Equilibrium and kinetic studies for the biosorption system of copper(II) ion from aqueous solution using *Tectona grandis* L.f. leaves powder

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Abstract

The biosorption of copper(II) ions from aqueous solution by *Tectona grandis* L.f. was studied in a batch adsorption system as a function of pH, metal ion concentration, adsorbent concentration and adsorbent size. The biosorption capacities and rates of copper(II) 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 with maximum adsorption capacity of 15.43 mg/g of copper(II) ion on *T. grandis* L.f. leaves powder. The kinetic experimental data 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.
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Keywords: Tectona grandis L.f.; Biosorption capacities; Biosorption rates; Adsorption isotherm

1. Introduction

Due to their extreme toxicity, metal ions are nowadays among the most important pollutants both in surface water and in ground water. Since levels of metals in the environment have increased because of industrial pollution [1,2], the elimination of such ions from water is essential to protect public health. In addition, these toxic elements can seriously affect plants and animals, causing a large number of afflications.

Traditional technologies for heavy metal removal, including ionic exchange and precipitation, are frequently inefficient and or expensive when applied for removal of metal ions in low concentrations. New technologies with acceptable costs are necessary to reduce the concentration of heavy metals in the environment to acceptable levels. Biosorption, the passive non-metabolically mediated process of metal ion binding by living or dead biomass has a great potential to reach these objectives [3,4]. The discovery and the development of biosorption is the base of a new technology of heavy metal removal from dilute solutions (1–100 mg/l) [5]. Compared with traditional technologies, biosorption has advantages such as the high purity of treated wastewater and the use of cheap raw material as biosorbents. These may be waste products from others industries (e.g. fermentation by-products) or naturally abundant biomass (e.g. marine algae) [6].

Biosorption is a process that utilizes inexpensive biomass to sequester toxic heavy metals and is particularly useful for the removal of contaminants from industrial effluents [7,8]. Compared with conventional methods for removing toxic metals from industrial effluents, such as precipitation with lime, ion exchange and precipitation with biosulphide (H_2S produced by sulphate-reducing bacteria), the biosorption process offers several advantages, such as low operating cost, minimization of the volume of chemical and/or biological sludge to be disposed of, high efficiency in detoxifying very dilute effluents and no nutrient requirements. These advantages are the primary incentives for developing full-scale biosorption processes to clean up heavy metal pollution [9].

Living and dead microbial cells are able to remove heavy metal ions from aqueous solutions. Uptake of heavy metal ions

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by microorganisms may offer an alternative method for their removal from wastewater [9]. Metal ion uptake by biomass is believed to occur through interactions with functional groups that are native to the proteins, lipids, and carbohydrates that make up the cell wall. To maximize the efficiency of the biomass, the identity of the functional groups responsible for metal binding is very important. The information obtained from these determinations would be useful for future attempts at chemically or biosynthetically altering the biomass to enhance the adsorption capacity to selectively adsorb specific metal ions. The identity of the functional groups would also be helpful for determining the mechanisms responsible for the binding of targeted metal ions.

Copper is essential to human life and health but, like all heavy metals, is potentially toxic as well. The excessive intake of copper results in its accumulation in the liver and produces gastrointestinal problems, kidney damage, anemia and continued inhalation of copper-containing sprays is linked with an increase in lung cancer among exposed workers [10,11]. For these reason US EPA has regulated drinking water concentrations not to exceed 1.3 ppm for copper [12]. In the present investigation, untreated *Tectona grandis* L.f. leaves powder was examined in an attempt to remove copper(II) in aqueous solution.

Many researchers [13,14,32–45] have done their research work on removal of heavy metals from aqueous solutions using different adsorbents, but no information was available for the removal of copper from aqueous solution using *T. grandis* L.f. as adsorbent.

The aim of the present study is to remove copper from aqueous solution using *T. grandis* L.f. as adsorbent material for various parameters like pH, contact time, initial metal concentration, adsorbent concentration and adsorbent size. The adsorption capacity of this at room temperature was estimated using equilibrium studies.

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. A large to very large deciduous tree having height upto 35 m; bark having brown or grey colour and shallow longitudinal furrows; leaves simple, opposite, broadly elliptical or obovate, acute or acuminate, coriaceous, possessing minute glandular dots; flowers white, many, small, having pleasant smell, in large erect terminal branched tomentose cymose bladder like calyx; seeds usually 1–3, ovate, marble white.

2.2. Preparation of biosorbent

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

2.3. Chemical

Analytical grades of $CuSO_4 \cdot 5H_2O$, HCl and NaOH were purchased from Merck, India. Cupric (Cu^{2+}) ions were prepared by dissolving its corresponding sulphate 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 copper concentrations. After 3 h 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:

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

where Q is the metal uptake (mg/g); C_0 and C_f the initial and equilibrium metal concentrations in the solution (mg/l), respectively; V the solution volume (l); 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 sorption model was chosen for the estimation of maximum copper sorption by the biosorbent. The Langmuir isotherm can be expressed as

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

where Q_{max} indicates the monolayer adsorption capacity of adsorbent (mg/g) and the Langmuir constant b (l/mg) is related to the energy of adsorption. For fitting the experimental data, the Langmuir model was linearized as

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

The Freundlich model is represented by the equation:

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

where K (mg/g) is the Freundlich constant related to adsorption capacity of adsorbent and n is the Freundlich exponent related to adsorption intensity (dimensionless). 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 model is represented by the equation:

$$q_e = \frac{AC_e}{1 + BC_e^g} \tag{6}$$

where A (l/g) and B (l/mg) 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

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

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 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) 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 copper concentrations. Samples were taken at different time periods and analyzed for their copper concentration.

3. Results and discussion

3.1. The effect of contact time

The data obtained from the adsorption of copper 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 copper concentrations at the end of 180 min are given as the equilibrium values (q_e, mg/g; C_e, mg/l), respectively (Fig. 1).

3.2. Effect of adsorbent concentration

Fig. 2 shows the effect of adsorbent concentration on the amount of copper adsorbed, q_e (mg/g) and on the % removed at equilibrium conditions. It was observed that the amount of copper adsorbed varied with varying adsorbent concentration. The amount of copper adsorbed increases with an increase in adsorbent dosage from 0.1 to 0.5 g. The percentage copper removal was increased from 84.93% to 85.92% for an increase in biomass concentration from 0.1 to 0.5 g. The increase in the adsorption of the amount of solute is obvious due to increasing biomass surface area. Similar trend was also observed for copper removal using *Ulva fasciata* sp. as adsorbent [15].
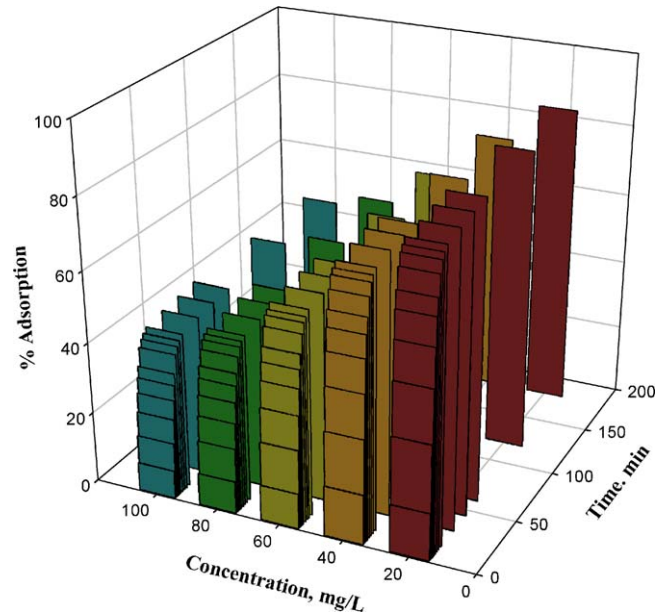

Fig. 1. The influence of contact time on adsorption capacities on *T. grandis* L.f. of copper (adsorbent concentration = 0.1 g/30 ml, adsorbent size = 75 μm and pH 5).

3.3. Effect of particle size

The effect of different adsorbent particle sizes on percentage removal of copper is investigated and showed in Fig. 3. It reveals that the adsorption of copper on *T. grandis* L.f. decrease from 85.67% to 64.18% with the increased particle size from 75 to 212 μm at an initial concentration of 20 mg/l. 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
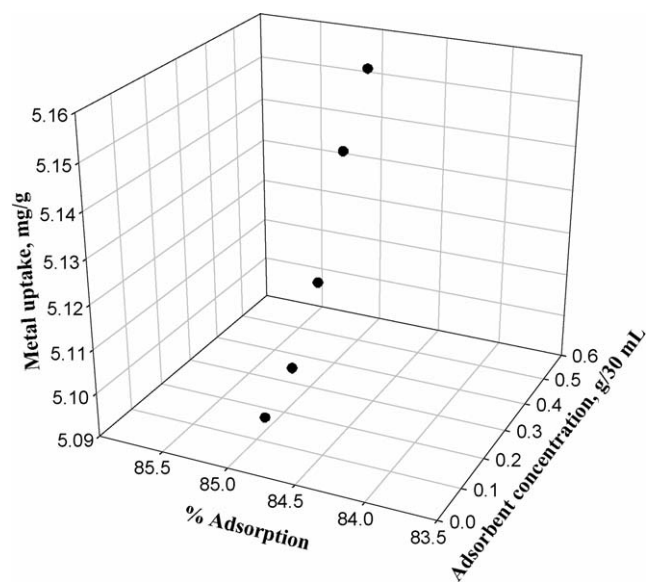

Fig. 2. Effect of adsorbent concentration in percentage adsorption and the equilibrium by *T. grandis* L.f. (initial metal ion concentration = 20 mg/l, adsorbent size = 75 μm and pH 5).
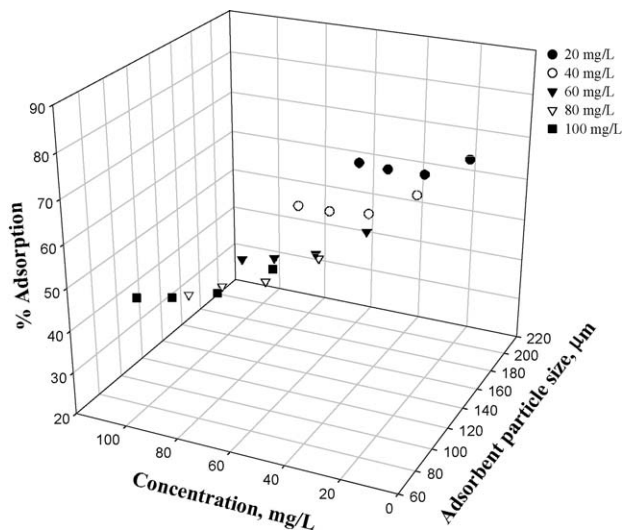
Fig. 3. Effect of particle size on adsorption of copper(II) (pH 5 and adsorbent concentration = 0.1 g/30 ml).

area, which in turn increases the adsorption capacity. A similar result was also obtained for the copper adsorption on saw dust [7].

3.4. Influence of initial 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 [16–20].

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, at least in theory, very liable to the influence of the pH. As shown in Fig. 4, the uptake of free ionic copper depends on pH, increasing with the increase in pH from 2.0 to 3.0 and then reaching a plateau in
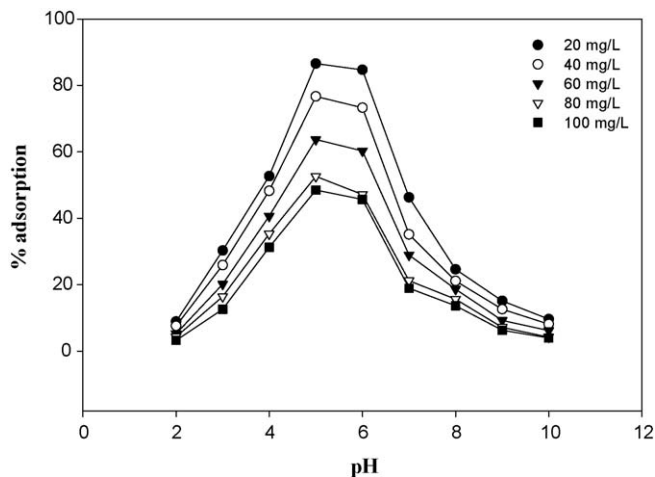
the range 4.0–5.0. Similar results were reported in literature for different Cu(II) biomass systems [21–23]. At pH values lower than 2.0 copper removal was inhibited, possibly as a result of the competition between hydrogen and copper ions on the sorption sites, with an apparent preponderance of hydrogen 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 copper(II) hydroxide starts precipitating from the solution, so that adsorption rate was decreased [15]. In this study, these copper(II) 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 copper(II) adsorption was found as 5 and the other adsorption experiments were performed at this pH value.

4. Biosorption equilibrium

The equilibrium biosorption of copper(II) on the T. grandis L.f. as a function of the initial concentration of copper(II) is shown in Fig. 5. There was a gradual increase of adsorption for copper(II) ions until equilibrium was attained. An equilibrium concentration of copper(II) ions was reached at about 100 mg/l for T. grandis L.f. Adsorption isotherm is important to describe how solutes interact with adsorbent. 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 copper(II) on the T. grandis L.f. was correlated well with the Langmuir equation as compared to Freundlich, Redlich–Peterson and Temkin equation under the concentration range studied. Examination of the Redlich–Peterson and Temkin data shows that these two

Fig. 4. Effect of pH on the copper adsorption (initial metal concentration = 20–100 mg/l, adsorbent concentration = 0.1 g/30 ml, adsorbent size = 75 μm and pH 5).
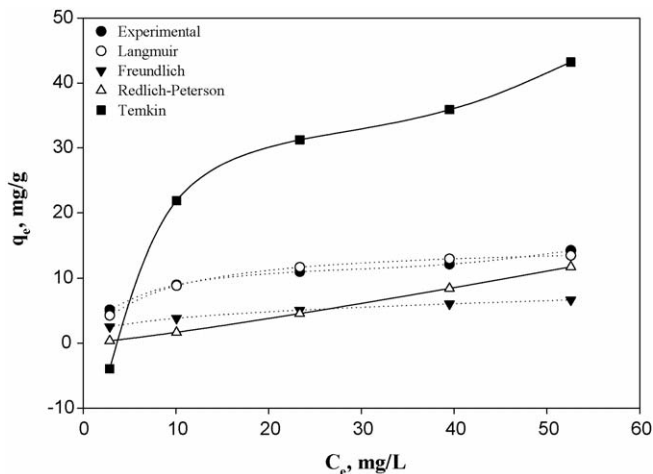

Fig. 5. Equilibrium curves for copper onto T. grandis L.f. (pH 5, adsorbent concentration = 0.1 g/30 ml and adsorbent size = 75 μm).

Table 1
Langmuir, Freundlich, Redlich–Peterson and Temkin isotherm constants and correlation coefficients for *T. grandis* L.f.

Langmuir				Freundlich		
Q (mg/g)	b (l/mg)	R^2		K_f (mg/g)	n	R^2
15.43	0.134	0.985		1.7885	0.3313	0.976

Redlich–Peterson				Temkin		
A (l/g)	B (l/mg)	g	R^2	A_T (l/mg)	b_T	R^2
0.4011	3.163	−0.3488	0.1117	0.1787	54.39	0.7923

isotherms are not modeled as well across the concentration range studied.

5. Kinetics of adsorption

In order to examine the controlling mechanism of adsorption processes such as mass transfer and chemical reaction, the first- and second-order equations are used to test the experimental data. The first-order kinetic model is given as [24,25]:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \tag{9}$$

where q_e and q_t are the amounts of copper adsorbed on adsorbent (mg/g) at equilibrium and at time t, respectively, and k_1 is the rate constant of first-order adsorption (min^{-1}). The straight-line plots of $\log(q_e - q_t)$ against t were used to determine the rate constant, k_1 and correlation coefficient, R values of the Cu(II) under different concentration range were calculated from these plots. The second-order equation may be expressed as [26–28]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{10}$$

where k_2 is the rate constant of second-order adsorption (g/mg min). The straight-line plots of t/q_t against t have been tested to obtain rate parameters and it suggests the applicability of this kinetic model to fit the experimental data.
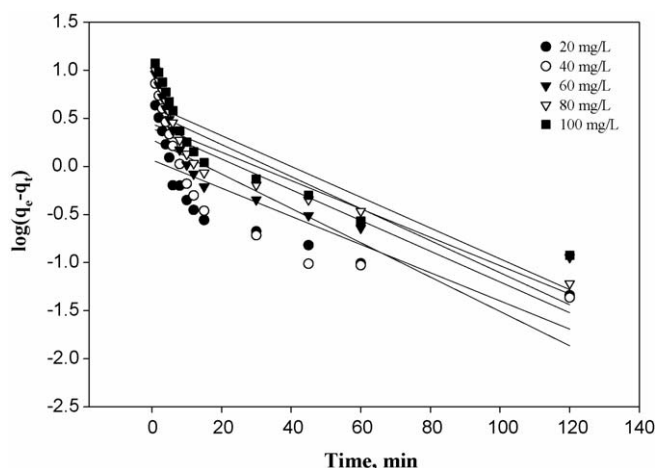

Fig. 6. Test of first-order equation for adsorption of copper using *T. grandis* L.f. (pH 5, adsorbent concentration = 0.1 g/30 ml and adsorbent size = 75 µm).
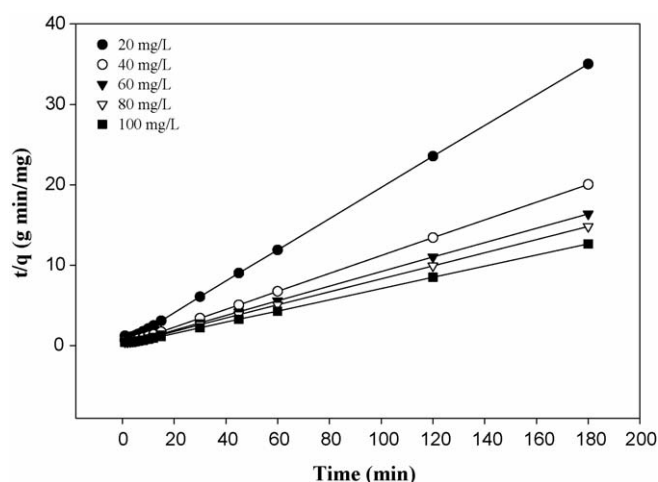

Fig. 7. Test of second-order equation for adsorption of copper using *T. grandis* L.f. (pH 5, adsorbent concentration = 0.1 g/30 ml and adsorbent size = 75 µm).

The validity of both kinetic models is checked and depicted in Figs. 6 and 7 by each linear plot of $\log(q_e - q_t)$ against t and t/q_t against t, respectively. The first-order kinetic model fits the experimental data poorly as shown in Fig. 6. Fig. 7 shows a good agreement of dynamical data with second-order kinetic model. The results of the kinetic parameters for copper(II) biosorption are given in Table 2. Based on the correlation coefficients, the biosorption of copper(II) is best described by the second-order equation. In many cases the first-order equation of Lagergren does not fit well to the whole range of contact time and is generally applicable over the initial stage of the adsorption processes [29]. The first-order kinetic process has been used for reversible reaction with an equilibrium being established between liquid and solid phases. Whereas, the second-order kinetic model assumes that the rate-limiting step may be chemical adsorption [28,30]. In many cases, the second-order equation correlates well to the adsorption studies [26]. It is more likely to predict that the adsorption behaviour may involve valency forces through sharing of electrons between transition metal cations and adsorbent.

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 parameters for copper biosorption on *T. grandis* L.f.

Concentration (mg/l)	Pseudo first-order		Pseudo second-order	
	k_1	R^2	k_2	R^2
20	0.0338	0.6774	0.0827	0.9995
40	0.0412	0.6902	0.0500	0.9997
60	0.0341	0.6831	0.0360	0.9996
80	0.0385	0.8086	0.0310	0.9997
100	0.0368	0.7706	0.0229	0.9996

Table 3
Adsorption capacity of copper on different adsorbents

Adsorbent	Q_{max} (mg/g)	Source
Kraft lignin	87.05	[32]
Moroccan stevensite	19.2	[33]
Black gram husk	27.7	[34]
Gracillaria sp.	37.5	[35]
Ulva sp.	47.6	[35]
Padina sp.	62.9	[35]
Chlorella vulgaris algal cells	58.8	[36]
Ceratophyllum demersum	6.17	[37]
Myriophyllum spicatum	10.37	[38]
Granular activated carbon	5.08	[39]
Powder activated carbon	4.45	[39]
Duolite GT-73	61.6	[40]
Amberlite IRC-718	127	[40]
Lewatit TP207	85.09	[41]
Penicillium chrysogenum	8.89	[42]
Rhizopus arrhizus	10.16	[42]
Sugar beet pulp	20.95	[43]
Activated sludge	48.89	[44]
Anaerobic biomass	55.24	[45]
T. grandis L.f.	15.43	Present study

6. 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 303 to 333 K:

$$\Delta G^\circ = -RT \ln K_a \tag{11}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{12}$$

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

where R is universal gas constant (8.314 J/mol K) 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 $\ln K_a$ (not shown).

The values of ΔG°, ΔH° and ΔS° for the adsorption process were calculated to be -12.67, -9.89 kJ/mol, and 41.8 kJ/mol K, respectively. The negative value of ΔG° confirms the feasibility of the process and the spontaneous nature of sorption with a high preference for copper(II) 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 [31]. The positive value of ΔS° shows the increasing randomness at the solid/liquid interface during the sorption of copper(II) onto *T. grandis* L.f.

7. Conclusions

The present study shows that the *T. grandis* L.f. was an effective biosorbent for the adsorption of copper 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, initial metal ion concentration, adsorbent concentration and adsorbent size on process equilibrium were studied. The uptake of copper ions by *T. grandis* L.f. was increased by increasing 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. 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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