



## Biosorption of nickel from aqueous solutions by *Acacia leucocephala* bark: Kinetics and equilibrium studies

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### ABSTRACT

The biosorption of nickel(II) ions from aqueous solution by *Acacia leucocephala* bark was studied in a batch adsorption system as a function of pH, initial metal ion concentration, adsorbent dosage, contact time and temperature. The maximum Ni(II) adsorption was obtained at pH 5. Further, the biosorbents were characterized by Fourier Transformer Infrared Spectroscopy (FTIR). The experimental data were analysed using three sorption kinetic models viz., the pseudo-first- and second-order equations and the intraparticle diffusion model. Results show that the pseudo-second-order equation provides the best correlation for the biosorption process. The equilibrium nature of Ni(II) adsorption at different temperatures of 30, 40 and 50 °C have been described by the Langmuir and Freundlich isotherm models. The equilibrium data fit well Langmuir isotherm. The monolayer adsorption capacity of *A. leucocephala* bark as obtained from Langmuir isotherm at 30 °C was found to be 294.1 mg/g. The Chi-square ( $\chi^2$ ) and Sum of the square errors (SSE) tests were also carried out to find the best fit adsorption isotherm and kinetic model. Isotherms have been used to determine thermodynamic parameters of the process, viz., free energy change ( $\Delta G^\circ$ ), enthalpy change ( $\Delta H^\circ$ ), and entropy change ( $\Delta S^\circ$ ) were calculated indicating that this system was a spontaneous and endothermic process. Present investigation emphasized that *A. leucocephala* bark may be utilized as a low cost adsorbent for nickel removal.

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### 1. Introduction

The heavy and toxic metal contaminants in aqueous waste streams can cause serious water pollution problems being faced the world over. The heavy metals, such as lead, copper, cadmium and nickel are among the most common pollutants found in industrial effluents. The removal of these heavy metals from aqueous environment has received considerable attention in recent years due to their toxicity and carcinogenicity which may cause damage to various systems of the human body. Even at low concentrations, these metals can be toxic to humans [1]. They also can be readily adsorbed by marine animals and directly enter the human food chains, thus presenting a high health risk to consumers [2].

Different methods were investigated and applied to remove nickel ions from water such as adsorption, chemical precipitation, ion exchange, filtration, membrane separation and reverse osmosis [2]. Since these methods are either inefficient or expensive when heavy metals exist in low concentrations, the use of agricultural residues or industrial by-product having biological

activities has been received with considerable attention [3]. In recent years, a number of inexpensive and abundant biosorbents, such as agricultural originating waste biomass [3], woody materials [4], agricultural husk [5], chaff [6,7], rice milling [8], rice husk [9], activated sludge [10], eucalyptus bark [11], etc. were used in heavy metal removal from wastewaters.

Nickel is an essential trace element and is used in the production of several types of alloys and electroplating industries. Toxic action associated with Ni is the inhibition of oxidative enzyme activity. Acute poisoning causes nausea, vomiting, chest pain and rapid respiration. Dermatitis or nickel-itch is common among workers involved in making Ni containing jewellery and those using nickel-plated watches and Ni containing detergents. It is highly carcinogenic and high levels of Ni induce the reduction of nitrogen and impaired growth. The deficiency of Ni in animals results in impaired growth and an increased foetal death rate.

The aim of the present study is to remove nickel from aqueous solution using *Acacia leucocephala* bark as adsorbent material. The effect of various parameters such as pH, initial metal ion concentration, adsorbent dosage, contact time and temperature was studied. The pseudo-first-order, pseudo-second-order and intraparticle diffusion kinetic models were applied to the kinetics of adsorption. The data were fitted to Langmuir and Freundlich isotherm models.

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## 2. Material and methods

### 2.1. Chemical

Analytical grade ammonium nickel sulphate from S.D. Fine Chemicals, Mumbai, India was used as source of nickel(II). Hydrochloric acid and sodium hydroxide used for pH adjustment and for the treatment of bark were obtained from Ranbaxy Fine Chemicals, Mumbai, India and S.D. Fine Chemicals respectively. Bromine, ammonia and dimethyl glyoxime were purchased from S.D. Fine Chemicals. Doubly distilled water was used in all experimental works.

All the experiments were repeated three times and the average values have been reported. Also, blank experiments were conducted to ensure that no adsorption was taking place on the walls of the apparatus used.

### 2.2. Preparation of biosorbent

The *A. leucocephala* bark is collected from Pullampet, Kadapa District, Andhra Pradesh, India. Bark is washed with deionized water to remove dirt particles. The dried bark was ground to fine powder and used as biosorbent without any pretreatment for Ni(II) adsorption.

### 2.3. Batch adsorption studies

The sorption capacity of *A. leucocephala* bark was studied by adding 0.1 g of adsorbent to 100 mL of Ni(II) solutions of different concentrations in 125 mL Erlenmeyer flasks. The flasks, sealed with glass stoppers and para film, were placed in an oscillating shaker and shaken for 4 h at 150 rpm. Initial adsorption experiments showed that this period of time was adequate to ensure equilibrium between nickel adsorbed and nickel unadsorbed. After the equilibrium period, samples were filtered through Whatmann No. 5 filter paper. The first portion of the filtrate was discarded to eliminate the effect of any adsorption of nickel on filter paper.

The concentration of Ni(II) was determined spectrophotometrically by using dimethyl glyoxime as a complexing agent. 2 mL of solution was pipetted into 100 mL standard flask and made up to the mark with bromine water, ammonia solution and dimethyl glyoxime and double distilled water. The concentration of Ni(II) was determined spectrophotometrically at 490 nm.

In order to explore the effect of influencing factors, such as effect of pH, initial metal ion concentration, adsorbent dosage, contact time and temperature of Ni(II), a series of batch experiments were conducted with solutions of initial concentrations of 50, 100, 150, 200 ppm. The pH of the suspension at the start of the experiment was adjusted using 0.1 N HCl and 0.1 N NaOH, after agitating the samples for 4 h. Then the concentration of Ni(II) in the filtrate was determined as discussed earlier. The amount adsorbed per unit mass of adsorbent at equilibrium was obtained using the equation,

$$Q_e = \left( \frac{C_0 - C_e}{m} \right) V \quad (1)$$

where  $Q_e$  (mg/g) was the adsorption capacity at equilibrium,  $C_0$  and  $C_e$  are respectively initial and equilibrium concentrations (mg/L) of nickel(II),  $m$  is the mass of adsorbent in grams and  $V$  is volume of the solution in liters.

## 3. Results and discussion

### 3.1. Fourier transform infrared spectral analysis of adsorbent

The FTIR spectral analysis is important to identify the characteristic functional groups, which are responsible for adsorption of

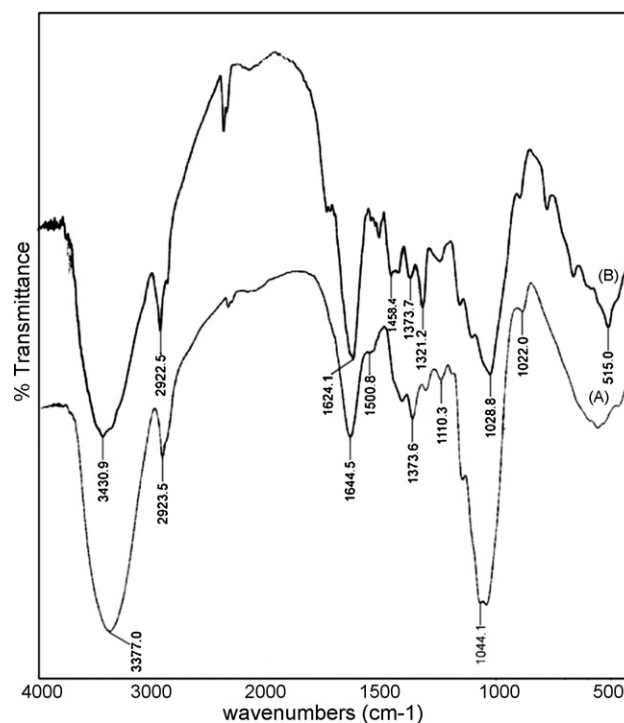


Fig. 1. FTIR spectra of *Acacia leucocephala* bark before adsorption (A) and after adsorption of nickel (B).

metal ions. FTIR spectrum of *A. leucocephala* bark (Fig. 1A) shows distinct peaks at 3377, 2923.5, 1644.5, 1500.8, 1373.6, 1110.3, 1044.1 and 1022  $\text{cm}^{-1}$ . The broad and strong band at 3377  $\text{cm}^{-1}$  may be due to overlapping of  $-\text{OH}$  and  $-\text{NH}$  stretching. The peaks at 1110.3 and 1044.1  $\text{cm}^{-1}$  are assigned to alcoholic  $\text{C}-\text{O}$  and  $\text{C}-\text{N}$  stretching vibration, thus showing the presence of hydroxyl and amine groups on the biomass surface. The strong peak at 1644.5  $\text{cm}^{-1}$  can be assigned to a  $\text{C}=\text{O}$  stretching in carboxyl or amide groups. The bands at 2923.5 and 1500.8  $\text{cm}^{-1}$  are attributed to  $\text{C}-\text{H}$  stretching and  $\text{N}-\text{H}$  bending, respectively. Fig. 1B shows the spectrum of *A. leucocephala* bark after the sorption of nickel. The peak at 1500.8  $\text{cm}^{-1}$  corresponding to  $\text{N}-\text{H}$  bending shifts to the lower frequency (1460  $\text{cm}^{-1}$ ) after nickel uptake. Thus, it can reasonably be concluded that the amino group may be the main adsorption site for nickel attachment on the *A. leucocephala* bark. In addition, the FTIR spectrum shows the shift in peaks at wavenumbers 3377 and 1110.3  $\text{cm}^{-1}$ , which may be attributed to the intensity of  $-\text{OH}$  and  $-\text{NH}_2$  groups with the sorbate. The decrease in the wavenumber of the peak at 1644.5–1624.1  $\text{cm}^{-1}$ , suggests that Ni(II) interacts with carbonyl functional group present in *A. leucocephala* bark. Hence, FTIR spectra reveal that functional groups like  $-\text{NH}_2$ ,  $-\text{OH}$  and  $-\text{C}=\text{O}$  present on the *A. leucocephala* bark surface are involved in nickel adsorption.

### 3.2. Effect of pH

The pH of solution greatly influences metal sorption, and the pH of maximum adsorption optima depends on the nature of the biosorbent and the metal [12–14]. Further, pH influences surface properties of the adsorbent by way of functional group dissociation and also surface charges [15,16]. Adsorption of nickel by *A. leucocephala* bark had been found to increase with increase in pH and reach maximum at 5.0 and then decrease with further increase in pH up to 8.0 (Fig. 2A). The effect of pH was not studied beyond pH 8.0 because of the precipitation of nickel as hydroxide. At low pH, nickel ions and protons compete for binding sites on the adsorbent result-

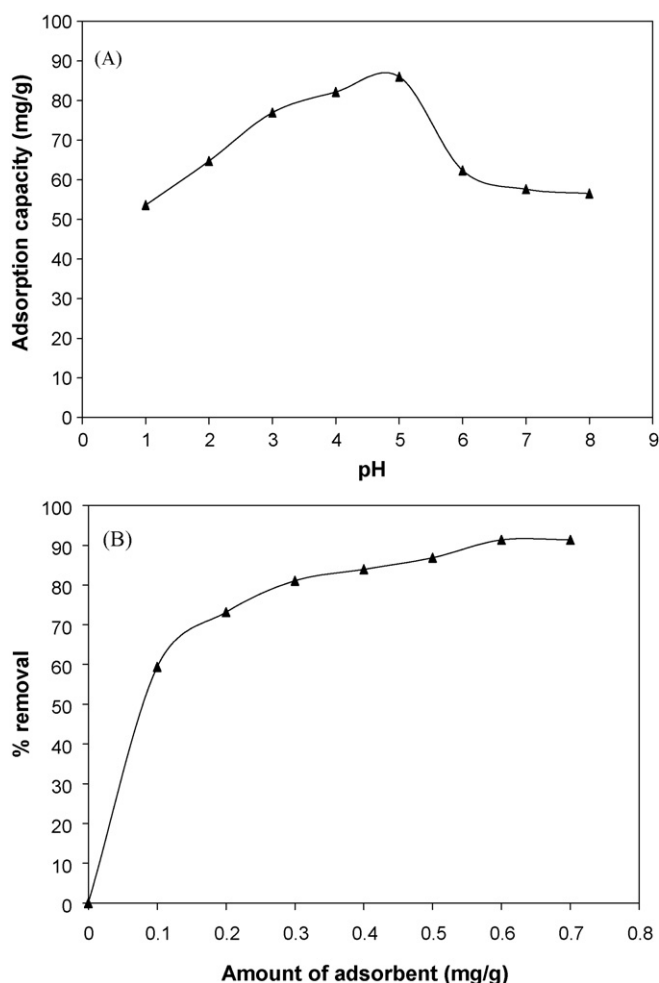


Fig. 2. (A) Effect of pH and (B) amount of *Acacia leucocephala* bark on percent removal of Ni(II).

ing in low adsorption of nickel. It has been suggested that at low pH,  $H_3O^+$  ions are close to the binding sites of the bark and this restricts the approach of nickel ions due to repulsion [17]. With increase in pH, more ligands with negative charges are expected to be exposed and this will attract more positively charged nickel ions for binding. Above the pH of maximum adsorption with decreased in adsorption may be attributed to reduced solubility and precipitation of nickel [18,19].

### 3.3. Effect of sorbent dose

The dependence of adsorption of Ni(II) on the amount of *A. leucocephala* bark is studied at room temperature and at pH 5.0 by varying the adsorbent doses from 0.1 to 0.7 g, while keeping the volume and concentration of the metal solution constant. The results are graphically shown in Fig. 2B. It is apparent that the percent removal of Ni(II) increases rapidly with increase in the dose of adsorbent due to the greater availability of the adsorption sites. Maximum percentage removal is about 91% with *A. leucocephala* bark for Ni(II).

### 3.4. Effect of contact time

The adsorption capacity of *A. leucocephala* bark towards Ni(II) as a function of time at different initial concentration of Ni(II) was studied. Increase in agitation time increases the uptake of metal ions and reaches equilibrium. The equilibrium time is 120 min for *A. leucocephala* bark. The rate of uptake is rapid in the early stages,

gradually decreases and becomes constant when equilibrium is attained. This result is important for considering the treatment of wastewaters and the other similar applications. The data obtained from the experiment was further used to evaluate the kinetic parameters of the adsorption process.

### 3.5. Adsorption kinetics study

The study of adsorption kinetics describes the solute uptake rate and evidently this rate controls the residence time of adsorbate uptake at the solid–solution interface including the diffusion process. The mechanism of adsorption depends on the physical and chemical characteristics of the adsorbents as well as on the mass transfer process [20].

The results obtained from the experiments were used to study the kinetics of metal ion adsorption. The rate kinetics of Ni(II) adsorption on the *A. leucocephala* bark analysed using pseudo-first-order [21], pseudo-second-order [22], and intra-particle diffusion [23] models. The conformity between experimental data and the model predicted values was expressed by correlation coefficients ( $R^2$ ).

#### 3.5.1. Lagergren model

The pseudo-first-order kinetic model was proposed by Lagergren [21]. The linearized form of the model generally expressed as follows:

$$\log(q_e - q_t) = \log q_e - \frac{K_{ad}t}{2.303} \quad (2)$$

where  $q_e$  (mg/g) and  $q_t$  (mg/g) are the amounts of adsorbed metal on the sorbent at the equilibrium and at time  $t$ , respectively, and  $K_{ad}$  is the first order rate constant of adsorption.

#### 3.5.2. Pseudo-second-order model

The kinetics of adsorption process may also be described by pseudo-second-order rate equation [22]. The linearized form of equation is expressed as

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \quad (3)$$

where  $K_2$  (g/(mg min)) is the pseudo-second-order rate constant.

#### 3.5.3. Intra-particle diffusion model

The intra-particle diffusion model is based on the theory proposed by Weber and Morris [23]. According to this theory

$$q_t = K_{id}t^{0.5} + c \quad (4)$$

where  $q_t$  (mg/L) is the amount adsorbed at time  $t$  (min),  $K_{id}$  ( $mg/g \text{ min}^{-0.5}$ ) is the rate constant of intra-particle diffusion.  $C$  is the value of intercept which gives an idea about the boundary layer thickness, i.e. the larger intercept; the greater is the boundary effect. The Weber–Morris plot for adsorption of Ni(II) is given in Fig. 3. If the intra-particle diffusion is the sole rate determining step, the plots of  $q_t$  versus  $t^{0.5}$  should be linear and pass through the origin. The plots in the figure are multi-linear with three distinct regions. The initial curved region corresponds to the external surface uptake, the second stage relates the gradual uptake reflecting intra-particle diffusion as the rate limiting step and final plateau region indicates equilibrium uptake. Based on the results it may be concluded that the intra-particle diffusion is only the rate determining step.

The values of rate constants and correlation coefficients for each model are shown in Table 1. The correlation coefficients  $R^2$ , show that the adsorption process follows pseudo-second-order model. In addition, the sum of the squares of the errors (SSE) was also carried out to support the best fit adsorption model. Lower values of SSE

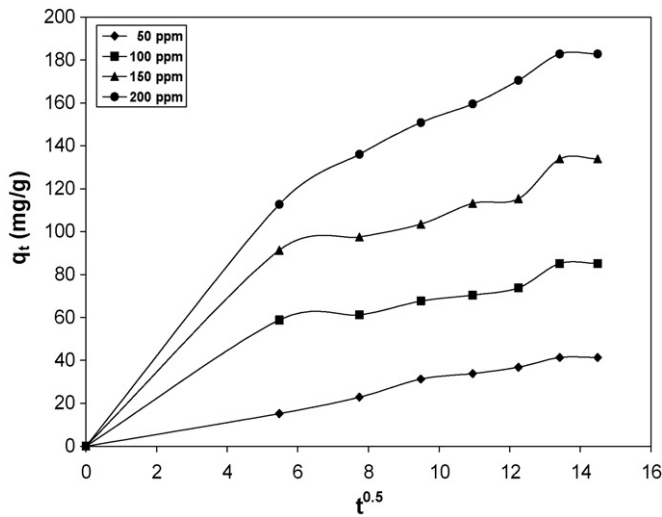


Fig. 3. Weber–Morris model for adsorption of Ni(II) on *Acacia leucocephala* bark.

indicate better fit to sorption data and can give an indication of the sorption mechanism.

$$SSE = \sum \left( \frac{(q_{t,e} - q_{t,m})^2}{q^2} \right) \quad (5)$$

where  $q_{t,e}$  and  $q_{t,m}$  are the experimental sorption capacity of nickel (mg/g) at time  $t$  and the corresponding value which is obtained from the kinetic models. SSE values of reaction-based and diffusion-based kinetic models were computed and summarized in Table 1. It is assumed that the model which gives the lowest SSE values is the best model for this system and then the mechanism of sorption can be explained based on that model. It is observed from Table 1 that pseudo-second-order model gives a better fit than the other two models (pseudo-first-order and intra-particle diffusion models).

### 3.6. Adsorption isotherms

The equilibrium adsorption isotherm is of importance in the design of adsorption systems [24]. The adsorption isotherms for Ni(II) adsorption onto *A. leucocephala* bark at the temperature of 30, 40 and 50 °C are shown in Fig. 4A and B.

The Langmuir treatment, based on the assumption that a maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface, that the energy of adsorption is constant, and there is no transmigration of adsorbate in the plane of the surface [25], is represented by,

$$q_e = \frac{Q_0 b C_e}{1 + b C_e} \quad (6)$$

where  $q_e$  is the amount of metal adsorbed (mg/g),  $C_e$  is the equilibrium concentration of solution (mg/L).  $Q_0$  and  $b$  are Langmuir constants indicating adsorption capacity and energy, respectively. The plots of  $1/C_e$  versus  $1/Q_e$  at different temperatures were found to be linear, this indicates the applicability of the Langmuir model. The parameters  $Q_0$  and  $b$  have been calculated and the values are

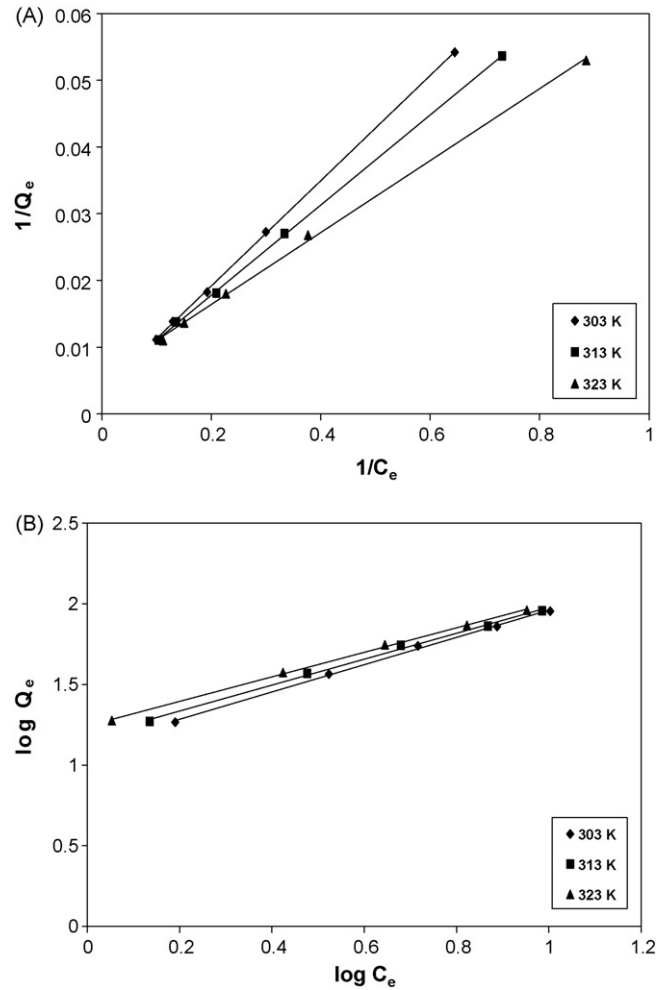


Fig. 4. (A) Langmuir and (B) Freundlich plots for nickel adsorption from aqueous solution on *Acacia leucocephala* bark at different temperatures.

presented in Table 2. The adsorption capacity of *A. leucocephala* bark for Ni(II) uptake found in this work is significantly higher than reported for other biosorbents in literature [26–36] given in Table 3.

The Freundlich equation general form:

$$q_e = K_f C_e^{1/n} \quad (7)$$

where  $K_f$  and  $1/n$  are Freundlich constants related to adsorption capacity and adsorption intensity, respectively. The plots of  $\log C_e$  versus  $\log Q_e$  at different temperatures are found to be linear indicating the applicability of the Freundlich model. The Freundlich parameters are represented in Table 2. The correlation coefficients ( $R^2$ ) and the Chi-square ( $\chi^2$ ) test were also carried out to find the best fit adsorption isotherm model. The equation for evaluating the best fit model is to be written as

$$\chi^2 = \sum \left( \frac{(q_e - q_{e,m})^2}{q_{e,m}} \right) \quad (8)$$

Table 1  
Kinetic parameters for adsorption of Ni(II) by *Acacia leucocephala* bark.

Metal ion	Lagergren first order			Pseudo-second-order			Weber and Morris			
	$K_{ad}$	$R^2$	SSE	$K_2$	$R^2$	SSE	$K_{id}$	$C$	$R^2$	SSE
Ni(II)	0.01	0.9911	0.9993	0.0002	0.9905	0.2085	3.0091	0.0961	0.9887	0.8598
	0.02	0.9704	0.9996	0.0002	0.9885	0.0497	5.3915	13.049	0.8931	0.8774
	0.01	0.9689	0.9999	0.0002	0.9765	0.0131	8.4956	20.201	0.8965	0.7211
	0.01	0.9850	0.9998	0.0002	0.9954	0.0195	12.173	24.601	0.9272	0.7490

**Table 2**  
Langmuir and Freundlich isotherm parameters for the adsorption of Ni(II) on *Acacia leucocephala* bark at different temperatures.

Metal ion	Temperature (K)	Langmuir					Freundlich				
		$Q_0$ (mg/g)	$b$ (L/mg)	$K_L$	$R^2$	$\chi^2$	$K_f$ (mg/g)	$1/n$	$n$	$R^2$	$\chi^2$
Ni(II)	303	294.1	0.039	11.47	0.9998	141.7	13.02	0.846	1.1820	0.998	454.6
	313	232.6	0.062	14.42	0.9998	86.9	14.95	1.1747	0.8513	0.996	380.1
	323	178.6	0.104	18.57	0.9989	42.9	17.49	0.7603	1.3153	0.9989	309.1

where  $q_{e,m}$  is equilibrium capacity obtained by calculating from the model (mg/g) and  $q_e$  is the experimental data of the equilibrium capacity (mg/g). If the data from the model are similar to the experimental data,  $\chi^2$  will be a small number, while if they differ;  $\chi^2$  will be a bigger number. Therefore, it is necessary also to analyse the data set using the non-linear Chi-square test to confirm the best-fit isotherm for the sorption system. The  $\chi^2$  values are calculated using Eq. (8) and are given in Table 2. The  $\chi^2$  values of both the isotherms are comparable and hence the adsorption of nickel(II) follows both Freundlich and Langmuir isotherms and better fits to Langmuir as its  $\chi^2$  value is less than that of Freundlich model.

### 3.7. Thermodynamic parameters

In environmental engineering practice, both energy and entropy factors must be considered in order to determine what processes will occur spontaneously. Gibb's free energy change,  $\Delta G^\circ$ , is the fundamental criterion of spontaneity. Reactions occur spontaneously at a given temperature if  $\Delta G^\circ$  is a negative value. The thermodynamic parameters of  $\Delta G^\circ$ , enthalpy change,  $\Delta H^\circ$ , and entropy change,  $\Delta S^\circ$ , for the adsorption processes are calculated using the following equations for the temperature range 303–323 K;

$$\Delta G^\circ = -RT \ln K_L \quad (9)$$

where  $T$  is the temperature in kelvin and  $R$  is the gas constant ( $8.314 \times 10^{-3}$  kJ/mol K), enthalpy change ( $\Delta H^\circ$ ) calculated from the following equation:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (10)$$

$$\ln K_L = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (11)$$

The plot of  $\ln K_L$  versus  $1/T$  (not shown) gives the straight line from which  $\Delta H^\circ$  and  $\Delta S^\circ$  are calculated from the slope and intercept of the linearized form. Table 4 shows the values of thermodynamic parameters of Ni(II) adsorption on *A. leucocephala* bark. The negative values of  $\Delta G^\circ$  confirms the spontaneity of adsorption process with increasing temperature and the positive value of  $\Delta H^\circ$  suggests that the adsorption is endothermic in nature. The negative value of  $\Delta S^\circ$  shows the increasing randomness at the solid/liquid interface during the sorption of nickel(II) onto *A. leucocephala* bark.

**Table 3**  
Comparison of adsorption capacity *Acacia leucocephala* bark with the biosorbents reported in the literature.

Adsorbent	$Q_0$ (mg/g)	Reference
Cassia fistula (ponds bark)	188.40	[26]
Rice bran	100.00	[27]
Polyporous versicolor	57.00	[28]
Cork biomass	10.10	[29]
Waste of tea factory	18.42	[30]
PAC	31.08	[31]
Cone biomass of Thuja orientalis	12.42	[32]
Enteromorpha prolifera	65.07	[33]
Waste pomace of olive factory	14.80	[34]
Orange (fruit peels)	80.00	[35]
Slag (blast furnace)	55.75	[36]
<i>Acacia leucocephala</i> bark	294.11	Present study

**Table 4**  
Thermodynamic parameters for the adsorption of Ni(II) on *Acacia leucocephala* bark at different temperatures.

Metal ion	Temperature (K)	$\Delta G^\circ$ (kJ/mol)	$\Delta S^\circ$ (kJ/mol K)	$\Delta H^\circ$ (kJ/mol)
Ni(II)	303	-6.147	-0.055	10.389
	313	-6.945	-0.055	
	323	-7.847	-0.056	

## 4. Conclusion

The present study shows that the *A. leucocephala* bark was an effective biosorbent for the adsorption of nickel ions from aqueous solution. The effect of operating parameters such as pH, initial metal ion concentration, adsorbent dosage, contact time and temperature on the extent of adsorption of Ni(II) was evaluated. The maximum uptake of Ni(II) ions occurred at pH 5. Further, the biosorbents were characterized by Fourier Transformer Infrared Spectroscopy (FTIR). Biosorption equilibrium was better described by the Langmuir isotherm model than the Freundlich model. The monolayer biosorption capacity of *A. leucocephala* bark for Ni(II) was found to be 294.1 mg/g ions. Kinetic study of the equilibrium data showed that the biosorption of Ni(II) ions onto *A. leucocephala* bark followed pseudo-second-order kinetic model. The thermodynamic parameters such as free energy change ( $\Delta G^\circ$ ), enthalpy change ( $\Delta H^\circ$ ) and entropy change ( $\Delta S^\circ$ ) were calculated and the adsorption process was endothermic.

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