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Zinc biosorption on *Tectona grandis* L.f. leaves biomass: Equilibrium and kinetic studies

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Abstract

The biosorption of zinc ions from aqueous solution by *Tectona grandis* L.f. was studied in a batch adsorption system as a function of pH, contact time, zinc ion concentration, adsorbent concentration and adsorbent size. The biosorption capacities and rates of zinc ions onto *T. grandis* L.f. were evaluated. The Langmuir, Freundlich, Redlich–Peterson and Temkin adsorption models were applied to describe the isotherms and isotherm constants. Biosorption isothermal data could be well interpreted by the Langmuir model followed by Temkin model with maximum adsorption capacity of 16.42 mg g^{-1} of zinc ion on *T. grandis* L.f. leaves biomass. The kinetic experimental data was properly correlated with the second-order kinetic model. Various thermodynamic parameters such as ΔG°, ΔH°, and ΔS° were calculated indicating that this system was a spontaneous and exothermic process.

Keywords: *Tectona grandis* L.f.; Biosorption; Adsorption isotherm; Kinetic studies; Thermodynamic parameters

1. Introduction

Enhanced industrial activity during recent decades has led to the discharge of unprecedented volumes of wastewater, which is a serious cause of environmental degradation. Heavy metals, due to their high toxicity, pose a serious threat to biota and the environment. The high degrees of industrialization and urbanization have resulted in environmental pollution [1–3]. The presence of heavy metals in the environment is of major concern because of their extreme toxicity and tendency for bioaccumulation in the food chain even in relatively low concentrations [4–6]. Heavy metals pollute the environment from various industries such as metal plating, electroplating, mining, ceramic, batteries, pigment manufacturing [7,8].

In 1978, the United States Environmental Protection Agency (USEPA) prepared a list of organic and inorganic pollutants, which found in wastewater and constitute serious health hazards. The following 13 metals found in this list are antimony, arsenic, beryllium, cadmium, chromium, copper, lead, mercury, nickel, selenium, silver, thallium and zinc [9].

Zinc is one of the most important metal often found in effluents discharged from industries involved in acid mine drainage, galvanizing plants, natural ores and municipal wastewater treatment plants and not biodegradable and travels through the food chain via bioaccumulation. Therefore there is significant interest regarding zinc removal from wastewaters [10] and its toxicity for humans at levels of 100–500 mg/day [11]. World Health Organization (WHO) recommended the maximum acceptable concentration of zinc in drinking water as 5.0 mg L^{-1} [6].

Removal of heavy metals from aqueous solutions by biosorption plays an important role in water pollution control [12]. Biosorption can be defined as the ability of biological materials to accumulate heavy metals through metabolically mediated or physico-chemical pathways of uptake [10]. It has been showed that heavy metals can be removed by inexpensive biological materials such as fungi, bacteria and algae [13–16]. Biosorption is a rapid, reversible, economical and ecofriendly technology in contrast to traditional methods used for removal of heavy metals from aqueous streams such as chemical precipitation and reverse osmosis [17,18].

The present work investigates the potential use of untreated *Tectona grandis* L.f. biomass as metal sorbent for zinc from aqueous solution. *T. grandis* L.f. was chosen as a biosorbent because of the relative lack of information about its sorption

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ability. Environmental parameters affecting the biosorption process such as pH, contact time, metal ion concentration, adsorbent concentration and adsorbent size were evaluated. The equilibrium adsorption data were evaluated by Langmuir, Freundlich, Redlich–Peterson and Temkin isotherm models. Thermodynamic parameters were also evaluated.

2. Materials and methods

2.1. Biosorbent

T. grandis L.f. is a well known for its high-grade timber. Although it is known less for its medicinal properties and uses but in India, its different plant parts are in use as medicine since generations. Leaves simple, opposite, broadly elliptical or obovate, acute or acuminate, coriaceous, possessing minute glandular dots.

2.2. Preparation of biosorbent

The green *T. grandis* L.f. leaves were collected from Andhra University College of Engineering campus of Visakhapatnam, Andhra Pradesh, India. Leaves were washed with deionized water several times to remove dirt particles. The dried leaves of 75–212 μm particle size were used as biosorbent without any pretreatment for zinc adsorption.

2.3. Chemical

Analytical grades of $ZnSO_4 \cdot 7H_2O$, HCl and NaOH were purchased from Merck, India. Zinc (Zn^{2+}) ions were prepared by dissolving its corresponding sulfate salt in distilled water. The pH of solutions was adjusted with 0.1 M HCl and NaOH.

All the experiments were repeated five 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.

2.4. Biosorption experiments

Biosorption experiments were performed in a rotary shaker at 180 rpm using 250 mL Erlenmeyer flasks containing 30 mL of different zinc concentrations. After 3 h of contact (according to the preliminary sorption dynamics tests), with 0.1 g *T. grandis* L.f. leaves biomass, equilibrium was reached and the reaction mixture was centrifuged for 5 min. The metal content in the supernatant was determined using Atomic Absorption Spectrophotometer (GBC Avanta Ver 1.32, Australia) after filtering the adsorbent with Whatman filter paper. The amount of metal adsorbed by *T. grandis* L.f. leaves was calculated from the differences between metal quantity added to the biomass and metal content of the supernatant using the following equation:

$$Q = (C_0 - C_f) \times \frac{V}{M} \tag{1}$$

where Q is the metal uptake (mg g^{-1}), C_0 and C_f are the initial and equilibrium metal concentrations in the solution (mg L^{-1}), respectively, V the solution volume (L), and M is the mass of biosorbent (g). The pH of the solution was adjusted by using 0.1 M HCl and 0.1 M NaOH.

The Langmuir [19] sorption model was chosen for the estimation of maximum zinc sorption by the biosorbent. The Langmuir isotherm can be expressed as:

$$Q = \frac{Q_{\max} b C_f}{1 + b C_f} \tag{2}$$

where $Q_{\max}$ indicates the monolayer adsorption capacity of adsorbent (mg g^{-1}) and the Langmuir constant b (L mg^{-1}) is related to the energy of adsorption. For fitting the experimental data, the Langmuir model was linearized as:

$$\frac{1}{Q} = \frac{1}{Q_{\max}} + \frac{1}{b Q_{\max} C_f} \tag{3}$$

The Freundlich [20] model is represented by the equation:

$$Q = K C_f^{1/n} \tag{4}$$

where K (mg g^{-1}) is the Freundlich constant related to adsorption capacity of adsorbent and n is the Freundlich exponent related to adsorption intensity. For fitting the experimental data, the Freundlich model was linearized as follows:

$$\ln Q = \ln K + \frac{1}{n} \ln C_f \tag{5}$$

The Redlich–Peterson [21] model is represented by the equation:

$$q_e = \frac{A C_e}{1 + B C_e^{g}} \tag{6}$$

where A (L g^{-1}) and B (L mg^{-1}) are the Redlich–Peterson isotherm constants and g is the Redlich–Peterson isotherm exponent, which lies between 0 and 1. The linearized form of equation is given by:

$$\ln\left(\frac{A C_e}{q_e} - 1\right) = g \ln(C_e) + \ln(B) \tag{7}$$

Redlich–Peterson isotherm equation contains three unknown parameters A, B and g. Therefore a minimization procedure is adopted to maximize the coefficient of determination, between the theoretical data for q_e predicted from the linearized form of Redlich–Peterson isotherm equation and the experimental data.

The Temkin [22] isotherm has generally been applied in the following form:

$$q_e = \frac{RT}{b_T} \ln(A_T C_e) \tag{8}$$

where A_T (L mg^{-1}) and b_T are Temkin isotherm constants.

2.5. Biosorption kinetics

The kinetics studies were carried out by conducting batch biosorption experiments with different initial zinc concentrations. Samples were taken at different time periods and analysed for their zinc concentration.

3. Results and discussion

3.1. The effect of contact time

The data obtained from the biosorption of zinc ions on the *T. grandis* L.f. showed that a contact time of 180 min was sufficient to achieve equilibrium and the adsorption did not change significantly with further increase in contact time. Therefore, the uptake and unadsorbed zinc concentrations at the end of 180 min are given as the equilibrium values (q_e, mg g^{-1}; C_e, mg L^{-1}), respectively (Fig. 1).

3.2. Effect of pH

It is well known that the pH of the medium affects the solubility of metal ions and the concentration of the counter ions on the functional groups of the biomass cell walls, so pH is an important parameter on biosorption of metal ions from aqueous solutions [23–27].

T. grandis L.f. presents a high content of ionizable groups (carboxyl groups from mannuronic and guluronic acids) on the cell wall polysaccharides, which makes it, very liable to the influence of the pH. As shown in Fig. 2, the uptake of zinc increased with the increase in pH from 2.0 to 5.0 and then decreased with increasing pH from 5.0 to 10.0. Similar results were also reported in literature for different biomass systems [28–30]. At pH values lower than 2.0 zinc removal was inhibited, possibly as a result of the competition between hydrogen and zinc ions on the sorption sites, with an apparent preponderance of hydrogen ions, which restricts the approach of metal cations as in consequence of the repulsive force. As the pH increased, the ligands such as carboxylate groups in *T. grandis* L.f. would be exposed, increasing the negative charge density on the biomass surface, increasing the attraction of metallic ions with positive charge and allowing the biosorption onto the cell surface.

Above pH 5, insoluble zinc hydroxide starts precipitating from the solution, so that adsorption rate was decreased [31]. In this study, these zinc cations at around 5 would be expected to interact more strongly with the negatively charged binding sites in the adsorbent. As a result, the optimum pH for zinc adsorption was found as 5 and the other adsorption experiments were performed at this pH value.

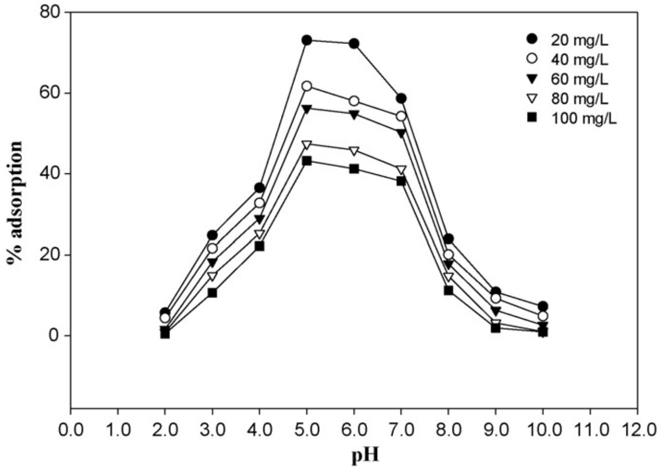

Fig. 2. Effect of pH on zinc adsorption by *Tectona grandis* L.f. for 20–100 mg L^{-1} of metal and 0.1 g/30 mL of biomass concentration.

3.3. Effect of metal ion concentration

Fig. 3 shows the effect of metal ion concentration on the adsorption of zinc by *T. grandis* L.f. The data shows that the metal uptake increases and the percentage adsorption of zinc decreases with increase in metal ion concentration. This increase (4.3868–12.9702 mg g^{-1}) is a result of increase in the driving forces, i.e. concentration gradient. However, the percentage adsorption of zinc ions on *T. grandis* L.f. was decreased from 73.11% to 43.23%. Though an increase in metal uptake was observed, the decrease in percentage adsorption may be attributed to lack of sufficient surface area to accommodate much more metal available in the solution. The percentage adsorption at higher concentration levels shows a decreasing trend whereas

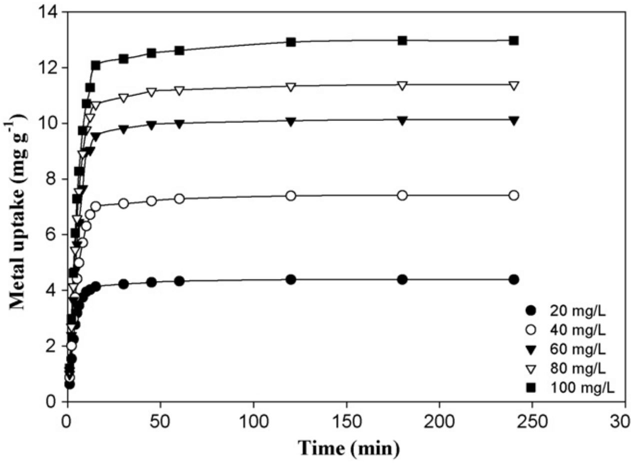

Fig. 1. Effect of contact time on zinc metal uptake by *Tectona grandis* L.f. for 20–100 mg L^{-1} of metal and 0.1 g/30 mL of adsorbent concentration.

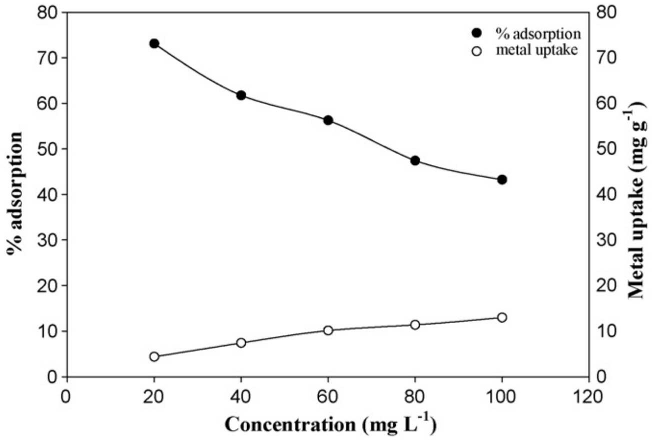

Fig. 3. Effect of initial metal concentration on the adsorption of zinc by *Tectona grandis* L.f.

the equilibrium uptake of zinc displays an opposite trend. At lower concentrations, all zinc ions present in solution could interact with the binding sites and thus the percentage adsorption was higher than those at higher zinc ion concentrations. At higher concentrations, lower adsorption yield is due to the saturation of adsorption sites. As a result, the purification yield can be increased by diluting the wastewaters containing high metal ion concentrations.

3.4. *Effect of adsorbent concentration*

Fig. 4 shows the effect of adsorbent concentration on the % removed at equilibrium conditions. It was observed that the amount of zinc adsorbed varied with varying adsorbent concentration. The amount of zinc adsorbed increases with an increase in adsorbent concentration from 0.1 to 0.5 g. The percentage zinc removal was increased from 73.11% to 82.62% for an increase in biomass concentration from 0.1 to 0.5 g at initial concentration of 20 mg L^{-1}. The increase in the adsorption of the amount of solute is obvious due to increasing biomass surface area. Similar trend was also observed for zinc removal using *Ulva fasciata* sp. as adsorbent [31].

3.5. *Effect of adsorbent size*

The effect of different adsorbent particle sizes on metal uptake is investigated and showed in Fig. 5. It reveals that the metal uptake of zinc on *T. grandis* L.f. decrease from 4.3866 to 3.2568 with the increased particle size from 75 to 212 μm at an initial concentration of 20 mg L^{-1}. The smallest size obtained was 75 μm due to the limitation of available grinder configuration. It is well known that decreasing the average particle size of the adsorbent increases the surface area, which in turn increases the adsorption capacity.

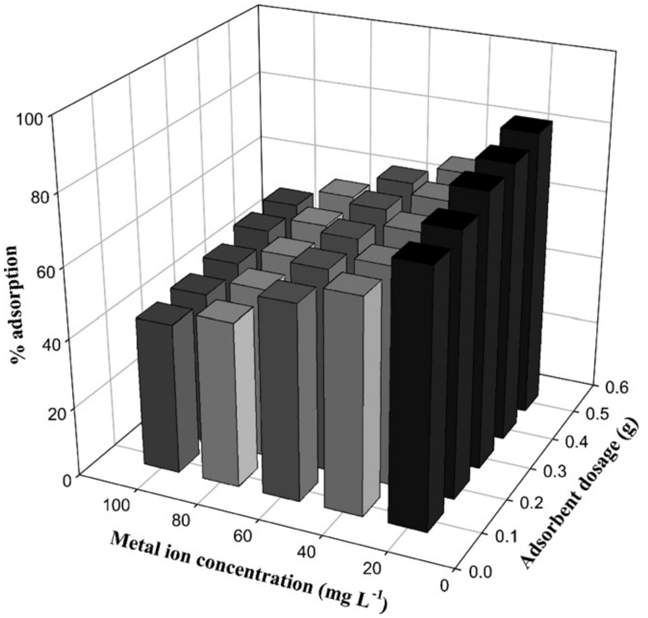

Fig. 4. Effect of *Tectona grandis* L.f. dosage on adsorption of zinc.

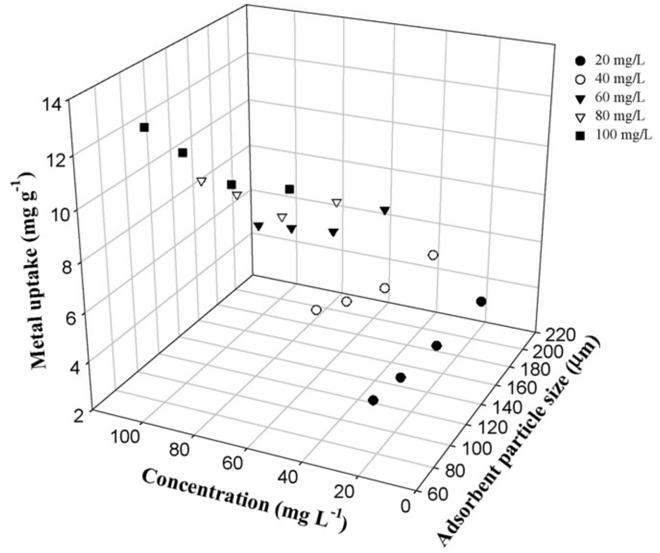

Fig. 5. Effect of *Tectona grandis* L.f. particle size on adsorption of zinc for 20–100 mg L^{-1} of metal and 0.1 g/30 mL of biomass concentration.

3.6. *Biosorption equilibrium*

The equilibrium biosorption of zinc on the *T. grandis* L.f. as a function of the initial concentration of zinc is shown in Figs. 6–10. There was a gradual increase of adsorption for zinc ions until equilibrium was attained. The Langmuir, Freundlich models are often used to describe equilibrium sorption isotherms and Redlich–Peterson and Temkin models are also applied to describe equilibrium sorption isotherms. The calculated results of the Langmuir, Freundlich, Redlich–Peterson and Temkin isotherm constants are given in Table 1.

It is found that the adsorption of zinc on the *T. grandis* L.f. was correlated well with the Langmuir equation and Temkin equation as compared to Freundlich and Redlich–Peterson equations under the concentration range studied. Examination of the Freundlich and Redlich–Peterson data shows that these two isotherms are not modeled as well across the concentration range studied.

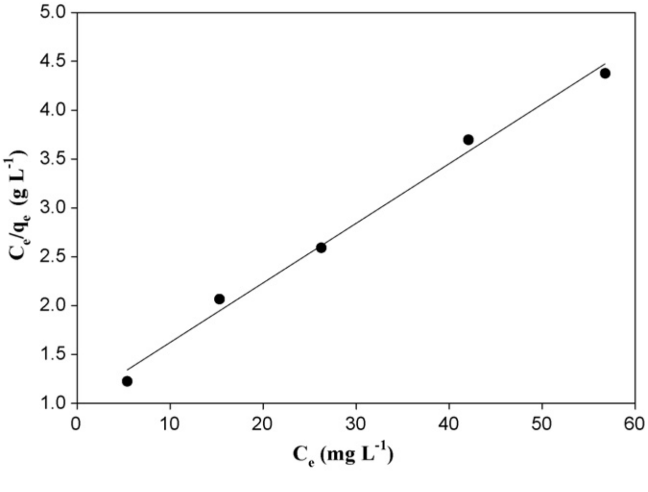

Fig. 6. Langmuir adsorption isotherm for zinc at 0.1 g/30 mL of biomass concentration.

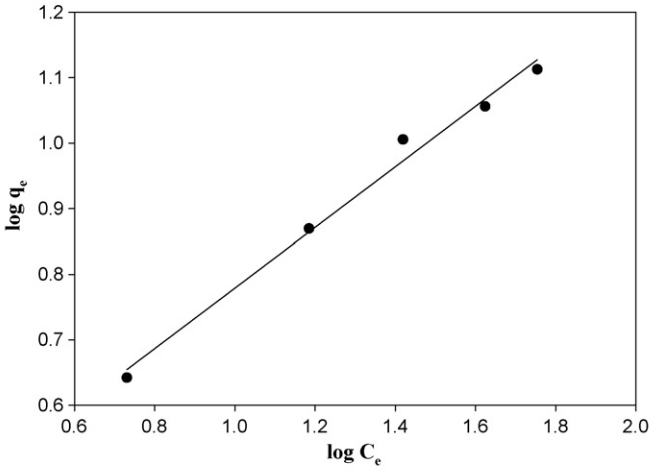

Fig. 7. Freundlich adsorption isotherm for zinc at 0.1 g/30 mL of biomass concentration.

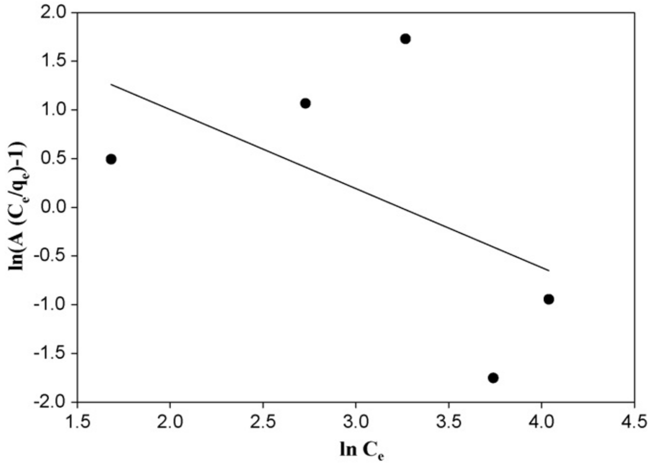

Fig. 8. Redlich–Peterson adsorption isotherm for zinc at 0.1 g/30 mL of biomass concentration.

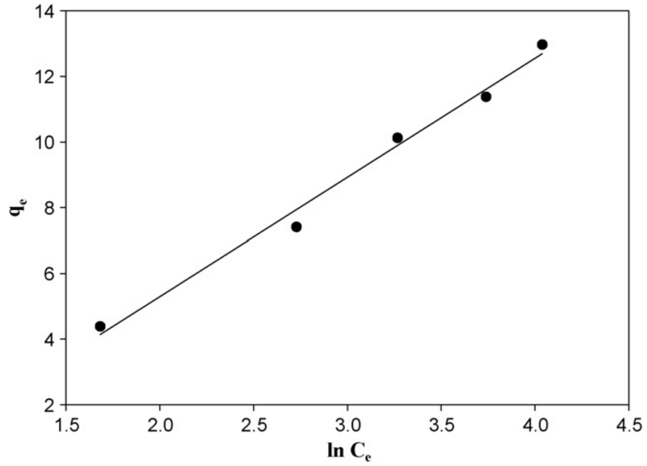

Fig. 9. Temkin adsorption isotherm for zinc at 0.1 g/30 mL of biomass concentration.

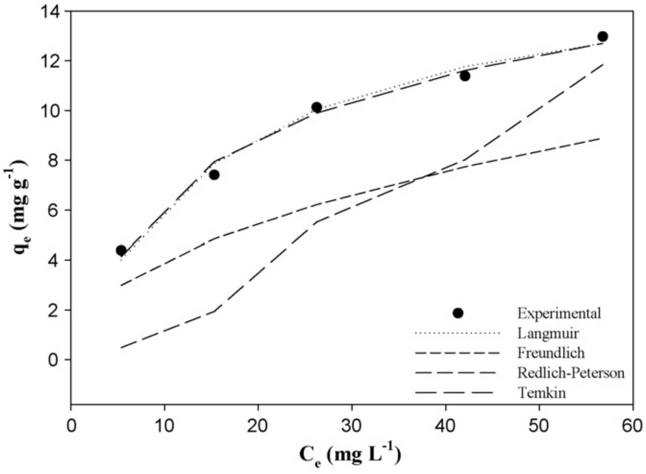

Fig. 10. Equilibrium curves for zinc onto *Tectona grandis* L.f.

3.7. Kinetics of adsorption

The prediction of adsorption rate gives important information for designing batch adsorption systems. Information on the kinetics of solute uptake is required for selecting optimum operating conditions for full-scale batch process. Fig. 1 shows the plot between amount adsorbed, q_e (mg g^{-1}) versus time, t (min) for different initial solute concentrations. From the figure it was observed that q_e value increased with increase in initial zinc concentration. The adsorption rate within the first 5 min was observed to be very high and thereafter the reaction proceeds at a slower rate till equilibrium and finally a steady state was obtained after equilibrium. The saturation time was found to be 180 min based on the initial metal concentration. The kinetics of the adsorption data was analysed using two kinetic models, pseudo-first order and pseudo-second order kinetic model. These models correlate solute uptake, which are important in predicting the reactor volume. These models are explained as follows.

Table 1
Langmuir, Freundlich, Redlich–Peterson and Temkin isotherm constants and correlation coefficients

Tectona grandis L.f.	
Langmuir	
Q (mg g^{-1})	16.42
b (L mg^{-1})	0.06
R^2	0.9918
Freundlich	
K_f (mg g^{-1})	1.3724
n	0.4623
R^2	0.9887
Redlich–Peterson	
A (L g^{-1})	0.3174
B (L mg^{-1})	13.77
g	−0.8099
R^2	0.2751
Temkin	
A_T (L mg^{-1})	0.5818
b_T	694.05
R^2	0.9886

3.7.1. The pseudo-first order equation

The pseudo-first order equation of Lagergren and Kungliga [32] is generally expressed as follows:

$$\frac{\mathrm{d}q_{\mathrm{t}}}{\mathrm{d}t} = k_1(q_{\mathrm{e}} - q_t) \tag{9}$$

where q_{e} and q_t are the sorption capacities at equilibrium and at time t, respectively (mg g^{-1}) and k_1 is the rate constant of pseudo-first order sorption (1 min^{-1}). After integration and applying boundary conditions, $q_t = 0$–q_t at $t = 0$–t; the integrated form of Eq. (9) becomes:

$$\log(q_{\mathrm{e}} - q_t) = \log(q_{\mathrm{e}}) - \frac{k_1}{2.303}t \tag{10}$$

In order to fit Eq. (10) to experimental data, the equilibrium sorption capacity (q_{e}), must be known. The pseudo first order rate constant k_1 can be obtained from the slope of plot between $\log(q_{\mathrm{e}} - q)$ versus time, t. The pseudo first order rate constant k_1 values and their corresponding linear regression correlation coefficient values are shown in Table 2. The linear regression correlation coefficient values R_1^2 found in the range of 0.7178–0.8585, which shows that this model can be applied to predict the adsorption kinetic model.

3.7.2. The pseudo-second order equation

If the rate of sorption is a second order mechanism, the pseudo-second order chemisorption kinetic rate equation is expressed as:

$$\frac{\mathrm{d}q_t}{\mathrm{d}t} = k_2(q_{\mathrm{e}} - q_t)^2 \tag{11}$$

where q_{e} and q_t are the sorption capacity at equilibrium and at time t, respectively (mg g^{-1}) and k_2 is the rate constant of pseudo-second order sorption, (g mg^{-1} min^{-1}). For the boundary conditions $q_t = 0$–q_t at $t = 0$–t; the integrated form of Eq. (11) becomes:

$$\frac{1}{q_{\mathrm{e}} - q_t} = \frac{1}{q_{\mathrm{e}}} + k_2 t \tag{12}$$

which is the integrated rate law for a pseudo-second order reaction. Eq. (12) can be rearranged to obtain:

$$q_t = \frac{t}{(1/k_2 q_{\mathrm{e}}^2) + (t/q_{\mathrm{e}})} \tag{13}$$

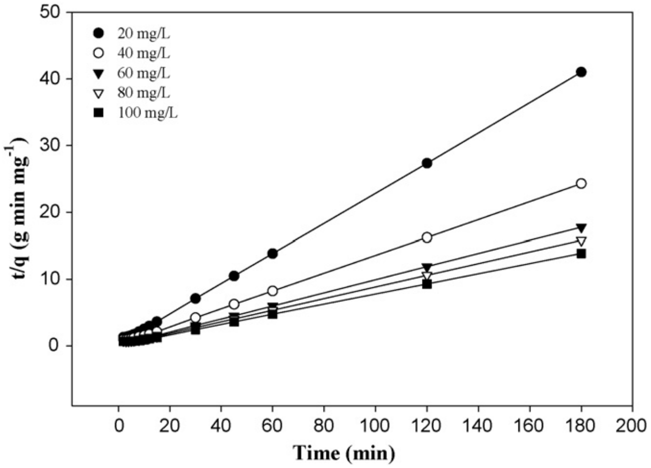

Fig. 11. Pseudo-second order kinetics for zinc onto *Tectona grandis* L.f.

which has linear form:

$$\frac{t}{q_t} = \frac{1}{kq_{\mathrm{e}}^2} + \frac{1}{q_{\mathrm{e}}}t \tag{14}$$

where t is the contact time (min), q_{e} (mg g^{-1}) and q_t (mg g^{-1}) are the amount of the solute adsorbed at equilibrium and at any time, t. Eq. (14) does not have the problem of assigning as effective q_{e}. If pseudo-second order kinetics are applicable, the plot of t/q_t against t of Eq. (14) should give a linear relationship, from which q_{e} and k_2 can be determined from the slope and intercept of the plot (Fig. 11) and there is no need to know any parameter beforehand.

The pseudo-second order rate constant k_2, the calculated q_{e} value and the corresponding linear regression correlation coefficient values R_2^2 are given in Table 2. At all initial copper concentrations, the linear regression correlation coefficient R_2^2 values were higher and ranged from 0.9993 to 0.9998. The higher R_2^2 values confirm that the adsorption data are well represented by pseudo-second order kinetics and supports the assumption behind the model that the adsorption is due to chemisorption.

A comparison of the maximum capacity $Q_{\max}$ of *T. grandis* L.f. with those of some other adsorbents reported in literature is given in Table 3. Differences of metal uptake are due to the properties of each adsorbent such as structure, functional groups and surface area.

Table 2
Kinetic constants for zinc onto *Tectona grandis* L.f.

Initial concentration in present study (20–100 mg L^{-1})	Pseudo-first order			Pseudo-second order		
	Rate constant, k_1	Amount of zinc adsorbed on adsorbent, q_{e} (mg g^{-1})	Correlation coefficient, R_1^2	Rate constant, k_2	Amount of zinc adsorbed on adsorbent, q_{e} (mg g^{-1})	Correlation coefficient, R_2^2
20	0.0642	1.2232	0.8108	0.0966	4.5537	0.9998
40	0.049	1.5558	0.8585	0.0346	7.9113	0.9996
60	0.0474	1.7732	0.8002	0.0203	11.0864	0.9994
80	0.0447	1.8428	0.7998	0.0198	12.3	0.9993
100	0.0428	2.0499	0.8369	0.0165	13.9275	0.9994

Table 3
Maximum adsorption capacities for zinc adsorption to different adsorbents

Adsorbent material	Operating conditions					Reference
	Adsorption capacity (mg g^{-1})	pH	Temperature (°C)	Initial concentration range (mg L^{-1})	Biomass (g L^{-1})	
Activated carbon	31.11	4.5	25	1–1000	4.0	[34]
Streptoverticillium cinnamoneum	21.3	5.5	28	50–1000	2.0	[35]
Fontinalis antipyretica	12 ± 1[a]	5.0	5	100	2.0	[36]
Aspergillus niger 405	4.70	5.0	25	10	10.0	[37]
Mucor rouxii (live)	4.89	5.0	n.a.	10	n.a.	[38]
Mucor rouxii (NaOH pre-treated)	5.63	5.0	n.a.	10	n.a.	[38]
Mucor rouxii (Na_2CO_3 pre-treated)	3.26	5.0	n.a.	10	n.a.	[38]
Mucor rouxii ($NaHCO_3$ pre-treated)	6.28	5.0	n.a.	10	n.a.	[38]
Phanerochaete chrysosporium[b]	39.0	7.0	25	30–600	n.a.	[39]
Sargassum sp.	24.35	4.5	30	98	4.0	[40]
Animal bones	11.55	5.0	20	15–79	4.0	[41]
Tectona grandis L.f.	16.42	5.0	30 ± 1 °C	20	0.1	Present study

[a] S.D. of the mean.
[b] Ca-alginate immobilized.

3.8. 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, ΔG°, is the fundamental criterion of spontaneity. Reactions occur spontaneously at a given temperature if ΔG° is a negative value. The thermodynamic parameters of ΔG°, enthalpy change ΔH°, and entropy change, ΔS° for the adsorption processes are calculated using the following equations for the temperature range of 303–333 K:

$$\Delta G^\circ = -RT \ln K_\mathrm{a} \qquad (15)$$

$$\Delta G^\circ = \Delta H^\circ - T\,\Delta S^\circ \qquad (16)$$

$$\ln K_\mathrm{a} = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \qquad (17)$$

where R is the universal gas constant (8.314 J mol^{-1} K^{-1}) and T is the absolute temperature in K. Enthalpy change ΔH° and entropy change ΔS° are determined from the slope and intercept of the plot $1/T$ versus $\ln K_\mathrm{a}$ (not shown). The free energy changes for the zinc adsorption to *T. grandis* L.f. was determined by using the equilibrium constants obtained from Langmuir isotherm model. The $-\Delta G^\circ$ and $T\Delta S^\circ$ values at different temperatures (303, 313, 323 and 333 K) are given in Table 4.

The values of ΔH° and ΔS° for the adsorption process were calculated to be −4.454 kJ mol^{-1}, and 54.08 kJ mol^{-1} K^{-1}, respectively. The negative value of ΔG° confirms the feasibility of the process and the spontaneous nature of sorption with a high preference for zinc to adsorb onto *T. grandis* L.f. The value of ΔH° was negative, indicating that the sorption reaction is exothermic. A similar result was also obtained for the lead adsorption on *Azadirachta indica* leaf powder [33]. The positive value of ΔS° shows the increasing randomness at the solid/liquid interface during the sorption of zinc onto *T. grandis* L.f.

Table 4
ΔG° and $T\Delta S^\circ$ values for the adsorption of zinc ions at different temperatures and at pH 5.0

Temperature (K)	K_a (L mg^{-1})	$-\Delta G^\circ$ (kJ mol^{-1})	$T\Delta S^\circ$ (kJ mol^{-1})
303	0.0600	11.94	16.39
313	0.0570	12.48	16.93
323	0.0520	13.02	17.47
333	0.0518	13.56	18.01

4. Conclusions

The present study shows that the *T. grandis* L.f. was an effective biosorbent for the adsorption of zinc ions from aqueous solution. The biosorption capacity of *T. grandis* L.f. was superior due to the higher content of hydroxyl and amine groups. The effect of process parameters like pH, metal ion concentration, adsorbent concentration and adsorbent size on process equilibrium were studied. The uptake of zinc ions by *T. grandis* L.f. was increased by increasing the metal ion concentration and the adsorbent concentration and decreased by increasing the adsorbent size. The uptake was also increased by increasing pH up to 5 and then decreased by increasing pH from 5 to 10. The adsorption isotherms could be well fitted by the Langmuir equation followed by Temkin equation. The biosorption process could be best described by the second-order equation. The thermodynamic parameters such as ΔG°, ΔH° and ΔS° were calculated and the adsorption process was exothermic.

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