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Biosorption of Cu(II), Cd(II) and Pb(II) by *Acacia leucocephala* bark powder: Kinetics, equilibrium and thermodynamics

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ABSTRACT

The kinetics, equilibrium and thermodynamics of the biosorption of Cu(II), Cd(II) and Pb(II) onto *Acacia leucocephala* bark powder from aqueous solution were investigated at different experimental conditions. The biosorption characteristics of Cu(II), Cd(II) and Pb(II) ions on the bark powder was investigated with respect to well-established effective parameters including the effect of pH, initial metal ion concentration, biosorbent dosage, contact time and temperature. Optimum adsorption of Cu(II), Cd(II) and Pb(II) took place at pH values of 6.0, 5.0 and 4.0, respectively. Further, the biosorbent was characterized by Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscopy (SEM). The Langmuir and Freundlich equilibrium adsorption models were studied and observed to fit well. The Langmuir model gives a better fit than the Freundlich model. The kinetic studies indicated that the biosorption process of the metal ions followed well pseudo-second-order model. The thermodynamic parameters Gibbs free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) changes were also calculated, and the values indicated that the biosorption process was exothermic and spontaneous. It was concluded that *A. leucocephala* bark powder can be used as an effective, low cost, and environmentally friendly biosorbent for the removal of Cu(II), Cd(II) and Pb(II) ions from aqueous solution.

1. Introduction

Heavy metals can enter a water supply from either industrial activities such as microelectronics, electroplating, battery manufacture, metallurgical, and fertilizer industries or acid rain breaking down soils and releasing heavy metals into streams, lakes, rivers, and groundwater. Heavy metals are taken into the body via inhalation, ingestion, and skin adsorption. Most are extremely harmful to humans, animals and plants mainly because of their accumulation in the body [1–4].

Cadmium is introduced into the water from smelting, metal plating, cadmium–nickel batteries, phosphate fertilizers, mining, pigments, stabilizers, alloy industries and sewage sludge [5]. The harmful effects of Cd(II) include acute and chronic metabolic disorders, such as itai-itai disease, renal damage, emphysema, hypertension and testicular atrophy. Copper is one of the major contaminants emanating from electrical, electroplating, and metal finishing industries. It is often found in high concentrations near mines, landfills and waste disposal sites. In human beings copper toxicity causes itching and dermatization, keratinization of the hands and soles of feet [6,7]. Severe gastro-intestinal irritation and possible changes in the liver and kidney occur due to intake of excessively large doses of copper [8]. Inhalation of copper spray increases the risk of lung cancer among exposed workers [9]. Lead is a particularly hazardous heavy metal because once it gets into human body. It disperses throughout the body immediately and causes harmful effects wherever it lands. For example, it can damage the red blood cells and limit their ability to carry oxygen to the organs and tissues. It can also affect the nervous system, kidneys and hearing [10]. In particular unborn babies and young children are at risk of health problems from lead poisoning because their smaller bodies make them more susceptible to absorbing lead ions. Lead compounds are known as metabolic poison and enzyme inhibitor [11].

The most widely used methods for heavy metal removal from wastewaters include chemical precipitation and filtration, electrochemical treatments, reverse osmosis, ion exchange, evaporation, preconcentration, adsorption and biosorption. Among these methods, biosorption is an emerging and attractive method which involves sorption of dissolved substances by a biomaterial. In addition, the main advantages of this technique can be ordered as follows: the reusability of biomaterial, low operating cost, improved selectivity for specific metals of interest, removal of heavy metals from effluent irrespective of toxicity, short operation

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time, and no production of secondary compounds. In recent years, a number of agricultural and forestry by-products such as rice husk [12], pine bark [13], saw dust [14], technical lignin [15], and cork biomass [16] have been used for heavy metal removal from waters and wastewaters.

Acacia leucocephala's native range through South and Southeast Asia is non-contiguous. Its largest continuous distribution is arid India through Sri Lanka, Bangladesh, Burma and much of Thailand. *A. leucocephala* is an important dry-season fodder and pasture tree throughout its range. Leaves, tender shoots and pods are eagerly eaten by goats, sheep and cattle. All mature *A. leucocephala* put on an annual layer of bark, which contributes to the increasing diameter of the stems. In some species the outermost layer dies and is annually deciduous either in long strips or in variably sized flakes. Due to the high number of *A. leucocephala* trees in India, massive amounts of barks (as waste) are disposed. Various biosorbents were chemically modified to increase the efficiency of metal ion removal. This chemical modification has either been too expensive or it has caused other problems, such as bleeding of excessive quantities of colored organic compounds, odor, or further pollution through the use of toxic chemicals. Hence attempts are made in this study to develop an inexpensive adsorbent for the removal of metal ions from aqueous solutions using *A. leucocephala* bark powder by simple treatment of washing with water.

The aim of the present work was to investigate the possible use of *A. leucocephala* bark powder as an alternative biosorbent material for removal of Cu(II), Cd(II) and Pb(II) ions from aqueous solutions. 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 and equilibrium isotherm models and thermodynamic parameters related with the process were performed.

2. Materials and methods

2.1. Materials

A. leucocephala bark was collected from a local *A. leucocephala* tree near Pullampet, Kadapa District, Andhra Pradesh, India, for the preparation of biosorbent. All the necessary chemicals $Cu(NO_3)_2{\cdot}3H_2O$, $Cd(NO_3)_2{\cdot}4H_2O$ and $Pb(NO_3)_2$ were of analytical grade and obtained from M/S Qualigens Fine Chemicals, Mumbai, India. HCl and NaOH, used to adjust pH, were obtained from S.D. Fine Chemicals, Mumbai, India. H_2SO_4 was used to remove color material from the biosorbent was purchased from S.D. Fine Chemicals, Mumbai, India. Atomic adsorption spectrophotometer (AAS; Model AA 6300, Shimadzu, Japan) was used for determination of Cu(II), Cd(II) and Pb(II) before and after adsorption. The pH of the solution was measured with a Digisun electronics digital pH meter using solid electrode calibrated with standard buffer solutions.

2.2. Preparation of biosorbent

A. leucocephala bark was thoroughly washed with distilled water to remove mud and dirt. Then *A. leucocephala* bark powder was soaked in 0.1N NaOH to remove lignin based color materials followed by 0.1N H_2SO_4. Finally it was washed with distilled water several times and dried in an oven at 80 °C for 6 h and cooled at room temperature in desiccators. The dried bark was ground to fine powder and used as biosorbent without any pretreatment for Cu(II), Cd(II) and Pb(II) adsorption.

2.3. Characterization of biosorbent

Characterization of the biosorbent was carried out by Fourier Transform Infrared Spectroscopy (FTIR; Model 200 series, Thermonicolet, Germany) to determine the type of functional groups on the biosorbent and Scanning Electron Microscopy (SEM; Model Evo15, Carl Zeiss, England) was used to study the surface morphology of the biosorbent.

FTIR shows the main functional groups of *A. leucocephala* bark powder are –COOH, –OH and $–NH_2$. To most adsorbents, the sites responsible for the adsorption process are due to the –COOH, –OH and $–NH_2$:

$$\text{S–COOH} + \text{M}^{n+} \rightarrow \text{S–COOH}^{(n-1)+} + \text{H}^+$$

$$\text{S–OH} + \text{M}^{n+} \rightarrow \text{S–OM}^{(n-1)+} + \text{H}^+$$

$$\text{S–NH}_2 + \text{M}^{n+} \rightarrow \text{S–NM}^{(n-2)+} + 2\text{H}^+$$

where S denotes of the adsorbent surface.

2.4. Preparation of Cu(II), Cd(II) and Pb(II) standards

The stock solutions containing 1000 mg/L of Cu(II), Cd(II) and Pb(II) were prepared by dissolving 3.801 g of $Cu(NO_3)_2{\cdot}3H_2O$, 2.744 g of $Cd(NO_3)_2{\cdot}4H_2O$ and 1.598 g of $Pb(NO_3)_2$. The desired concentrations were prepared from stock solutions for carrying out experiments.

2.5. Batch adsorption studies

In order to explore the effect of pH, contact time, temperature, quantity of adsorbent, and the initial concentration of adsorbate, a series of batch experiments were conducted. Batch adsorption experiments were performed by agitating specified amount of adsorbent in 100 mL of metal solution of desired concentration at varying pH in 125 mL stoppered bottles. The sample was then filtered using Whatman No. 42 filter paper and analyzed for the concentration of metal ions remaining in the solution. The adsorption studies were conducted at 30, 40, and 50 °C. The metal removal efficiency (R) is calculated from Eq. (1):

$$R = \frac{C_i - C_e}{C_i} \times 100 \qquad (1)$$

where C_i and C_e are initial and equilibrium metal concentrations, respectively. The metal uptake capacity, q, can also be calculated from Eq. (2):

$$q = \frac{(C_i - C_e)V}{M} \qquad (2)$$

where q (mg/g) is the adsorption capacity of the biosorbent at any time, M (g) is the adsorbent dosage, and V (L) is the volume of the solution.

3. Results and discussion

3.1. Characterization

FTIR spectra in the range of 4000–400 cm^{-1} for the raw *A. leucocephala* bark powder and the *A. leucocephala* bark powder loaded with Cu(II), Cd(II) and Pb(II) are shown in Fig. 1. The FTIR spectroscopic characteristics are shown in Table 1. FTIR spectral analysis demonstrated the existence negatively charged functional groups (carboxyl, hydroxyl and amine) on the surface of *A. leucocephala* bark powder. The broad band at 3434.8 cm^{-1} in pure bark powder is attributed due to hydroxyl (–OH) stretching or amine ($–NH_2$) stretching of polymeric compounds. This band appeared in the lower region 3409.4–3423.3 cm^{-1} in the FTIR spectra of bark powder loaded with Cu(II), Cd(II) and Pb(II). The C=O stretching of pure bark powder as at 1611.3 cm^{-1}. The IR band of C=O stretching shifted to higher frequency due to involvement of carboxyl

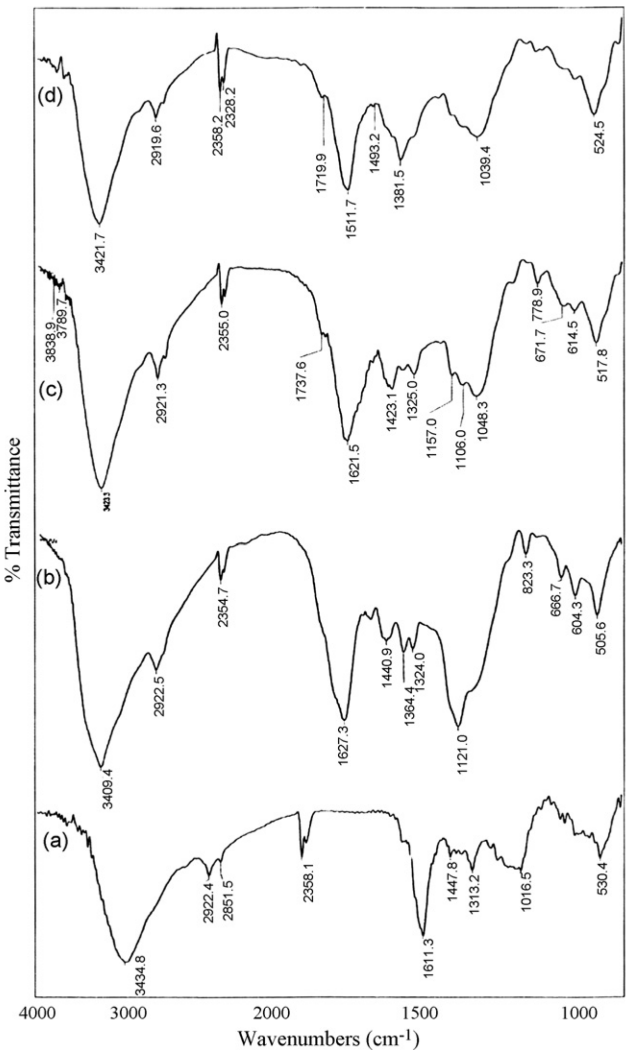

Fig. 1. FTIR spectra of *Acacia leucocephala* bark powder: (a) pure, (b) with Cu(II), (c) with Cd(II), and (d) with Pb(II).

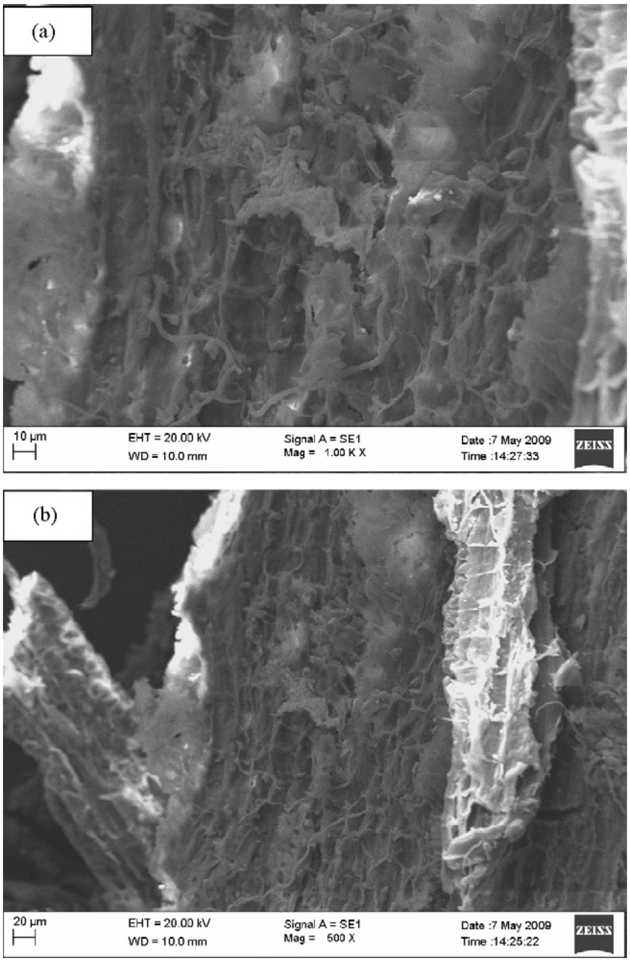

Fig. 2. SEM micrographs of *Acacia leucocephala* bark powder surface: (a) magnification100× and (b) 500× magnification.

(–C=O) group in the adsorption process of metal ions with pure bark powder. The other frequencies which were all most same in all the FTIR spectra of pure bark powder, bark powder loaded with Cu(II), Cd(II) and Pb(II). The $-CH_2$ symmetric stretching vibrations could be ascribed to the bands that appeared in the region 2922.4–2851.5 cm^{-1} and the bands present below 800 cm^{-1} are finger print zone of phosphate and sulphur functional groups. The analysis of the FTIR spectra showed the presence of ionizable functional groups (i.e. carboxyl, hydroxyl and amino) able to interact with protons or metal ions. It considered sufficient to give an idea about the presence of functional groups on the *A. leucocephala* bark powder.

Scanning electro-micrographs (SEM) show the surface texture and morphology of the biosorbent (Fig. 2). It is evident from the micrograph (100×) that the biosorbent has a well-defined rod clusters in net/mat format (100×). At 500× magnification, the single rod of the biosorbent was focused, where an uneven surface texture along with lot of irregular surface format was observed.

Table 1
Wave number (cm^{-1}) for dominant peak from FTIR.

Functional groups of bark powder	Pure bark powder	Bark powder loaded with Cu(II)	Bark powder loaded with Cd(II)	Bark powder loaded with Pb(II)
O–H or NH_2 stretching	3434.8	3409.4	3423.3	3421.7
CH_2 vibration	2922.4	2922.5	2921.3	2919.6
	2851.5	–	–	–
C=O stretching	1611.3	1627.3	1621.5	1611.7
CH bending	1447.8	1440.9	1423.1	1493.2
C–O stretching	–	1121.0	1106.0	–
	1016.5	–	1048.3	1039.4
Finger print –SH, $-PO_4$ functional groups	–	666.7	671.7	–
	–	604.3	614.5	–
	530.4	505.6	517.8	524.5

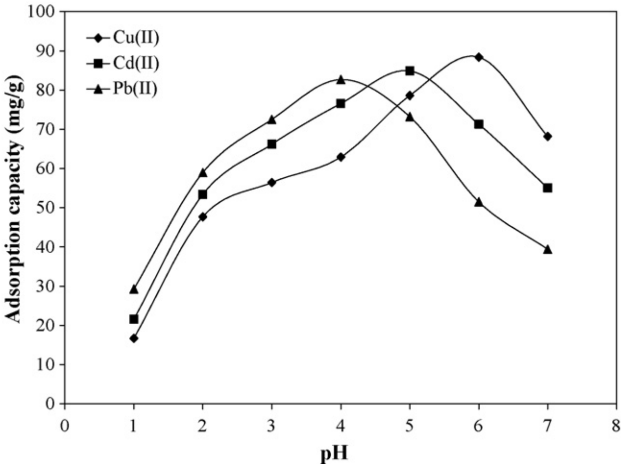

Fig. 3. Effect of pH on the biosorption of Cu(II), Cd(II) and Pb(II) onto *Acacia leucocephala* bark powder. Experimental conditions: for Cu(II): initial conc. 100 mg/L, contact time 4 h, agitation rate 150 rpm. For Cd(II): initial conc. 100 mg/L, contact time 4 h, agitation rate 150 rpm. For Pb(II): initial conc. 100 mg/L, contact time 4 h, agitation rate 150 rpm.

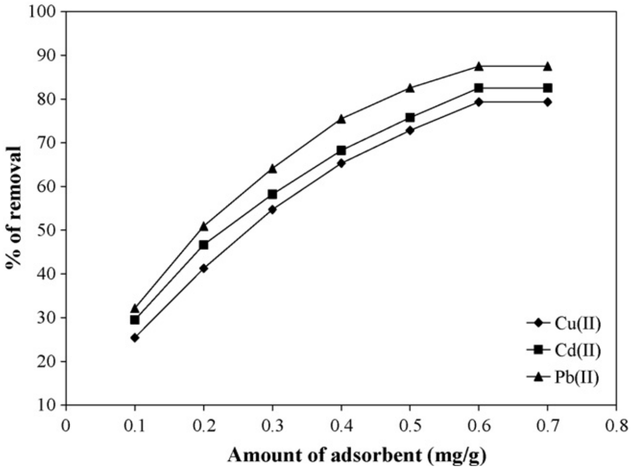

Fig. 4. Effect of biosorbent dosage level on the biosorption of Cu(II), Cd(II) and Pb(II) onto *Acacia leucocephala* bark powder. Experimental conditions: for Cu(II): initial conc. 100 mg/L, contact time 4 h, pH 6.0. For Cd(II): initial conc. 100 mg/L, contact time 4 h, pH 5.0. For Pb(II): initial conc. 100 mg/L, contact time 4 h, pH 4.0.

3.2. *Effect of pH*

The pH has been identified as one of the most important parameter that is effective on metal sorption. It is directly related with competition ability of hydrogen ions with metal ions to active sites on the biosorbent surface [17]. Generally, metal biosorption involves complex mechanisms of ion exchange, chelation, adsorption by physical forces, and ion entrapment in inter and intrafibrillar capillaries and spaces of the cell structural network of a biosorbent [18,19]. The FTIR spectroscopic analysis showed that the *A. leucocephala* bark powder has 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 values of the aqueous solutions these functional groups participate in metal ion bindings. The effect of pH on the biosorption of Cu(II), Cd(II) and Pb(II) ions onto *A. leucocephala* bark powder was studied at pH 1–7 and the results are given in Fig. 3. The maximum biosorption was observed at pH 6.0, 5.0 and 4.0 for Cu(II), Cd(II) and Pb(II), respectively. Therefore, the remaining all biosorption experiments were carried out at this pH values.

The biosorption mechanisms on the bark powder surface reflect the nature of the physicochemical interaction of the solution. At highly acidic pH ($\text{pH} < 1.0$), the overall surface charge on the active sites became positive and metal cations and protons complete for binding sites on cell wall, which results in lower uptake of metal. The biosorbent surface was more negatively charged as the pH solution increased from 1.0 to 6.0. The functional groups of the bark powder were more deprotonated and thus available for the metal ions. Decrease in biosorption yield at higher pH ($\text{pH} > 6$) is not only related the formation of soluble hydroxylated complexes of the metal ions (copper ions in the form of $Cu(OH)_2$, cadmium ions in form of $Cd(OH)_2$, and lead ions in the form of $Pb(OH)_2$) but also to the ionized nature of the cell wall surface of the bark powder under the studied pH.

3.3. *Effect of biosorbent dose on biosorption*

The biosorbent dosage is an important parameter because this determines the capacity of a biosorbent for a given initial concentration. The biosorption efficiency for Cu(II), Cd(II) and Pb(II) ions as a function of biosorbent dosage was investigated (Fig. 4). The percentage of the metal biosorption steeply increases with the biosorbent loading up to 0.6 g/0.1 L. This result can be explained by the fact that the biosorption sites remain unsaturated during the biosorption reaction whereas the number of sites available for biosorption site increases by increasing the biosorbent dose. Moreover, the maximum biosorption, 79.3% for Cu(II), 82.5% for Cd(II) and 87.5% for Pb(II), of the metal ions was attained at biosorbent dosage, 0.6 g/0.1 L. Therefore, the optimum biosorbent dosage was taken as 0.6 g/0.1 L for further experiments.

3.4. *Effect of contact time*

The rate of biosorption is important for designing batch biosorption experiments. Therefore, the effect of contact time on the biosorption of Cu(II), Cd(II) and Pb(II) was investigated. The biosorption yield of Cu(II), Cd(II) and Pb(II) increased considerably until the contact time reached 180 min. Further increase in contact time did not enhance the biosorption, so, the optimum contact time was selected as 180 min for further experiments.

3.5. *Biosorption kinetics*

The prediction of biosorption rate gives important information for designing batch biosorption systems. The Lagergren's pseudo-first-order, pseudo-second-order, and intraparticle diffusion model were performed to the experimental data to clarify the biosorption kinetics of Cu(II), Cd(II) and Pb(II) ions onto *A. leucocephala* bark powder.

The linear form of the pseudo-first-order rate equation by the Lagergren [20] is given as

$$\log(q_e - q) = \log q_e - \frac{K_1}{2.303}t \tag{3}$$

where q_e and q (mg/g) are the amounts of the metal ions sorbed at equilibrium time (mg/g) and t (min), respectively, and K_1 is the rate constant of the equation (min^{-1}). The sorption rate constants (K_1) can be determined experimentally by plotting of $\log(q_e - q)$ vs. t.

Experimental data were also tested by the pseudo-second-order kinetic model which is given in the following form [21]:

$$\frac{t}{q} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e}t \tag{4}$$

where K_2 (g/(mg min)) is the rate constant of the second-order equation, q (mg/g) is the amount of biosorption time t (min) and q_e is the amount of biosorption equilibrium (mg/g). The rate constants (K_2), the R^2 values are also given in Table 2.

Table 2
Parameters of pseudo-first-order, pseudo-second-order, and intraparticle diffusion models. Experimental conditions: for Cu(II): pH: 6.0, initial conc. 100 mg/L. Biosorbent dosage: 0.6 g/0.1 L. For Cd(II): pH: 5.0, initial conc. 100 mg/L. Biosorbent dosage: 0.6 g/0.1 L. For Pb(II): pH: 4.0, initial conc. 100 mg/L. Biosorbent dosage: 0.6 g/0.1 L.

Metal ion	Lagergren first-order			Pseudo-second-order			Weber and Morris		
	K_1 (min^{-1})	R^2	SSE	K_2 (g/(mg min))	R^2	SSE	K_{id} (mg/(g min$^{-0.5}$))	R^2	SSE
Cu(II)	0.02	0.972	0.999	0.0002	0.995	0.106	3.125	0.934	0.873
	0.02	0.990	1.000	0.0002	0.999	0.034	4.913	0.922	0.901
	0.02	0.987	1.000	0.0002	0.999	0.016	6.374	0.919	0.916
	0.02	0.987	1.000	0.0002	0.999	0.015	7.975	0.924	0.921
Cd(II)	0.02	0.988	0.999	0.0005	0.996	0.032	2.478	0.858	0.898
	0.02	0.978	0.999	0.0005	0.999	0.008	3.273	0.848	0.933
	0.01	0.952	0.999	0.0005	0.999	0.004	3.658	0.905	0.950
	0.02	0.932	0.999	0.0005	0.999	0.005	4.268	0.956	0.956
Pb(II)	0.02	0.982	0.999	0.0001	0.992	0.262	3.000	0.971	0.858
	0.01	0.991	0.999	0.0001	0.994	0.112	5.353	0.985	0.873
	0.01	0.988	0.999	0.0001	0.987	0.071	7.151	0.989	0.886
	0.02	0.939	0.999	0.0001	0.996	0.068	9.526	0.963	0.886

The intraparticle diffusion equation is expressed as [22]

$$q = K_{id}t^{0.5} + C \tag{5}$$

where q (mg/g) is the amount adsorbed at time t (min) and K_{id} (mg/(g min$^{-0.5}$)) is the rate constant of intraparticle 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 Cu(II), Cd(II) and Pb(II) is given in Fig. 5. If the intraparticle diffusion is the sole rate determining step, the plots of q vs. $t^{0.5}$ should be linear and passing through the origin. The plots in the figure are multimodal with three distinct regions. The initial curved region corresponds to the external surface uptake, the second stage relates the gradual uptake reflecting intraparticle diffusion as the rate limiting step and final plateau region indicates equilibrium uptake. Based on the results it may be concluded the intraparticle diffusion is only the rate determining step. The values of rate constants and correlation coefficients for each model are shown in Table 2.

As a result, compared to pseudo-first-order and intraparticle diffusion kinetic models, a good correlation coefficient was obtained for pseudo-second-order kinetic model, which indicates that the Cu(II), Cd(II) and Pb(II) biosorption on the bark powder follows pseudo-second-order rate expression.

Table 3
Langmuir and Freundlich isotherm constants and correlation coefficients for the biosorption of Cu(II), Cd(II) and Pb(II) onto *Acacia leucocephala* bark powder at different temperatures.

Metal ion	Temp. (K)	Langmuir					Freundlich			
		q_m (mg/g)	K_L (L/mg)	R^2	χ^2	K_f (mg/g)	1/n	n	R^2	χ^2
Cu(II)	303	147.1	2.94	0.998	43.25	4.35	0.780	1.28	0.998	911.1
	313	135.1	4.05	0.998	33.10	5.24	0.737	1.35	0.993	758.4
	323	131.6	5.26	0.999	27.10	8.01	0.680	1.47	0.985	509.7
Cd(II)	303	166.7	3.83	0.998	58.47	5.22	0.718	1.39	0.986	753.9
	313	147.1	4.71	0.999	40.43	6.24	0.795	1.26	0.989	650.6
	323	131.6	5.92	0.999	27.06	8.01	0.904	1.11	0.985	509.7
Pb(II)	303	185.2	7.41	0.996	57.13	7.47	0.804	1.24	0.987	748.2
	313	156.3	9.38	0.995	33.10	9.48	0.780	1.28	0.997	591.1
	323	144.9	11.6	0.994	23.93	12.23	0.749	1.33	0.999	451.5

Table 4
Comparison of biosorption capacity (mg/g) of *Acacia leucocephala* bark powder for Cu(II), Cd(II) and Pb(II) on different biosorbents in the literature.

Biosorbent	Cu(II)	pH	Cd(II)	pH	Pb(II)	pH	References
Rice husk	29	5–6	–	–	–	–	[26]
Newspaper pulp	30	5.5	–	–	–	–	[27]
Tobacco dust	36	5.5	–	–	–	–	[28]
Saw dust	6.58	–	–	–	21.05	–	[29]
Modified peanut husk	10.15	–	–	–	29.14	–	[29]
Expanded perlite (EP)	8.62	5.0	–	–	13.39	5.0	[30]
Mucor rouxii	–	–	20.31	6.0	–	–	[31]
Pantoea sp.	–	–	52	6.0	–	–	[32]
C. vulgaris	–	–	67	4.0	–	–	[33]
H. splendens	–	–	32.5	5.0	–	–	[34]
Ulva lactuca	–	–	29.2	5.0	34.7	5.0	[35]
Lactarius scrobicu latus	–	–	53.1	5.5	56.2	5.5	[36]
A. niger	–	–	–	–	32.60	4.0	[37]
P. putida	–	–	–	–	180.41	5.5	[38]
C. aphidicola	–	–	–	–	36.91	5.0	[39]
Parmelina tiliaceae	–	–	–	–	75.8	5.0	[40]
Lichen (*C. furcata*)	–	–	–	–	12.3	5.0	[41]
Syzygium cumini L.	–	–	–	–	32.47	6.0	[11]
Acacia leucocephala bark powder	147.1	6.0	167.7	5.0	185.2	4.0	Present study

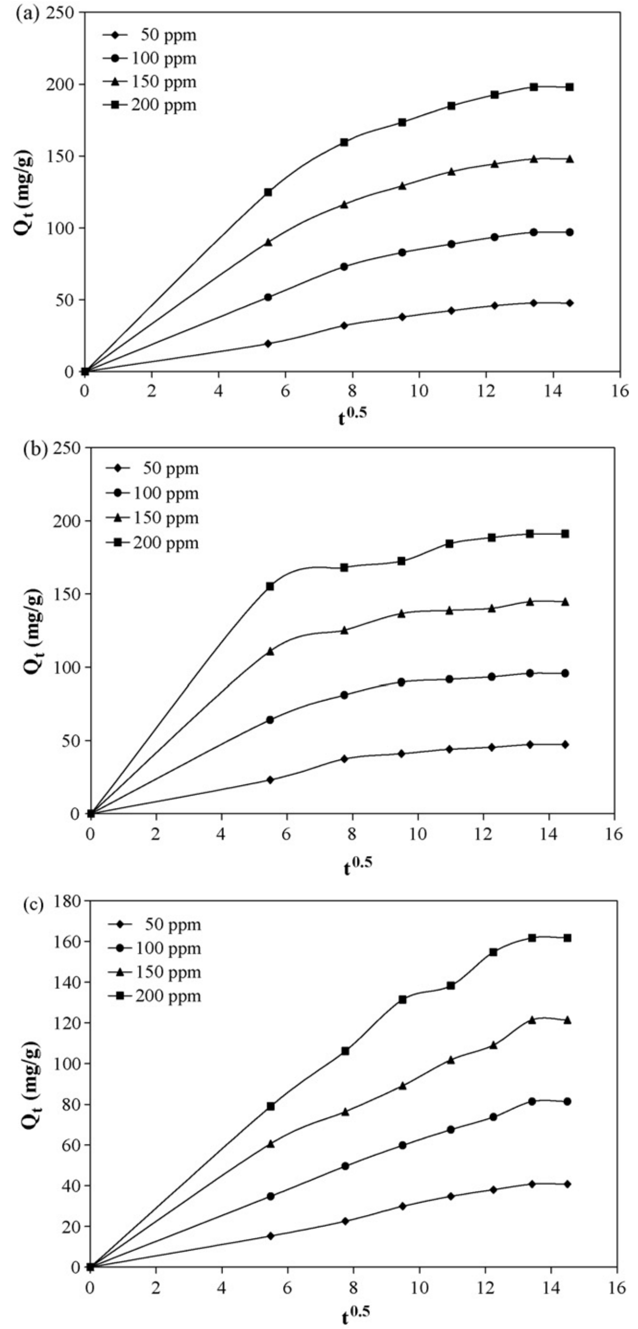

Fig. 5. Weber and Morris plots for the biosorption of (a) Cu(II), (b) Cd(II), and (c) Pb(II) onto *Acacia leucocephala* bark powder. Experimental conditions: for Cu(II): pH 6.0, initial conc. 100 mg/L, biosorbent dosage 0.6 g/0.1 L. For Cd(II): pH 5.0, initial conc. 100 mg/L, biosorbent dosage 0.6 g/0.1 L. For Pb(II): pH 4.0, initial conc. 100 mg/L, biosorbent dosage 0.6 g/0.1 L.

3.6. Fitness of the biosorption kinetic models

The best fit among the kinetic models is assessed by the squared sum of error (SSE) values. It is assumed that the model which gives the lowest SSE values is the best model for metal ion sorption on *A. leucocephala* bark powder. The SSE values were calculated by the equation:

$$\mathrm{SSE} = \sum \frac{(q_{t,e} - q_{t,m})^2}{q_{t,e}^2} \qquad (6)$$

where $q_{t,e}$ and $q_{t,m}$ are the experimental biosorption capacities of metal ions (mg/g) at time t and the corresponding values that are obtained from the kinetic models. SSE values for all the kinetic models are calculated and are summarized in Table 2. Pseudo-second-order model has lower SSE values indicating that the adsorption of Cu(II), Cd(II) and Pb(II) on the biosorbent follows second-order kinetic model.

3.7. Biosorption isotherm models

The capacity of bark powder can be described by equilibrium sorption isotherms which express the surface properties and affinity of the bark powder. In this study, the equilibrium adsorption data were analyzed by both the Langmuir and Freundlich adsorption isotherms.

The Langmuir sorption isotherm has been successfully applied to the biosorption processes of heavy metal ions. The 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 [23–25]:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \qquad (7)$$

where q_e is the equilibrium metal ion concentration on the sorbent (mg/g), C_e is the equilibrium metal ion concentration in the solution (mg/L), q_m is the monolayer sorption capacity of the sorbent (mg/g), and K_L is the Langmuir sorption constant (L/mg) related to the free energy of sorption. Fig. 6 shows the Langmuir plots at different temperature and the constants q_m and K_L are tabulated in Table 3.

On the other hand, Table 4 presents the comparison of biosorption capacity (q_m; mg/g) of *A. leucocephala* bark powder for Cu(II), Cd(II) and Pb(II) ions with that of various biosorbents reported in literature [26–41,11]. The biosorption capacity of *A. leucocephala* bark powder for Cu(II), Cd(II) and Pb(II) is higher than that of the majority of other biosorbents mentioned. Therefore, it can be noteworthy that the *A. leucocephala* bark powder has important potential for the removal of Cu(II), Cd(II) and Pb(II) ions from aqueous solution.

The Freundlich model assumes a heterogeneous sorption surface. The Freundlich model [42] is

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

where K_f is a constant relating the biosorption capacity and $1/n$ is an empirical parameter relating the biosorption intensity, which varies with the heterogeneity of the material. Fig. 7 shows the Freundlich plots at different temperature and the constants K_f and $1/n$ are tabulated in Table 3.

3.8. χ^2 analysis

To identify the suitable isotherm for biosorption of metal ions onto *A. leucocephala* bark powder, the χ^2 analysis is carried out. The mathematical statement for χ^2 analysis is to be written as [43]

$$\chi^2 = \sum \frac{(q_e - q_{e,m})^2}{q_{e,m}} \qquad (9)$$

where $q_{e,m}$ is the equilibrium capacity obtained by calculating from the model (mg/g) and q_e is the experimental data on the equilibrium capacity (mg/g). The χ^2 values are presented in Table 3. If the data from the model are similar to the experimental data, χ^2 will be a small number, while if they differ; χ^2 will be a bigger number. Therefore, it is necessary also to analyze the data set using the non-linear Chi-square test to confirm the best-fit isotherm for the biosorption system. The χ^2 values of both the isotherms are comparable and hence the adsorption of metal ions follows both

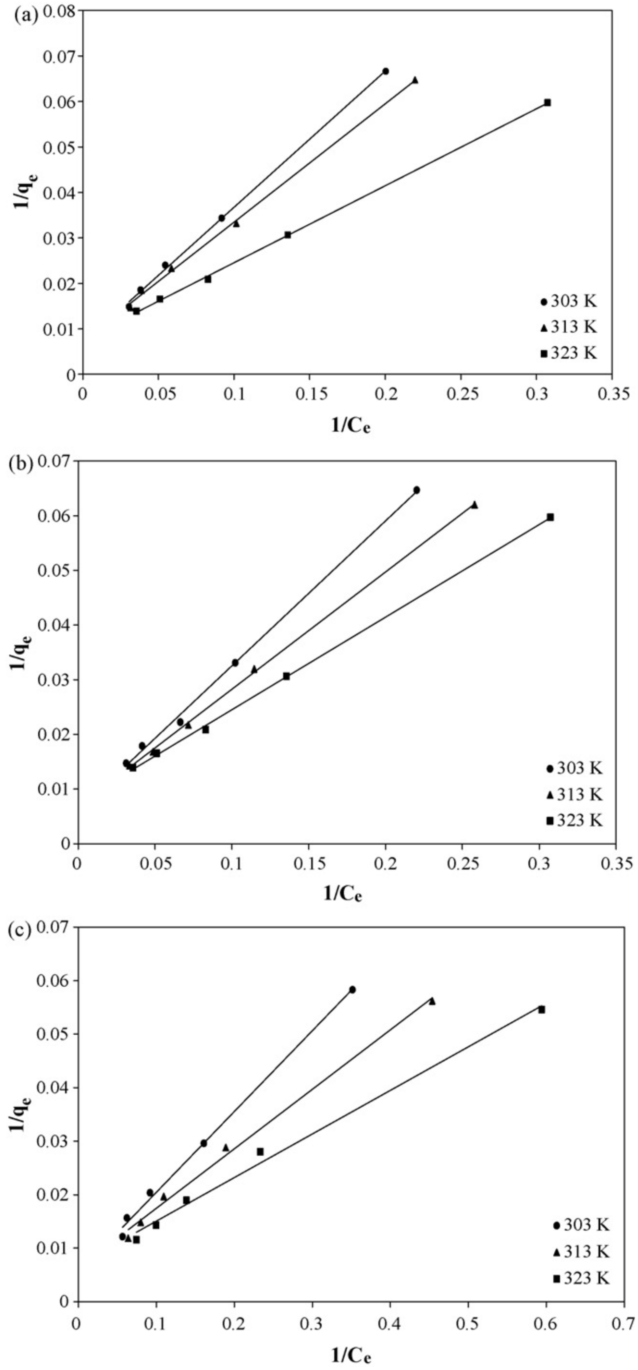

Fig. 6. Langmuir isotherm plots for the biosorption of (a) Cu(II), (b) Cd(II), and (c) Pb(II) onto *Acacia leucocephala* bark powder at different temperatures. Experimental conditions: for Cu(II): pH 6.0, biosorbent dosage 0.6 g/0.1 L. For Cd(II): pH 5.0, biosorbent dosage 0.6 g/0.1 L. For Pb(II): pH 4.0, biosorbent dosage 0.6 g/0.1 L.

Freundlich and Langmuir isotherms and better fits to Langmuir as its χ^2 value is less than that of Freundlich model.

3.9. Biosorption thermodynamics

In order to describe thermodynamic behaviour of the biosorption of Cu(II), Cd(II) and Pb(II) ions onto *A. leucocephala* bark powder, thermodynamic parameters including the change in free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were calculated from following equations:

$$\Delta G^\circ = -RT \ln K_D \tag{10}$$

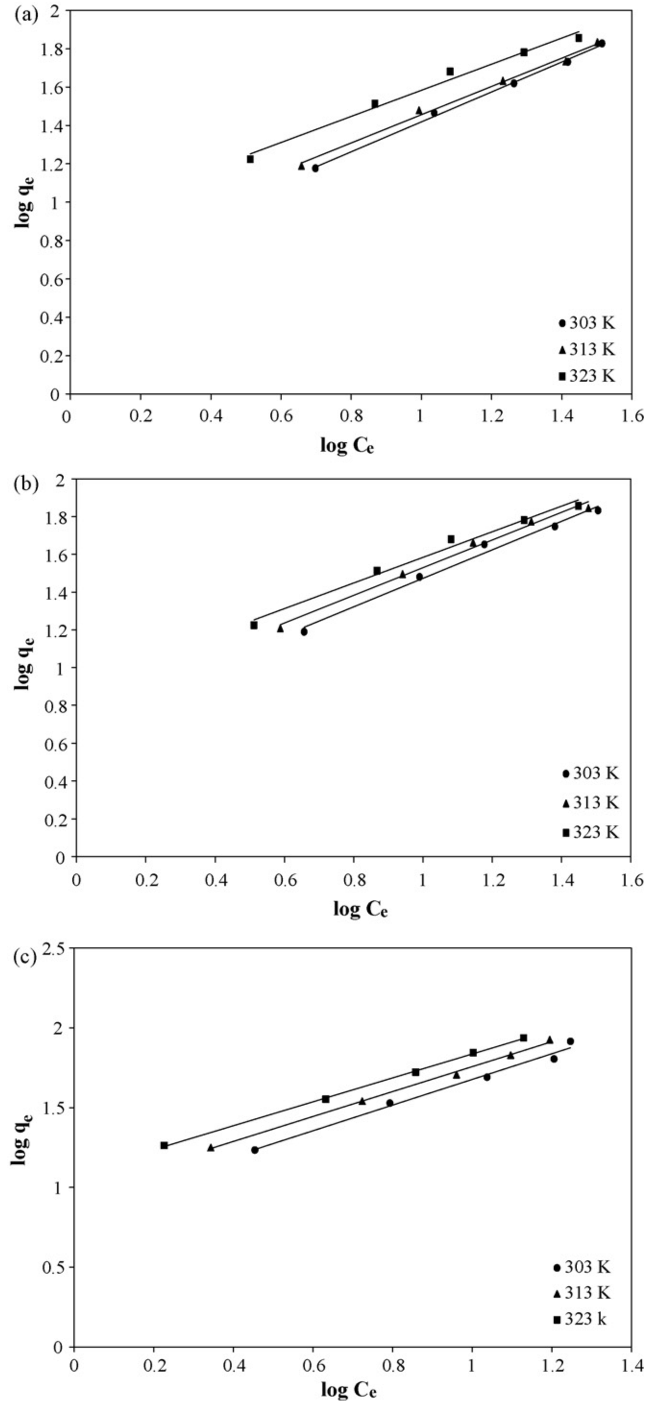

Fig. 7. Freundlich isotherm plots for the biosorption of (a) Cu(II), (b) Cd(II), and (c) Pb(II) onto *Acacia leucocephala* bark powder at different temperatures. Experimental conditions: for Cu(II): pH 6.0, biosorbent dosage 0.6 g/0.1 L. For Cd(II): pH 5.0, biosorbent dosage 0.6 g/0.1 L. For Pb(II): pH 4.0, biosorbent dosage 0.6 g/0.1 L.

where R is the universal gas constant (8.314×10^{-3} kJ/mol K), T is the temperature (K) and K_D (q_e/C_e) is the distribution coefficient [44,45].

The enthalpy (ΔH°) and entropy (ΔS°) parameters were estimated from the following equation:

$$\Delta G^\circ = \Delta H^\circ - T\,\Delta S^\circ \tag{11}$$

Eq. (11) can be written as

$$-RT\ \ln K_D = \Delta H^\circ - T\,\Delta S^\circ \tag{12}$$

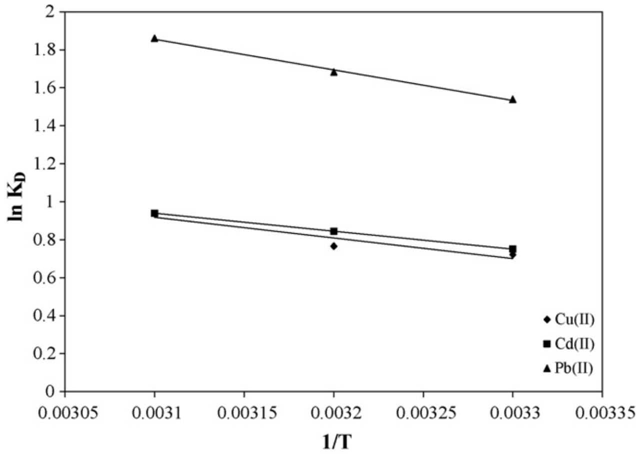

Fig. 8. Plot of $\ln K_L$ vs. $1/T$ for the estimation of thermodynamic parameters for biosorption of Cu(II), Cd(II) and Pb(II) onto *Acacia leucocephala* bark powder.

Table 5
Values of thermodynamic parameters for the biosorption of Cu(II), Cd(II) and Pb(II) ions onto *Acacia leucocephala* bark powder.

Metal ion	Temperature (K)	ΔG° (kJ/mol)	ΔS° (kJ/(mol K))	ΔH° (kJ/mol)
Cu(II)	303	−1.819	−0.036	−12.727
	313	−1.993	−0.036	−13.261
	323	−2.522	−0.036	−14.150
Cd(II)	303	−1.892	−0.032	−11.588
	313	−2.198	−0.032	−12.214
	323	−2.522	−0.032	−12.858
Pb(II)	303	−3.876	−0.057	−21.147
	313	−4.379	−0.057	−22.220
	323	−4.997	−0.057	−23.408

or

$$\ln K_D = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \tag{13}$$

According to Eq. (13), the ΔH° and ΔS° parameters can be calculated from the slope and intercept of the plot of $\ln K_D$ vs. $1/T$ yields, respectively (Fig. 8). The values of ΔG°, ΔH°, and ΔS° for the biosorption of Cu(II), Cd(II) and Pb(II) on the *A. leucocephala* brak powder are given in Table 5. Negative values of ΔH° suggests the exothermic nature of the adsorption and the negative values of ΔG° indicate the spontaneous nature of the adsorption process. However, the negative value of ΔG° decreased with an increase in temperature, indicating that the spontaneous nature of adsorption is inversely proportional to the temperature. The negative values of ΔS° show the increased randomness at the solid/solution interface during the adsorption process.

4. Conclusions

In this study, the use of *A. leucocephala* bark powder as a biosorbent was tested for removing of Cu(II), Cd(II) and Pb(II) ions from aqueous solution. The pH, initial metal ion concentration, biosorbent dosage, contact time, and temperature, were found to have an effect on the biosorption efficiency of Cu(II), Cd(II) and Pb(II). The biosorption capacity of *A. leucocephala* bark powder followed the order Pb(II) > Cd(II) > Cu(II) at optimum conditions of pH 4.0, 5.0, and 6.0. Further, the biosorbent was characterized by Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscopy (SEM) techniques. The kinetic studies revealed that the biosorption process best fit the pseudo-second-order kinetic model. The study on equilibrium sorption revealed that Langmuir isotherm model gave the best fit to experimental data. The calculated thermodynamic parameters showed the exothermic and spontaneous nature of the biosorption of Cu(II), Cd(II) and Pb(II) ion onto *A. leucocephala* bark powder. Thus, it may be concluded that *A. leucocephala* bark powder exhibited the potential for application in treatment of aqueous solutions containing Cu(II), Cd(II) and Pb(II) ions.

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