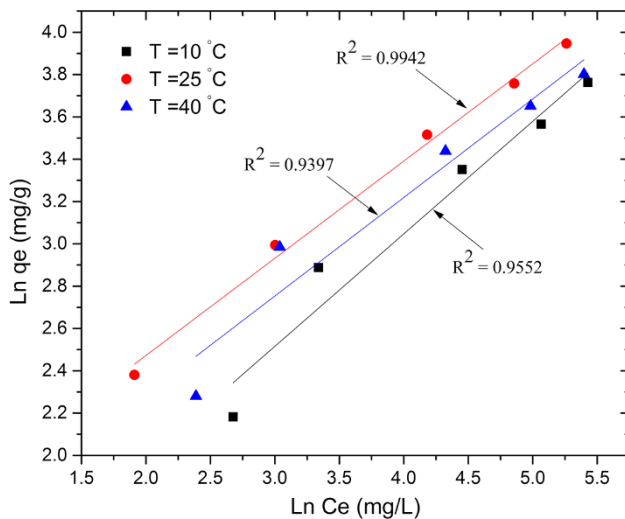
Fig. 5 Freundlich isotherm plot for the adsorption of chromium onto mangrove leaf powder at various temperatures (C_e equilibrium concentration, q_e amount of Cr(VI) adsorbed)

Fig. 6 Langmuir plots for the adsorption of chromium onto mangrove leaf powder at various temperatures (C_e equilibrium concentration, q_e amount of Cr(VI) adsorbed)

Table 2 Freundlich and Langmuir constants for the adsorption of Cr(VI) onto mangrove leaf powder at different temperatures and pH 2

	Temperature (°C)		
	10	25	40
Freundlich constants			
K_f (mg/g)	2.1552	3.6544	3.1006
n	1.8807	2.1767	2.1477
R^2	0.9552	0.9942	0.9397
Langmuir constants			
Q^0 (mg/g)	54.3478	60.2409	52.6315
b (1/mg)	0.0141	0.0243	0.0221
R^2	0.9824	0.9827	0.9913
R_L values			
C_o (mg/L)			
50	0.5864	0.4514	0.4748
100	0.4149	0.2915	0.3113
200	0.2617	0.1706	0.1843
300	0.1911	0.1206	0.1309
400	0.1505	0.0932	0.1015

Freundlich and Langmuir adsorption constants estimated from the isotherms at different temperatures and their correlation coefficients are presented in Table 2. The constant values derived from adsorption isotherm could express the surface properties and affinity of adsorbent. These constant values can also be useful to determine the adsorption capacity of the sorbent (Malkoc and Nuhoglu 2007).

The correlation coefficient values obtained from the Freundlich and Langmuir isotherms indicate that the adsorption pattern for Cr(VI) on MLP follows both the Freundlich isotherm ($R^2 > 0.9397$) and the Langmuir isotherm ($R^2 > 0.9824$) at all experimental temperatures

(Table 2). However, the Langmuir isotherm was best fitted for the adsorption of chromium ions on MLP at studied temperatures. It has been known that the magnitude of Freundlich model constant K_f indicates a measure of the adsorbent capacity. Among the studied temperatures, the maximum adsorption capacity (K_f) of 3.6544 mg/g was observed at 25 °C with an affinity value (n) of 2.1767. As indicated in Table 2, the affinity values (n) range 1.8–2.2 indicating a favorable adsorption of Cr(VI) on MLP.

According to Langmuir isotherm the equilibrium adsorption capacity (Q^0) of MLP increased from 54.34 to 60.24 mg/g with increase in the solution temperature from 10 to 25 °C. However, the adsorption capacity decreased from 25 to 40 °C (Table 2). The sorption constant 'b' also follows a similar pattern. From the Langmuir isotherm it is clear that the sorption of chromium on MLP is an endothermic process (Malkoc and Nuhoglu 2007).

The separation factor or equilibrium parameter (R_L) is a feature of Langmuir isotherm; it is a dimensionless constant and relates the isotherm shape which is used to predict whether a sorption system is 'favorable' or 'unfavorable'. Where $R_L > 1$ the isotherm is unfavorable, if $R_L = 1$ the isotherm is linear, if $0 < R_L < 1$ the isotherm is favorable and if the $R_L = 0$ the isotherm is irreversible (Malkoc and Nuhoglu 2007). The various R_L values obtained at different temperatures relating to initial chromium concentration are presented in Table 2. In the present study R_L values decreased with increasing initial Cr(VI) concentration at all studied temperatures. This indicates that sorption of Cr(VI) on MLP is more favorable at higher initial Cr(VI) concentrations. According to Das et al. (2000), any adsorption system which obeys both the Freundlich and Langmuir isotherms indicates that the solute forms a homogenous monolayer on the adsorbate. In the current study, the adsorption of Cr(VI) onto MLP obeyed both Freundlich and Langmuir isotherms suggesting that the Cr(VI) forms a monolayer on the surface of MLP.

Thermodynamic studies

Table 3 depicts various thermodynamic parameters calculated in the present study. The data indicated negative ΔG° values suggesting spontaneous nature of Cr adsorption on the MLP. The enthalpy change (ΔH°) and the entropy change (ΔS°) were calculated to be 41.92 kJ/mol and 138.53 J/mol/K, respectively. The positive value of ΔH° suggested that the adsorption is of endothermic nature. The positive value of ΔS° showed increased randomness at the solid/solution interface during the adsorption process, suggesting that the Cr ions replace some other molecules previously adsorbed on the surface of MLP. This may be explained based on the assumption that, the displaced molecules (may be water or other ions) gain more translation entropy than is lost by the Cr ions, thus allowing the prevalence of randomness in the system (Malkoc and Nuhoglu 2007).

Desorption and regeneration studies

Disposal of Cr(VI) loaded biosorbents in the environment is hazardous to the nature. Desorption of metals from sorbent helps in recovery of metals and reduces the

Table 3 Thermodynamic parameters for the adsorption of Cr(VI) onto mangrove leaf powder

T (K)	K_c	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol/K)
283	0.0127	−10.2735	41.92	138.53
298	0.897	−0.26932		
303	0.5752	−1.39325		

Table 4 Adsorption and desorption of Cr(VI) onto mangrove leaf powder (adsorbent dose = 4 g/L, particle size = 0.5, Cr(VI) = 400 mg/L)

Cycle no.	1	2	3	4	5
Cr adsorbed (mg/g)	51.77	47.94	38.70	36.41	35.47
Cr desorbed (mg/g)	48.85	40.83	28.28	26.23	24.88
% Adsorption decreased	–	7.40	25.25	29.67	31.49
% Desorption	94.34	85.16	73.07	72.03	70.13

disposal problem of metal-loaded sorbents. The regeneration capability of the biosorbent is one of the important parameter for considering their potential for commercialization. In the present study high amount of Cr(VI) was desorbed in the 0.1 N HCl solution compared with 0.1 N NaOH. Desorption studies showed that initially 94.34 % of Cr(VI) was desorbed from MLP, in subsequent cycles decreased desorption was noticed. At 5th cycle 70.13 % desorption was observed (Table 4). However, the adsorption capacity of MLP was decreased from 51.77 (1st cycle) to 35.37 mg/g (5th cycle). An overall 31.49 % reduction in the adsorption capability of MLP was observed at 5th cycle. The decreased adsorption and desorption during the repeated cycles attributed due to structural changes on the surface of sorbent and some of metal ions being held in the intrapores of MLP (Kaur et al. 2013). Kaur et al. (2013) observed that complete desorption of metal ions from the surface of agricultural residues is not possible even at high acid concentrations.

Conclusion

This study demonstrated that MLP could be used as an important component for the remediation of hexavalent chromium. It is an environmental friendly technology for cleaning-up the chromium-contaminated waste waters. The optimal operating conditions under laboratory conditions were evaluated. This study as well reveals that chromium sorption is affected by particle size of MLP, pH of the solution, concentration of sorbent and adsorption dose. The sorption isotherm studies revealed heterogeneous energetic distribution of chromium adsorption active sites on this material. Thermodynamic studies indicated that the

chromium sorption by this material is spontaneous in nature. Based on this study, it is rational to conclude that the use of natural and abundantly available materials best suits to immobilize and detoxify toxic compounds, such as chromium.

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