

Biosorption of Cd^{+2} by green plant biomass, *Araucaria heterophylla*: characterization, kinetic, isotherm and thermodynamic studies

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Abstract The present study attempted to analyze the biosorption behavior of novel biosorbent, *Araucaria heterophylla* (green plant) biomass, to remove Cd^{+2} from solutions against various parameters, i.e., initial metal ion concentration, pH, temperature, sorbent dosage and biomass particle size. The maximum biosorption was found to be 90.02% at pH 5.5 and biosorption capacity (q_e) of Cd^{+2} is 9.2506 mg g^{-1} . The Langmuir and Freundlich equilibrium adsorption isotherms were studied and it was observed that Freundlich model is the best fit than the Langmuir model with correlation co-efficient of 0.999. Kinetic studies indicated that the biosorption process of Cd^{+2} well followed the pseudo-second-order model with R^2 0.999. Thermodynamic studies observed that the process is

exothermic (ΔH° negative). Free energy change (ΔG°) with negative sign reflected the feasibility and spontaneous nature of the process. The chemical functional –OH groups, CH_2 stretching vibrations, C=O carbonyl group of alcohol, C=O carbonyl group of amide, P=O stretching vibrations and –CH groups were involved in the biosorption process. The XRD pattern of the *A. heterophylla* was found to be mostly amorphous in nature. The SEM studies showed Cd^{+2} biosorption on selective grains of the biosorbent. It was concluded that *A. heterophylla* leaf powder can be used as an effective, low-cost, and environmentally friendly biosorbent for the removal of Cd^{+2} from aqueous solution.

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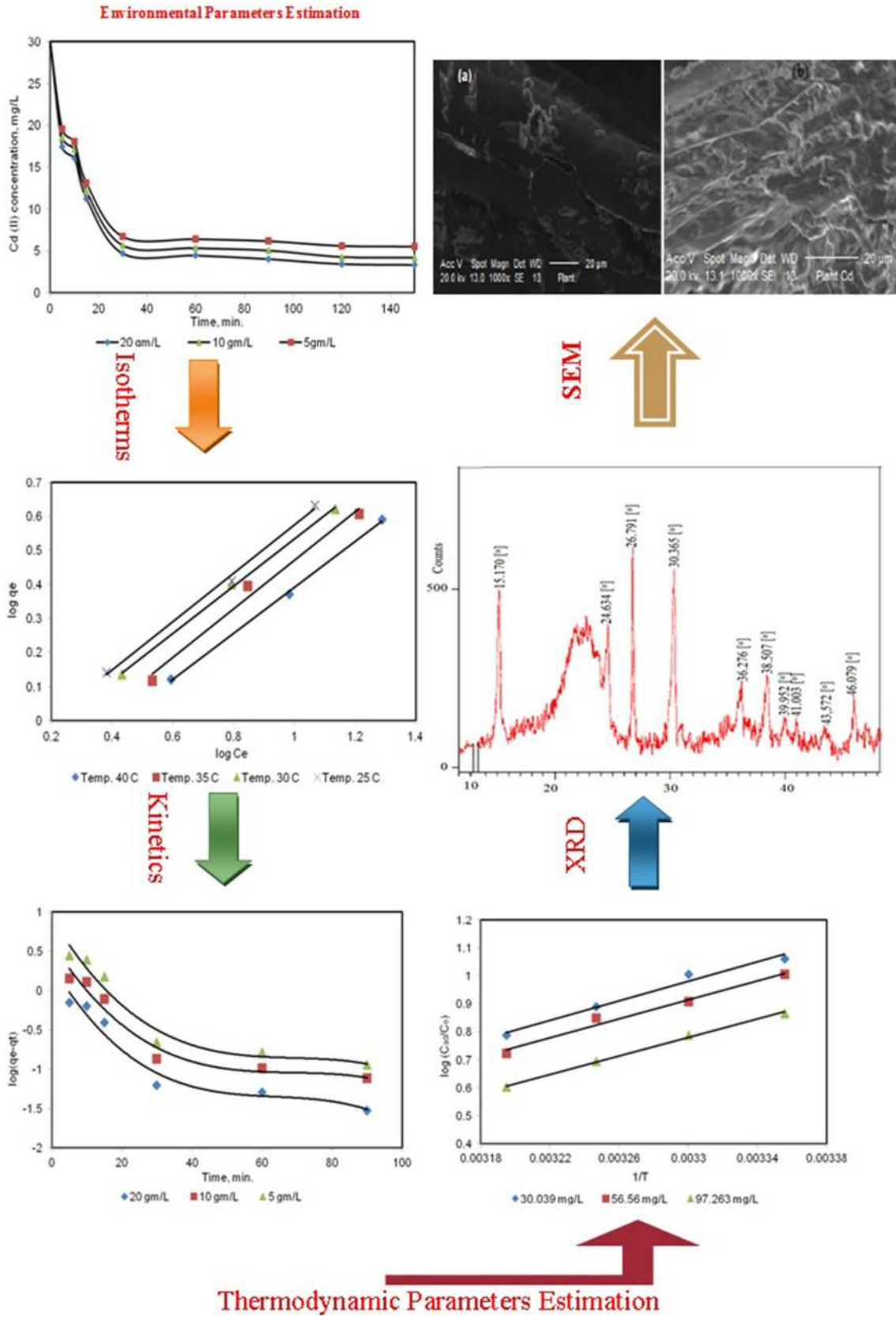
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Graphical Abstract



Keywords Biosorption · *Araucaria heterophylla* · Kinetics · Cadmium(II) · FTIR · SEM

Introduction

Battery manufacturing, metal plating, mining, pigment dye stuff, and chemical industries discharge many heavy metal ions into industrial wastewaters (Volesky 1990). Cadmium, zinc and lead are toxic heavy metals which constitute a global environmental problem in this manner. These heavy metals are toxic, non-biodegradable and become a source from which they are accumulated by absorption into living organisms (Victor et al. 2007). Metal plating, metallurgic alloying, ceramics, textile printing industry, photograph development, electroplating, alkaline battery manufacturing are the major industrial fields responsible for cadmium pollution (Kadirvelu et al. 2001; Zhu et al. 2007). In plants, absorption of Cd^{+2} is more when compared to other heavy metals. Cd^{+2} gains access to food chain readily and causes a grave health hazard (Mohapatra and Anand 2007). Cadmium is registered as List 1 in the Dangerous Substances Directive (2006/11/EC) of the European Union. The recommendations of WHO are much more stringent in this context as the maximum permissible limit of Cd^{+2} is fixed as 0.005 mg L^{-1} in drinking water. The water quality standards for cadmium is $1 \mu\text{g L}^{-1}$ for estuaries and marine waters and $0.5 \mu\text{g L}^{-1}$ for freshwater.

The kidneys are the critical target organ after ingestion causing renal dysfunction, hypertension and anemia (Zuane 1990; Cheung et al. 2001). Therefore, an adequate treatment of the polluted wastewater is practiced, i.e., chemical precipitation, membrane filtration, electrolysis, ion exchange, carbon adsorption and co-precipitation/adsorption. Nevertheless, the application of such processes is sometimes restricted because of technical or economic constraints (Rorrer 1998; Ekmeyapar et al. 2006). The search for new technologies for the removal of toxic metals has directed attention to biosorption phenomenon which is based on the metal binding capacity of agricultural wastes (Zacaria 2002). In recent years, a number of agricultural and forestry by-products such as rice husk (Ajmal et al. 2003), pine bark (Al-Asheh and Duvnjak 1998), saw dust (Bulut and Tez 2007), *Araucaria heterophylla* (Sarada et al., 2013), lignin (Srivastava et al. 1994), cork biomass (Chubar et al. 2004), *Lathyrus sativus* husk (Panda et al. 2008), *Zea mays* cob powder (Goyal and Srivastava, 2009), *Acacia leucocephala* bark powder (Munagapati et al., 2010), *Parthenium hysterophorus* weed (Ajmal et al., 2006), wheat bran (Nouri et al. 2007), *Eleocharis acicularis* (Miretzky et al., 2010), *Eichhornia crassipes* (Módenes et al., 2011), *Grape pomace* (Kishore et al.,

2013), orange peel (Feng et al., 2011) have been used for heavy metal removal from waters and wastewaters.

The biosorbent treatment/chemical modification has been causing other environmental problems, i.e., release of excessive quantities of colored organic compounds and toxic chemicals with an unpleasant smell. Hence, attempts are made in this investigation to develop a low-cost, renewable adsorbent for the removal of Cd^{+2} from aqueous solutions using *Araucaria heterophylla* leaf powder by simple treatment of washing with water and characterization of the biomass was attempted. *A. heterophylla* is a vascular trunk plant belonging to the family Araucariaceae. The study includes an evaluation of the effects of various process parameters such as pH, initial metal ion concentration, adsorbent dosage, contact time and temperature. The kinetic models, equilibrium isotherm models and thermodynamic parameters related to the process were studied.

Materials and methods

Preparation of biosorbent

The leaves of *Araucaria heterophylla* plant were collected from a Botanical garden in Ooty and was identified and authenticated by the botanist, Department of Botany, Andhra University, Visakhapatnam. The leaves were washed with distilled water, dried in an oven at $60 \text{ }^\circ\text{C}$ for 24 h and then ground to fine size. After grinding, the prepared adsorbent sample was sieved to get particles of uniform size. The biosorbent was kept in humidity control oven to maintain humidity for all equilibrium studies.

Preparation of adsorbate solutions

Cadmium chloride solution was prepared by dissolving 3.6178 g of cadmium chloride salt in 1000-mL standard volumetric flask with de-ionized water. The primary stock solution thus prepared had about 2222 ppm of Cd^{+2} in solution. From the stock solutions, experimental test solutions were prepared by diluting the primary stock solution with de-mineralized water. pH was maintained at 3–7 by addition of 0.1 N HCl.

Equilibrium studies

The experiments were carried out in 250-mL Erlenmeyer conical flasks, at a constant agitation speed (160 rpm) with 100 mL of solution and required amount of adsorbent weight using orbital shaker (Kemi make). Initially the effect of contact time (0–120 min) on the sorption capacity

of *A. heterophylla* was evaluated. The equilibrium time was obtained and the experiments were conducted for the same duration for all conditions. Batch experiments were carried out to investigate the adsorption behavior of Cd^{+2} on *A. heterophylla*.

Analysis of heavy metal ions

The concentrations of un-adsorbed Cd^{+2} ions in the sample supernatant liquid were determined using an atomic absorption spectrophotometer (PerkinElmer AA200) with an air–acetylene flame. C_t and q_t were then calculated and tabulated for subsequent analysis of the data. The metal uptake (q_t) was calculated using the general definition:

$$q_t = \frac{V(C_0 - C_e)}{M}, \quad (1)$$

where q_t is the metal uptake of Cd^{+2} g^{-1} biomass, V is the volume of metal solution in contact with the biosorbent in L , C_0 and C_e are the initial and residual concentration of metal in the solution mg L^{-1} , respectively, and M is the amount of added biosorbent in g ($5\text{--}20 \text{ g L}^{-1}$).

% removal of metal by *A. heterophylla* was determined by the following equation:

$$R(\%) = \frac{C_0 - C_e}{C_0} \times 100, \quad (2)$$

where R is the percentage of Cd^{+2} adsorbed by biomass, C_0 is the initial concentration of metal ions in mg L^{-1} and C_e is the concentration of metal ions at time t in mg L^{-1} .

Desorption and reuse

To determine the reusability of the biomass, three adsorption–desorption cycles were performed using the same biomass. Desorption of Cd^{+2} ions was performed by 2 N HCl solution. Biomass loaded with Cd^{+2} was placed in the desorption medium and stirred at 160 rpm for 2 h at 30 °C. The final Cd^{+2} ion concentrations in the desorption medium were determined using an AAS (AA400) as described above and calculated as in Eq. 1. Biomass desorption into the solution was calculated by the following equation:

$$q_{\text{des}} = C_{\text{des}} \frac{V}{W}, \quad (3)$$

where ‘ V ’ is the volume of solution and ‘ W ’ is the weight of biomass.

Desorption ratio was calculated from the amount of metal ions adsorbed on the biomass and the final Cd^{+2} concentration in the desorption medium:

$$\text{Desorption ratio} = \frac{\text{Amount of metal ions biosorbed} \times 100}{\text{Amount of metal ions desorbed}}. \quad (4)$$

Characterization of biomass

FTIR studies

The adsorbent samples, prior and after adsorption are dried and demineralized at 60 °C in humidity control oven. The powder was analyzed by Fourier transform infrared spectrophotometer (PerkinElmer No. 72425) by the potassium bromide (KBr) pellet method at wavenumber range 400.00–4000.00 Cm^{-1} .

Scanning electron microscopy

The dried biomass powder *A. heterophylla* and the corresponding metal ion-loaded powder were coated with ultra-thin film of gold by an ion sputter (JFC-1100), exposed under scanning electron microscope (JEOL, JX-8100) with voltage ranging from 10 to 25 kV.

X-ray diffraction

The X-ray diffraction (XRD) of the biomass was analyzed (XRD-6000 Shimadzu) and recorded as a function of 2Θ at a scan speed of $1.2^\circ \text{ min}^{-1}$ and XRD patterns were recorded from 10° to 70° .

Results and discussions

Biosorption studies

The experimental data for adsorption of Cd^{+2} onto *A. heterophylla* showed that an optimum contact time of 120 min is required to attain equilibrium. It can be observed from Fig. 1a that 42–56% of the metal was removed from the solution within 5 min of contact time and reached a maximum of 88.57% at 2 h. The metal uptake was faster at initial stages of contact and subsequently slowed down as the reaction approached equilibrium. In the initial stages of contact, a large number of vacant sites are available and hence the uptake is faster. The slowing down of metal uptake in later stages may be due to difficulty in occupying the remaining vacant sites. Repulsive forces between the solute molecules on the adsorbent and aqueous solution (bulk phase) may also most probably contribute to the slowing down of uptake of metal at equilibrium.

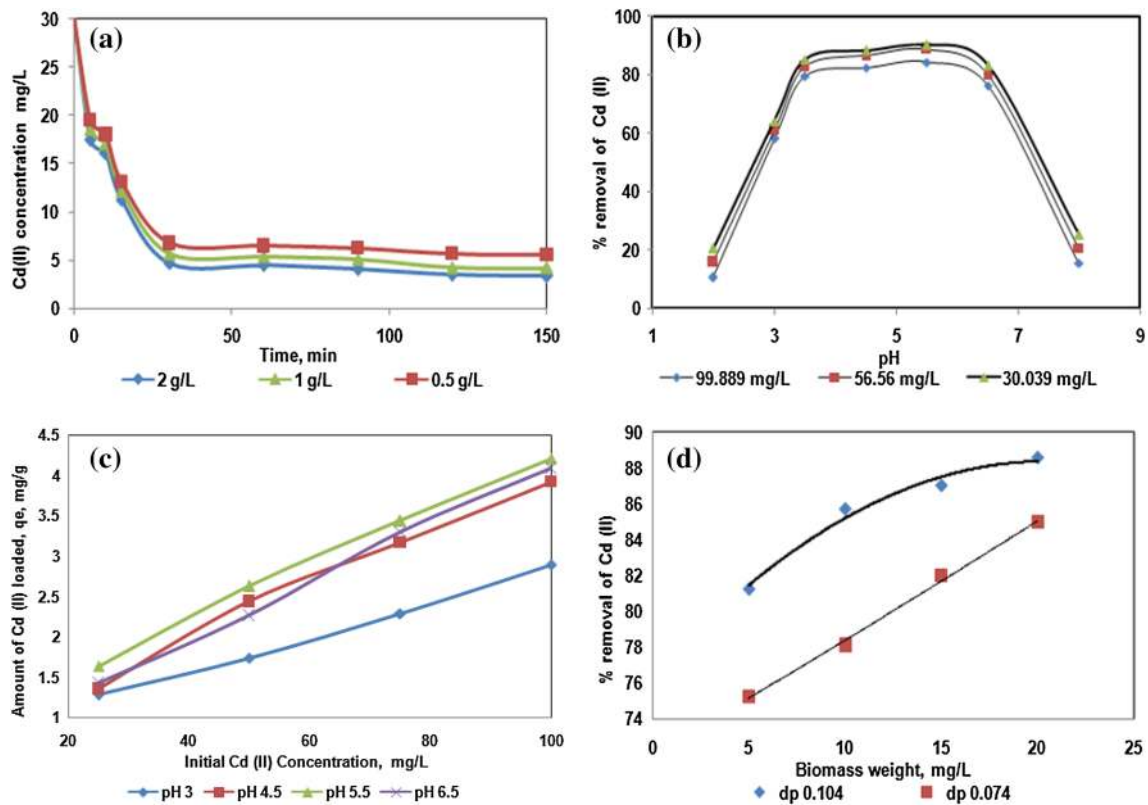


Fig. 1 Equilibrium time of *A. heterophylla* at 30 °C, CT 30.039 mg L⁻¹ and pH 4.5 (a), effect of pH at temp. 30°C, dp 0.074 mm and biomass weight 20 g L⁻¹ (b), effect of initial metal

concentration at dp 0.074 mm and biomass weight 20 g L⁻¹ (c), effect of biomass weight at temp 30°C, pH 4.5 and CT 30.039 mg L⁻¹ (d)

Effect of pH

pH of the biosorption medium is one of the essential parameters affecting the uptake of heavy metal ions from aqueous solutions by biosorbents (Yin et al. 1999). One of the factors significantly affecting biosorption of metal ions is its acidic nature. This parameter directly related the ability of hydrogen ions to that of the metal ions to bind themselves to active sites on the biosorbent surface (María and dos María 2010). Generally, metal biosorption involves complex mechanisms of ion exchange, chelation, adsorption by physical forces, and ion entrapment in inter- and intra-fibrillar capillaries and spaces of the cell structural network of biosorbents (Zhang and Banks 2006; Ahmet et al., 2008). The effect of pH on the biosorption of Cd⁺² ions onto *A. heterophylla* biomass was studied in the pH range 2–8 and the results are presented in Fig. 1b. The percent removal of biosorption was increased from (20.5%) to (90.02%) for Cd⁺² on *Araucaria heterophylla* at initial metal concentration of 30.039 mg L⁻¹ when pH was increased from 2.5 to 5.5, the decline was rapid beyond pH 5.5 and reached the lowest value when the pH was 8.0. The similar trend was followed for other initial metal ion concentrations (99.89 and 56.56 mg L⁻¹).

The pH dependency of metal uptake could be attributed to the functional groups attached to the biomass and their metal chemistry (Matheickal et al. 1999; Ahmet et al. 2008). At low pH values (pH < 2.0), poor biosorption of Cd⁺² could be due to the presence of H⁺ ions in abundance which are likely to claim their adsorption in preference to the metal ions in the solution. When the pH is increased (pH 2–5.5), biosorbent surface becomes deprotonated, thus facilitating the biosorption of more metal ions.

Essentially, carboxyl groups have the highest affinity for metal ions, since they are deprotonated over a wide range of pH (Matheickal et al. 1999; Chojnacka 2005). Decrease in biosorption at higher pH (pH > 5.5) (at pH 8.5, 20.8% removal) is not only attributed to the formation of soluble hydroxylated complexes of the metal ions, but also to the ionized nature of the cell wall surface of the biomass (Matheickal et al. 1999; Ahmet et al. 2008). The FTIR spectroscopic analysis showed that the biomass contains a variety of functional groups such as carboxyl, hydroxyl, and amine and these groups are involved in almost all potential binding mechanisms. Moreover, depending on the pH value of the aqueous solution these functional groups participate in metal ion binding. The effect of pH can be explained by ion-exchange mechanism of sorption in

which a significant role is played by the functional groups of biomass that have cation-exchange property.

Effect of initial metal concentration

The effect of initial metal concentration on the removal of Cd^{2+} using *A. heterophylla* is presented in Fig. 1c. An increase in the initial metal ion concentration from 25 to 100 mg L^{-1} increased the metal uptake from 1.634 to 4.205 at pH 5.5, further decreased the percent adsorption from 92.17 to 82.14%. It is reasonable that increase in metal ion concentration facilitated enhanced displacement of hydrogen ions on the surface of the biomass at pH 5.5 because of high concentration of the metal ions. This may be due to the saturation of the active sites with the biomass provided in the process. In addition, at low concentrations, biosorption sites took up the available metals more quickly. However, at higher concentrations, metal ions needed to diffuse to the biomass surface by intra-particle diffusion and greatly hydrolyzed ions diffused at a slower rate (Horsfall and Spiff 2004) and may be a cause for the reduction in the percentage adsorption.

Effect of adsorbent dosage

Biosorbent dosage determines the potential of biosorbent by the number of binding sites available to remove metal ions at a specified initial metal ion concentration. The effect of amount of biomass added to the aqueous solution on the biosorption of Cd^{2+} using *A. heterophylla* as biosorbent was studied and is shown in Fig. 1d. The amount of Cd^{2+} adsorbed increases with an increase in adsorbent dosage from 5 to 20 g L^{-1} . The percentage of Cd^{2+} removal was increased from 81.27 to 88.57% for an increase in biomass dosage due to increasing biomass surface area. Similar trend was also observed for lead removal using *Moringa oleifera* bark as biosorbents (Reddy et al. 2010).

Effect of adsorbent size

The effect of particle size in the range 0.074–0.150 mm on percentage adsorption of Cd^{2+} using *A. heterophylla* was investigated (Fig. 2a). About 10–12% decrease in the % adsorption was found with an increase in the particle size by twofold. The decrease in the average particle size of the adsorbent increased the surface area. The ion-exchange capacities depend much on the surface activity, in particular, specific surface area available for solute–surface interaction, which is accessible to solute. Consequently, it is expected that the ion-exchange capacity increased with increasing surface area of adsorbent. The rate of exchange is generally controlled by the rate of ion diffusion within

the particle and this is related to the size of particles (Kumar et al. 2006).

Effect of temperature

The effect of temperature on % removal of Cd^{2+} on (Fig. 2b) *A. heterophylla* decreased from 92 to 86% with increase in temperature in the range 25–40 °C at initial concentration of 30.039 mg L^{-1} . The same trend was observed for other initial metal concentrations. The results clearly indicated that Cd^{2+} uptake decreased with the increase in temperature. These findings suggested that Cd^{2+} uptake process was exothermic in nature. At high temperature, the thickness of the boundary layer decreased, due to increased tendency of the metal ion to escape from the biomass surface to the solution phase, which resulted in a decrease in the adsorption as temperature was increased (Horsfall and Spiff 2004). The decrease in adsorption with increasing temperature suggested the weak adsorption interaction between biomass surface and the metal ion, which supported the physisorption, although involvement of chemisorption cannot be completely neglected. A similar trend was also supported by the earlier reports (Aksu 2001; Cruz et al. 2004).

Biosorption isotherm models

The sorption equilibrium data are conveniently represented by sorption isotherms, which correspond to the relationship between the mass of the solute sorbed per unit mass of sorbent q_e and the solute concentration of the solution at equilibrium C_e . The biosorption isotherms were investigated using two equilibrium models, which are namely the Langmuir and Freundlich. A basic assumption of the Langmuir theory is that sorption takes place at specific homogeneous sites within the sorbent. This model can be written in non-linear form (Langmuir 1918) and is represented by the equation:

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \quad (5)$$

where q_m is the maximum amount of the metal ion per unit weight of adsorbent to form a complete monolayer on the surface bound at high C_e (mg g^{-1}), and b is a constant which accounts for the affinity of the binding sites (L mg^{-1}). q_m represents the limiting adsorption capacity when the surface is fully covered with metal ions and helps in the evaluation of adsorption performance, particularly in cases where the sorbent did not reach its full saturation during contact. From the plots between (C_e/q_e) and C_e the slope $(1/q_m)$ and the intercept $(1/b)$ can be calculated.

The linearized Langmuir adsorption isotherms of Cd^{2+} for the biosorbent obtained at different temperatures are

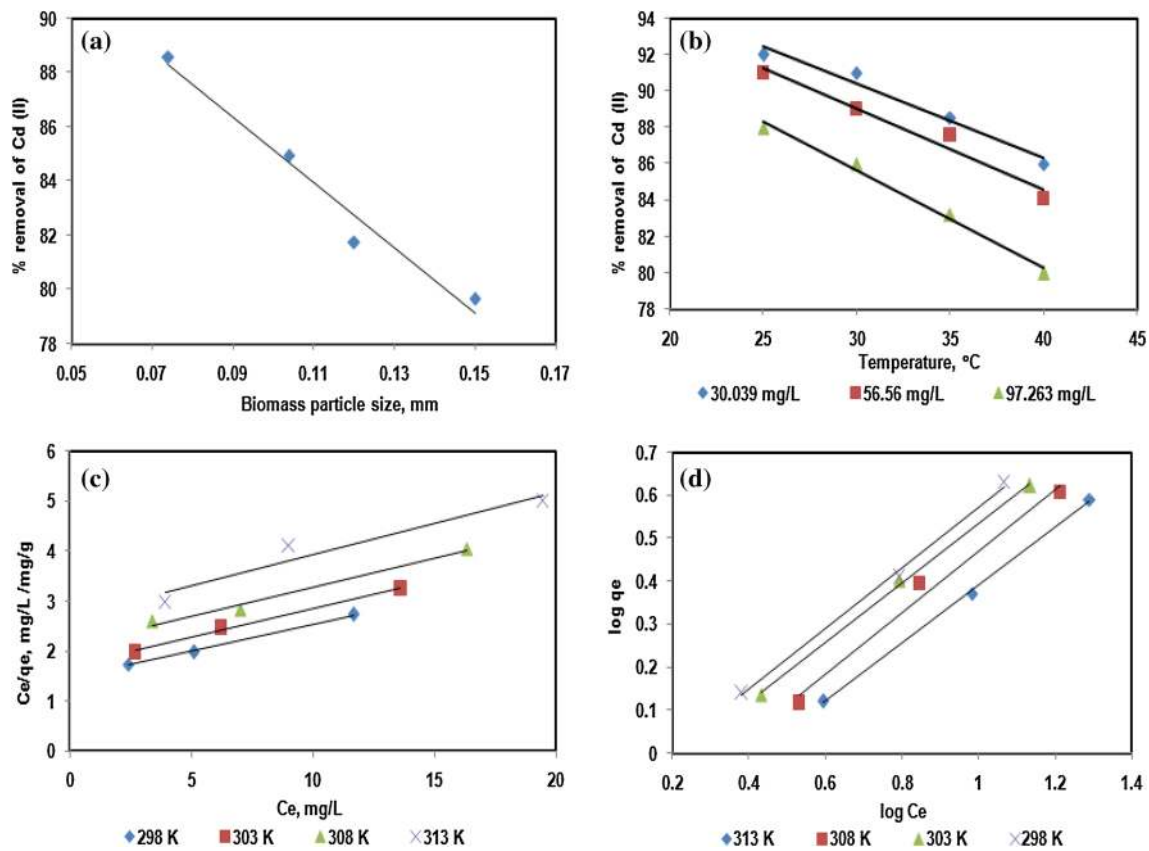


Fig. 2 Effect of biomass particle size using *A. heterophylla* at temp 30°C, pH 4.5 and C_T 30.039 mg L⁻¹ (a), effect of temperature at biomass weight 20 g L⁻¹ and pH 5.5 (b), Langmuir plots at various

temperatures, biomass weight 20 g L⁻¹ and at pH 5.5 (c), Freundlich plots at various temperatures with biomass weight 20 g L⁻¹ and at pH 5.5 (d)

Table 1 Langmuir and Freundlich isotherm model parameters for Cd(II) biosorption on *A. heterophylla*

Temp. (°K)	Langmuir constants			Freundlich constants			Separation factor	
	q_m (mg g ⁻¹)	b (L mg ⁻¹)	r^2	K_F	n_f	r^2	C_0 (mg/L)	R_L
298	9.250	0.157	0.997	0.730	1.408	0.996	30.039	0.0036
308	8.688	0.245	0.985	0.569	1.399	0.985	56.56	0.1008
313	7.905	0.332	0.954	0.521	1.485	0.999	97.263	0.0612

given in Fig. 2c. The Langmuir adsorption constants evaluated from the isotherms at different temperatures with correlation coefficients are presented in Table 1. From the Langmuir isotherm for cadmium, the biosorption affinity constants ‘ b ’ and maximum capacity (q_m) to form a complete monolayer on the surface of the *A. heterophylla* biomass at 25°C were estimated to be 0.1576 (L mg⁻¹) and 9.250 mg g⁻¹, respectively, with R^2 0.997 indicating the present sorption data could be best represented by the Langmuir model. The higher adsorption capacity, q_m ($\gg 1$), indicated the strong electrostatic force of attraction. From the value of b , a dimensionless parameter R_L at different initial metal ion concentrations was calculated and the values are shown in Table 1. Comparison of maximum

metal uptake (q_m) is illustrated in Table 2 for biosorption of cadmium with other biomass.

Freundlich adsorption isotherm was proposed by Boe-decker which was later modified by Freundlich (1926). The Freundlich adsorption equation can be written as:

$$q_e = K_f C_e^{\frac{1}{n_f}} \tag{6}$$

Taking logarithm on both sides

$$\ln q_e = \ln K_f + \frac{1}{n_f} \ln C_e, \tag{7}$$

where ‘ q_e ’ is the equilibrium adsorption capacity (mg g⁻¹), ‘ C_e ’ is the equilibrium concentration of the adsorbate in solution, ‘ K_f ’ and n_f are constants related to the adsorption

Table 2 Comparison of maximum metal uptake (q_m) for biosorption of cadmium with other biomass

Biosorbent	q_m (mg g ⁻¹)	References
<i>Moringa oleifera</i>	1.06	(Sharma et al. 2007)
<i>Juniperus monosperma</i> wood	2.84	(Shin and Rowell, 2005)
Wheat straw	4.25	(Farooq et al. 2011)
Hazelnut shells	5.6	(Cimino et al. 2000)
Corncoobs	8.99	(Vaughan et al. 2001)
<i>Araucaria heterophylla</i>	9.28	Present study

process such as adsorption capacity and intensity, respectively. The plots in Fig. 2d give the Freundlich isotherm for biosorption of Cd⁺² onto the plant *A. heterophylla*. The values of n_f and K_f are found to be (1.40) and (0.730), respectively, at 25 °C. n_f and K_f values at 35, 40 °C were also calculated and are shown in Table 1. This is also suggestive that the metal ion under study could well be separated from its aqueous solution with high adsorption capacity.

Adsorption kinetic models

The kinetic data help in tracing the rate-determining step of transport mechanism. Thus, the kinetics of metal ion sorption is another important parameter for designing sorption systems and is required for selecting optimum operating conditions for full-scale batch or continuous process. In the present study pseudo-first-order and pseudo-second-order kinetic models have been attempted to fit the present biosorption data.

Pseudo-first-order/Lagergren kinetic model

The pseudo-first-order or Lagergren kinetic rate equation for the adsorption of liquid–solid system was derived based on solid adsorption capacity. It is one of the most widely used adsorption rate equations for adsorption of a solute from a liquid solution (Taqvi et al. 2006; Suddhodan and Mishra 2006).

The pseudo-first-order kinetic equation can be expressed as:

$$\frac{dq}{dt} = k_1(q_e - q_t), \quad (8)$$

where ' q_e ' is the amount of solute adsorbed at equilibrium per unit mass of adsorbent (mg g⁻¹), ' q_t ' is the amount of solute adsorbed at any given time ' t ' and ' k_1 ' is the rate constant. Using the boundary conditions and simplifying, Eq. 8 yields:

$$\ln(q_e - q_t) = \ln q_e - k_1 t. \quad (9)$$

' k_1 ' can be computed from the slope of the linear plot between $\ln(q_e - q_t)$ and ' t ' for different adsorption parameters such as pH, temperature, adsorbate concentration, adsorbent

dose, and particle size. The first-order kinetic plots were drawn for Cd⁺² metal using *A. heterophylla* at a given temperature and pH. The pseudo-first-order rate constant k_1 could be obtained from the slope of the plot between $\log(q_e - q_t)$ and time, t . Lagergren pseudo-first-order kinetic plot (Fig. 3a) does not fit well for the adsorption of Cd⁺² *A. heterophylla* as R^2 values are very less than unity and q_e calculated is not coinciding with q_e experimental.

In view of the above, the fitness of the sorption data was tested using pseudo-second-order reaction model. The pseudo-second-order reaction model could be expressed by the rate expression (Ahmet et al. 2008; Ho and McKay 1999, 2000) as:

$$\frac{dq}{dt} = k_2(q_e - q_t)^2. \quad (10)$$

On integration for boundary conditions when $t = 0$ to $t > 0$ and $q_t = 0$ to $q_t > 0$ and further simplifications, Eq. (10) becomes,

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (11)$$

The plots Fig. 3(b) of t/q_t versus t of Eq. (11) gave a linear relationship from which the q_e and k_2 values were determined. The rate constants and the correlation coefficients for pseudo-second-order kinetic model were calculated and are summarized in Table 3. These values showed that the pseudo-second-order kinetic plots fit well the adsorption data of cadmium metal for both the biosorbents. This kinetic model can be aptly proposed to predict the kinetics of adsorption of Cd⁺² on the plant biomass.

Thermodynamic parameters

Gibbs free energy ΔG° is the basic criterion for deciding whether the chemical process does occur/proceed or not. The spontaneity of the reaction can also be judged by the sign and magnitude of ΔG° . A negative sign for ΔG° is an indicative of the spontaneity of any chemical process. To design any chemical process system one should have the knowledge of changes that are expected to occur during chemical reaction. The rate and extent of changes are more informative in the design of process equipment.

In view of the above, analysis has been carried out on the effect of thermodynamic parameters on the biosorption of Cd⁺² on *A. heterophylla* plant biomass. The thermodynamic parameters such as changes in standard free energy change ΔG° , enthalpy ΔH° and entropy ΔS° for any given adsorption process could be determined from the following equations:

$$\Delta G^\circ = -RT \ln K_c, \quad (12)$$

where ΔG° is the free energy change, expressed as J mol⁻¹. K_c is the apparent equilibrium constant for the process. K_c can be derived from:

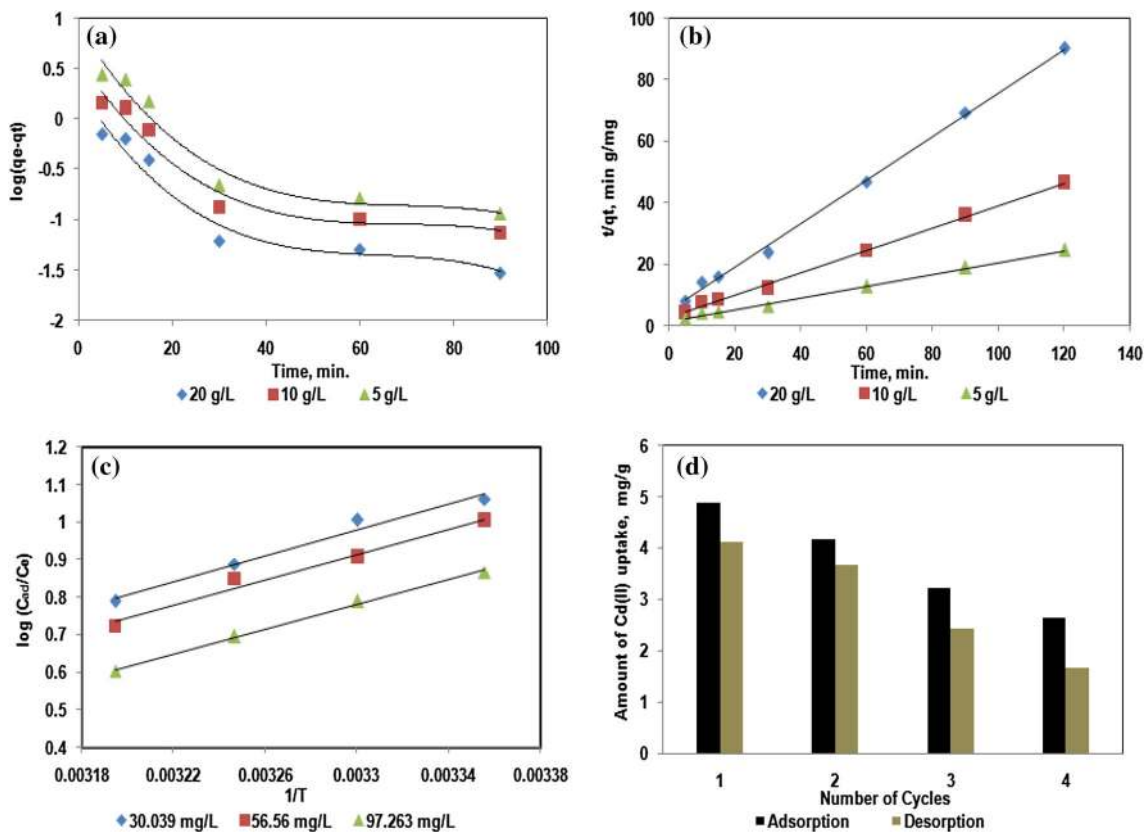


Fig. 3 First-order kinetics of Cd^{+2} on *A. heterophylla* at 30 °C, CT 30.039 mg L^{-1} and pH 4.5 (a), second-order kinetics at 30 °C, CT 30.039 mg L^{-1} and pH 4.5 (b), Van't Hoff plot at biomass weight 20 g L^{-1} and pH 5.5 (c) and desorption cycle of Cd(II) (d)

Table 3 Kinetic parameters for cadmium(II) biosorption on *A. heterophylla*

W (g L^{-1})	K_2 (g/mg-min)	q_e (cal) (mg g^{-1})	q_e (exp) (mg g^{-1})	r^2
5	0.0245	5.227	4.882	0.9969
10	0.0482	2.741	2.574	0.9974
20	0.1024	1.410	1.33	0.9979

$$K_c = \frac{C_{ad}}{C_e}, \quad (13)$$

$$\text{Log} \frac{C_{ad}}{C_e} = -\frac{\Delta H^0}{2.303RT} + \frac{\Delta S^0}{R}, \quad (14)$$

C_{ad}/C_e can be defined as ‘adsorption affinity’. The enthalpy changes (ΔH^0) and entropy changes (ΔS^0) for the adsorption process for Cd^{+2} using *A. heterophylla* for all the initial metal concentrations in the aqueous solutions obtained from the plots of $\text{Log}(C_{ad}/C_e)$ drawn against $1/T$ are shown in Fig. 3c. The calculated thermodynamic data are compiled in Table 4.

Large negative value of ΔG^0 for both the biosorbents indicates the spontaneity of biosorption process at a given temperature. The free energy values increased positively with increase in temperature for the adsorption of Cd^{+2}

which showed that the spontaneity of the biosorption process reduces with increase in temperature. The negative ΔH^0 values indicated exothermic nature of the adsorption. The negative values of ΔS^0 suggested a decrease in the randomness at solid/solution interface during the adsorption of Cd^{+2} ions onto *A. heterophylla*.

Desorption and regeneration

Desorption studies were performed on *A. heterophylla* (4.89 mg g^{-1}) with 2 N HCl (Chen et al. 2005) and maximum 84.45% desorption was achieved (Fig. 3d). In the second cycle, it adsorbed only 85.27% of Cd^{+2} which were desorbed up to 88.1%. In the third cycle, this desorbed biomass adsorbed 77.21% Cd^{+2} , which was desorbed up to 75.46%. The material in the last cycle was 73.29%

Table 4 Thermodynamic parameters for Cd(II) biosorption on *A. heterophylla*

C_0 (mg L ⁻¹)	ΔH° (KJ mol ⁻¹)	ΔS° (J mol ^o K ⁻¹)	ΔG° (KJ mol ⁻¹)	Temp (°K)
30.039	-33.2471	-90.95	-6.144	298
56.56	-32.4123	-89.59	-5.689	303
97.263	-31.5315	-89.12	-5.234	308

adsorbed followed by desorption up to 63.49%. Desorption ratios of *A. heterophylla* were noted as 118.40, 113.62, 132.51 and 157.48 for first, second, third and fourth cycles, respectively. In the fourth cycle desorption ratio was elevated, this may be possibly owed to corroded biomass. Absolute recovery was not attainable, perhaps due to the suitable association of non-electrostatic forces in between the biomass and Cd⁺².

Biomass characterization

FTIR studies

The FTIR differences of spectra in pure plant biomass adsorbent were compared to the spectra obtained in metal ion-loaded (Table 5) plant biomass to determine whether the observed differences are due to the interaction of the metal ions with functional groups (Fig. 4a). The absorption peaks of unloaded biomass and Cd⁺²-loaded plant biomass are tabulated in Table 5 which also explained the functional groups involved in the biosorption process. The broad absorption peak at 3420.21 cm⁻¹ indicates the presence of amino groups (Rajesh et al., 2010; Munagapati et al., 2010) and it is shifted to 3290.94 cm⁻¹, which might be due to the strong interaction with Cd⁺² metal ion. These results indicated the involvement of these functional groups in biosorption process.

The CH₂ stretching vibrations showed characteristic absorption peaks at about 2935.31 cm⁻¹ for unloaded biomass and shifted to 2918.55 cm⁻¹. This may be due to the strong interaction with Cd⁺² metal ion (Fig. 4b). The stretching vibration band (Suleman et al., 2009) 1618.67 cm⁻¹ is due to olefinic C=C and carbonyl C=O stretching and shifted to the 1621.93 cm⁻¹. The band at 1376.07 cm⁻¹ is due to the -CH₂ bending vibrations and the peak shifted to 1375.79 cm⁻¹ for Cd⁺²-loaded biomass. The band at 1238.04 cm⁻¹ is due to the -SO₃ group and the peak shifted very slightly to 1241.32 cm⁻¹ for Cd⁺²-loaded biomass. These results indicated the involvement of these functional groups in biosorption process. The absorption peaks around 1060.91 cm⁻¹ are indicative of P=O stretching and shifted to 1033.49 cm⁻¹.

These functional groups were involved in the chemisorption process. The bands present below 800 cm⁻¹ were finger print zone of phosphate and sulfur functional groups and N-containing bioligands. The appearance of new peaks at 1431.37, 1736.09 and 2850.35 cm⁻¹ was probably due to the modification of the surface functional groups by the interaction of Cd⁺² ions. These band positions revealed the functional groups C=O carboxylic acid of amide, C=O carboxylic acid of alcohol and CH₂ stretching, respectively. The analysis of the FTIR spectra showed the presence of ionizable functional groups (i.e., carboxyl, hydroxyl and amino) that are able to interact with metal ions Cd⁺².

Table 5 Band positions of *A. heterophylla* unloaded and loaded with Cd(II)

Band position cm ⁻¹		Description
Unloaded biomass	Loaded with Cd ⁺²	
3420.21	3290.94	Hydroxyl (-OH) stretching or amine (-NH ₂) stretching
2935.31	2918.55	CH ₂ stretching vibrations
-	2850.35	CH ₂ stretching
-	1736.09	C=O carboxylic acid of alcohol
1618.67	1621.93	Olefinic C=C and carbonyl C=O stretching
-	1431.37	C=O carboxylic acid of amide
1376.07	1375.79	-CH ₂ bending vibrations
1317.42	1317.82	-CH ₂ bending vibrations
1238.04	1241.32	-SO ₃ group
1060.91	1033.49	P=O stretching vibrations
781.20	781.33	N-containing bioligands
604.82	667.09	N-containing bioligands

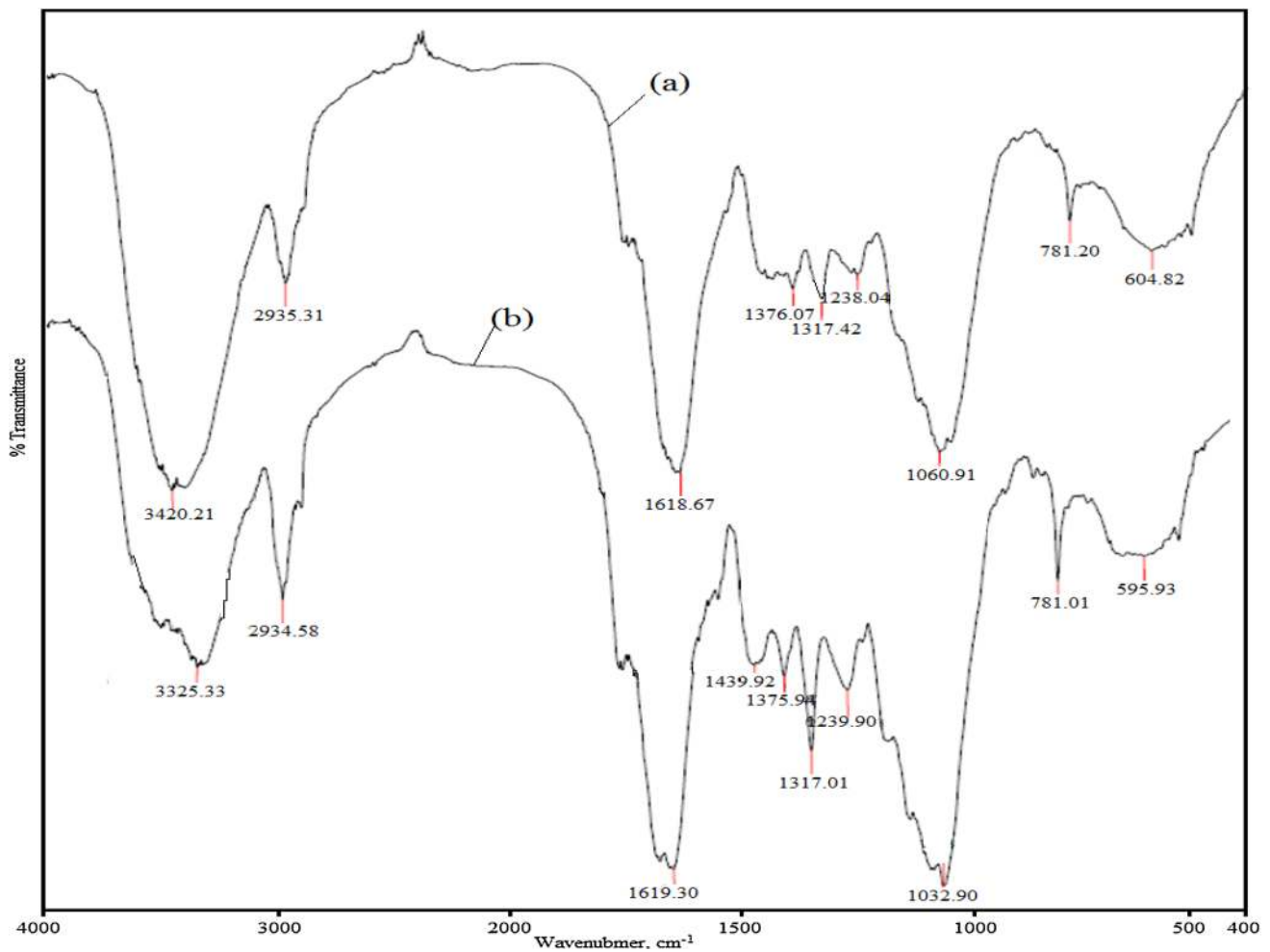


Fig. 4 FT-IR of *A. heterophylla* **a** before and **b** after Cd^{+2} loading

SEM studies

SEM is a useful technique in the study of both the natural sorbent morphology and its modification derived from sorbate interactions. SEM is an electron microscope which provides images of the sample surface by scanning it with a high-energy beam of electrons. The electron interactions with the atoms of the sample produce signals that contain information about topography, morphology, and composition of the sample surface (Valeria et al. 2010). In this investigation, possible mechanisms involved in the sorption of the toxic elements in the biomasses and differences due to the application of the amendments were investigated using scanning electron microscopy. The SEM images were taken by applying 10 kV voltage with different magnification times for the clarification of surface.

The SEM micrographs of *A. heterophylla* plant biomass before and after biosorption are depicted in Fig. 5. It is evident from analysis that the surface areas of plant biomass are uneven, heterogeneous with pores on the surfaces. SEM

images of native biomass (Fig. 5a) show the number of pores with different diameters and different pore areas. The change in morphology indicates the accumulation of liquid phase concentration of charge moieties onto plant biomass surface areas (Fig. 5b). Further, pores facilitate the good possibility for metal ions to be adsorbed. At $500\times$ magnification an uneven surface texture along with lot of irregular surface format was observed. After adsorption, the particles have granular, complex, uneven and porous surface textures that were not found in the native biomass of *A. heterophylla*. Similar results were observed in the case of Cd^{+2} and Cu^{+2} on the surface of *Acacia leucocephala* bark powder (Munagapati et al. 2010).

X-ray diffraction studies

The diffracted X-ray intensities were recorded as a function of 2Θ using copper target, at a scan speed of $1.2^\circ \text{ min}^{-1}$. XRD patterns recorded from 10° to 70° for *A. heterophylla* before and after biosorption are depicted in Fig. 5c, d

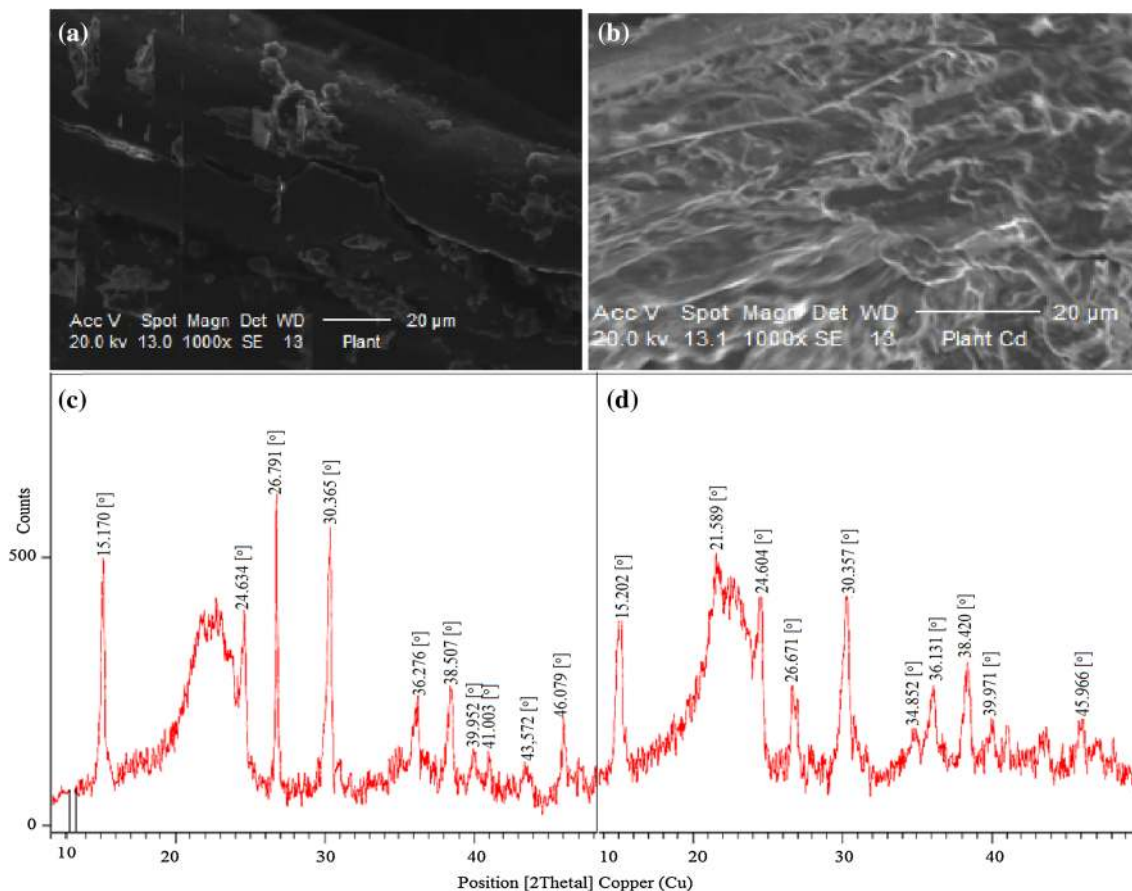


Fig. 5 SEM of *A. heterophylla* (a) before and (b) after Cd^{+2} loading. XRD pattern of the *A. heterophylla* (c) before and (d) after Cd^{+2} loading

which indicates poor crystallinity of pure *A. heterophylla* biomass. Further, the shifts in 2Θ and d-spacing values were observed in Cd^{+2} -loaded biomass (Zhu et al. 2009; Adan et al. 2011). These observations reveal that there was a change in crystallinity of biomass *A. heterophylla* after biosorption.

Conclusions

The percent removal of biosorption was increased from 21.5 to 90.02% for Cd^{+2} at initial metal concentration of 30.294 mg L^{-1} when pH was increased from 2.5 to 5.5. At pH beyond 5.5, the biosorption yield for Cd^{+2} ions showed a rapid decline. The maximum biosorption was found to be 92.01% at pH 5.5. The increase in initial Cd^{+2} from 30.294 to $101.877 \text{ mg L}^{-1}$ increased adsorption capacity (q_e) from 1.382 to 4.279 mg/g . The maximum adsorption capacity (q_m) of the biomass was 9.250 mg/g . The amount of Cd^{+2} adsorbed increases with an increase in adsorbent dosage from 5 to 20 g L^{-1} . About 10–12% decrease in the % adsorption was found with an increase in the particle size by twofold.

The effect of temperature on % removal of Cd^{+2} on *A. heterophylla* decreased from 92 to 86% with increase in temperature in the range of 25–40 °C at initial concentration of 30.039 mg L^{-1} . Both Langmuir and Freundlich equilibrium isotherm models proved to be good fits for the experimental data of Cd^{+2} biosorption on *A. heterophylla* biomass. The kinetics of the biosorption of Cd^{+2} described by a pseudo-second-order kinetic model with R^2 0.999. Free energy change (ΔG°) with negative sign reflects the feasibility and spontaneous nature of the process. The negative enthalpy values indicate exothermic nature and negative entropy value point towards decrease in randomness at solid–liquid interface. The SEM studies showed Cd^{+2} biosorption on selective grains. After adsorption the particles have granular, complex, uneven and porous surface textures that were not found in the native biomass of *A. heterophylla*. The FTIR spectra indicated bands corresponding to –OH, CH_2 stretching vibrations, C=O carbonyl group of alcohol, C=O carbonyl group of amide, P=O stretching vibrations and –CH groups were involved in the biosorption process. The XRD pattern of the *A. heterophylla* showed poor crystallinity of pure biomass. Desorption studies of biomass showed insignificant loss of

adsorption capacity in the third regeneration; hence, the biomass is used for several cycles.

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