

Sorption of copper(II) ion from aqueous solution by *Tectona grandis* l.f. (teak leaves powder)

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Abstract

Studies on a batch sorption system using *Tectona grandis* l.f. as adsorbent was investigated to remove copper(II) from aqueous solutions. The adsorption experiments were performed under various conditions such as different initial concentrations, pH, adsorbent dosage and adsorbent particle size. The data showed that 0.1 g of *Tectona grandis* l.f. was found to remove 71.66% of 20 mg/L copper(II) from 30 mL aqueous solution in 180 min. The experimental equilibrium data were adjusted by the adsorption isotherms from Langmuir and Freundlich models and their equilibrium parameters were determined. The best-adjusted model to the experimental equilibrium data for *Tectona grandis* l.f. was the Langmuir model. Using the Langmuir model equation, the monolayer sorption capacity of *Tectona grandis* l.f. was evaluated and found to be 95.40 mg/g. The optimum pH value was found to be 5.5. The pseudo-first-order and pseudo-second-order kinetic models were used to describe the kinetic data. The dynamic data fitted the pseudo-second-order kinetic model.

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1. Introduction

The presence of heavy metals in the environment is of great concern because of their increased discharge, toxic nature and other adverse effects on receiving waters. The majority of toxic metal pollutants are waste products of industrial and some domestic processes. Their concentrations have to be reduced to meet ever increasing legislative standards. Since most heavy metals are non-degradable, their concentrations must be reduced to acceptable levels before discharging them into the environment. In advanced countries, removal of heavy metals in wastewater is normally achieved by advanced technologies such as ion exchange, chemical precipitation, ultra filtration, or electrochemical deposition. But these technologies do not seem to be economically feasible because of their relatively high costs and that developing countries may not afford such technologies. Therefore, there is a need to look into alternatives to investigate a low-cost method, which is effective and economical. To over-

come this difficulty there is a strong need to develop economical adsorbents, which can be used in developing countries.

Copper is essential to human life and health, but like all heavy metals, it is potentially toxic, especially at high concentrations. Copper may be found as contaminant in food, especially shellfish, liver, mushrooms, nuts, and chocolate [1]. Copper has been found to cause stomach and intestinal distress, kidney damage, and anemia [2], and prolonged inhalation of copper-containing fumes has been linked to increase in lung cancer [1]. The main treatment process for the removal of metal ions include: chemical precipitation, membrane separation, and sorption/ion exchange. Sorption/ion exchange processes have significant benefits. The treated water is often sufficiently pure that it can be recycled and re-used, and the sorbed metals can often be recovered and purified in well-designed regeneration processes [3].

The adsorbent used in this study is teak leaves (*Tectona grandis* l.f.) powder, in which the adsorption takes place on surface of insoluble cell walls of the teak leaves. The insoluble cell walls of teak leaves are largely made up of cellulose and hemicelluloses, lignin, condensed tannins and structural proteins. In other words, one-third of the total dry matter in teak leaves should have

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good potential as metal scavengers from solutions and waste waters since the above constituents contain functional groups. The responsible groups in lignin, tannin or other phenolic compounds are mainly carboxylate, aromatic carboxylate, phenolic hydroxyl and oxyl groups [4].

1.1. Theory

1.1.1. Adsorption isotherms

1.1.1.1. Langmuir isotherm. The Langmuir sorption isotherm [5] has been successfully applied to many pollutant adsorption processes and has been the most widely used adsorption isotherm for the adsorption of a solute from a liquid solution. A basic assumption of the Langmuir theory is that adsorption takes place at specific homogeneous sites within the adsorbent. It is then assumed that once a metal ion occupies a site, no further adsorption can take place at that site. The rate of adsorption to the surface should be proportional to a driving force, which times an area. The driving force is the concentration in the solution, and the area is the amount of bare surface. If the fraction of covered surface is f , the rate per unit of surface is:

$$r_a = k_a C(1 - f) \quad (1)$$

The desorption from the surface is proportional to the amount of surface covered:

$$r_d = k_d f \quad (2)$$

where k_a and k_d are rate coefficients, r_a is adsorption rate, r_d desorption rate, C concentration in the solution, and f fraction of the surface covered. At equilibrium, the two rates are equal, and:

$$f = \frac{k_a C_e}{k_d + k_a C_e} \quad (3)$$

and

$$b = \frac{k_a}{k_d} \quad (4)$$

Since q_{eq} is proportional to f :

$$f = \frac{q_{eq}}{q_{max}} \quad (5)$$

The saturated monolayer adsorption capacity, q_{max} , can be obtained when f approaches 1, then $q_{eq} = q_{max}$. The saturated monolayer isotherm can be represented as:

$$q_{eq} = \frac{q_{max} b C_{eq}}{1 + b C_{eq}} \quad (6)$$

The above Eq. (6) can be rearranged to the following linear form:

$$\frac{C_{eq}}{q_{eq}} = \frac{1}{b q_{max}} + \frac{1}{q_{max}} C_{eq} \quad (7)$$

where C_{eq} is the equilibrium concentration (mg/L), q_{eq} the amount of metal ion sorbed (mg/g), q_{max} is q_{eq} for a complete monolayer (mg/g), and b sorption equilibrium constant (L/mg). A plot of C_{eq}/q_{eq} versus C_{eq} should indicate a straight line of slope $1/q_{max}$ and an intercept of $1/bq_{max}$.

1.1.1.2. Freundlich isotherm. In 1906, Freundlich studied the sorption of a material onto animal charcoal [6]. He found that if the concentration of solute in the solution at equilibrium, C_{eq} , (mg/L) was raised to the power m , the amount of solute adsorbed being q_{eq} , then C_{eq}^m/q_{eq} was a constant at a given temperature. This fairly satisfactory empirical isotherm can be used for non-ideal sorption and is expressed by the following equation:

$$q_{eq} = K_f C_{eq}^m \quad (8)$$

The equation is conveniently used in the linear form by taking the logarithm of both sides as:

$$\log q_{eq} = \log K_f + m \log C_{eq} \quad (9)$$

An adsorption isotherm is characterized by certain constants, the values of which express the surface properties and affinity of the sorbent and can also be used to compare biosorptive capacity of biomass for different metal ions. Out of several isotherm equations, two have been applied for this study, the Freundlich and Langmuir isotherms.

The purpose of the present study was to investigate the adsorption capacity of copper on *Tectona grandis* l.f. The experiments were done in batch systems and copper adsorption was investigated with respect to initial copper ion concentration at optimum conditions. Langmuir and Freundlich isotherms were used to determine the adsorption characteristics of *Tectona grandis* l.f. This study showed that the biomass can accumulate a high amount of copper(II) from aqueous solutions and it is a suitable adsorbent for practical metal recovery applications. The aim of this study was to investigate the adsorption of copper(II) ions from aqueous solution on the *Tectona grandis* l.f., on which no studies are available.

2. Materials and methods

2.1. Preparation of *Tectona grandis* l.f. for adsorption

The green colored Teak leaves (*Tectona grandis* l.f.) used in the present study were collected from the College of Engineering, Andhra University, Visakhapatnam, Andhra Pradesh, India. The collected leaves were washed with deionised water several times to remove dirt particles. The washing process was continued till the wash water contains no dirt. The washed leaves were then completely dried in sunlight for 10 days. The resulting product was directly used as adsorbent. The dried leaves were then cut into small pieces and powdered using domestic mixie. In the present study the powdered materials in the range of 75–212 μ m particle size were then directly used as adsorbents without any pre-treatment.

2.2. Metal solution

Stock solution of copper concentration 1000 mg/L was prepared by dissolving 3.93 g of 100% $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ in 1000 mL of distilled water. The solution was prepared using standard flasks. The range of concentration of the prepared metal solutions varied between 20 and 100 mg/L, and they were prepared by diluting

the copper stock solution, which were obtained by dissolving in deionized water.

2.3. Chemicals

Metal ion solutions were prepared by diluting stock metal ion solutions, which were obtained by dissolving weighed quantity of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ of analytical reagent grade obtained from Merck in double distilled water.

2.4. Batch adsorption studies

2.4.1. Effect of contact time

The effect of contact time was determined by shaking 0.1 g of adsorbent in 30 mL aqueous solution of initial metal concentration 20 mg/L with a pH of 5.5. The experiment is repeated for different time intervals like 1, 2, 3 min, etc. upto 240 min at constant agitation speed. After each interval of time the sample is filtered and is analyzed for determination of copper ion. This gives an opportunity for determination of optimum contact time.

2.4.2. Effect of initial metal ion concentration

To study the effect of initial metal concentration, 0.1 g of adsorbent is added to 30 mL stock solution of initial metal concentration of 20 mg/L and is kept for shaking for optimum time. Then the same procedure is repeated at pH 5.5 with 30 mL of stock solution, with different initial concentrations 40, 60, 80, 100 mg/L keeping the agitation speed and room temperature constant. Then the samples are filtered from adsorbent and they are analyzed for metal ion.

2.4.3. Effect of pH

The effect of initial solution pH on the equilibrium uptake of copper(II) was analyzed over a pH range from 2 to 10. The pH was adjusted using 0.1N NaOH and 0.1N HCl solutions. In this study, 30 mL of metal solution of concentration 20 mg/L was agitated with 0.1 g of adsorbent at room temperature for 180 min at a constant agitation speed. Samples are filtered from adsorbent and they are analyzed for metal ion.

2.4.4. Effect of adsorbent dosage

The effect of adsorbent dosage on the amount of metal adsorbed was obtained by agitating 30 mL of copper(II) solution of concentration 20 mg/L with 0.1, 0.2, 0.3, 0.4 and 0.5 g of adsorbent at room temperature for 180 min at a constant stirring speed.

2.4.5. Effect of adsorbent particle size

Thirty milliliters of 20 mg/L copper(II) solution is added to 0.1 g of a known size of adsorbent particle size, i.e. 75 μm , and it is kept for shaking for the optimum time. The sample is filtered from adsorbent and analyzed for concentration of copper metal ion. This experiment is repeated at constant agitation speed and at room temperature with different particle sizes of adsorbent from 75 to 212 μm .

2.5. Analysis

Metal concentration: The total metal concentration in solution was determined with atomic absorption spectrophotometer (GBC Avanta Ver 1.32, Australia) at a wavelength of 327.4 nm.

2.6. Metal uptake

The copper uptake was calculated by the simple concentration difference method [7]. The initial concentration C_i (mg/L) and final metal concentration C_{eq} (mg/L) at any time, were determined and the metal uptake q_{eq} (mg metal adsorbed/g adsorbent) was calculated from the mass balance as follows:

$$q_{eq} = \frac{V(C_i - C_{eq})}{w1000} \quad (10)$$

where V is the volume of the solution in milliliters and w is the mass of the adsorbent in gram. Preliminary experiments had shown that copper(II) adsorption losses to the flask walls and to the filter paper were negligible.

3. Results and discussion

The adsorption of copper(II) ions on the *Tectona grandis* l.f. was investigated as a function of the contact time, initial concentration, pH, adsorbent dosage and adsorbent particle size. The performance of *Tectona grandis* l.f. for the copper(II) removal using the experimental equilibrium data for Langmuir and Freundlich adsorption isotherms was tested.

3.1. Effect of contact time

Time course profiles for the adsorption of copper(II) from a solution of 20 mg/L are shown in Fig. 1. The data obtained from the adsorption of copper(II) ions on the *Tectona grandis* l.f. showed that a contact time of 180 min was sufficient to achieve equilibrium and the adsorption did not change with further increase in contact time. Therefore, the uptake and unad-

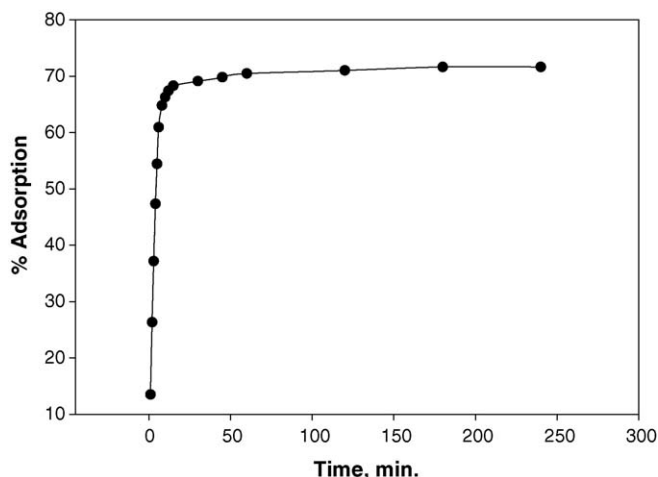


Fig. 1. Effect of contact time on adsorption of copper by *Tectona grandis* l.f. for 20 mg/L of metal and 0.1 g/30 mL of adsorbent concentrations.

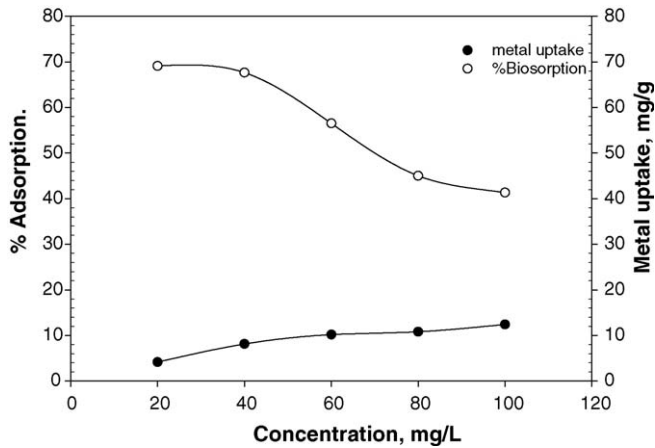


Fig. 2. Effect of initial metal concentration on the adsorption of copper by *Tectona grandis* l.f. at 0.1 g/30 mL of adsorbent concentration.

sorbed copper(II) concentrations at the end of 180 min are given as the equilibrium values, q_{eq} (mg/g) and C_{eq} (mg/L) as 42.99 and 5.67, respectively.

3.2. Effect of initial metal ion concentration

Several experiments were undertaken to study the effect of initial copper(II) concentration on the copper(II) removal from the solution. The results obtained are shown in Fig. 2 and the data show that the metal uptake increases and percentage adsorption of the copper(II) decreases with increase in initial metal ion concentration. This increase (42.99–87.80 mg/g) is a result of the increase in the driving force, i.e. concentration gradient. However, the percentage adsorption of copper(II) ions on *Tectona grandis* l.f. was decreased from 71.66 to 43.81%. 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 the equilibrium uptake of copper(II) displays an opposite trend. At lower concentrations, all copper(II) ions present in solution could interact with the binding sites, and thus the percentage adsorption was higher than those at higher initial copper(II) 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.

3.3. Influence 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, thus pH is an important parameter on adsorption of metal ions from aqueous solutions. *Tectona 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. 3 the uptake

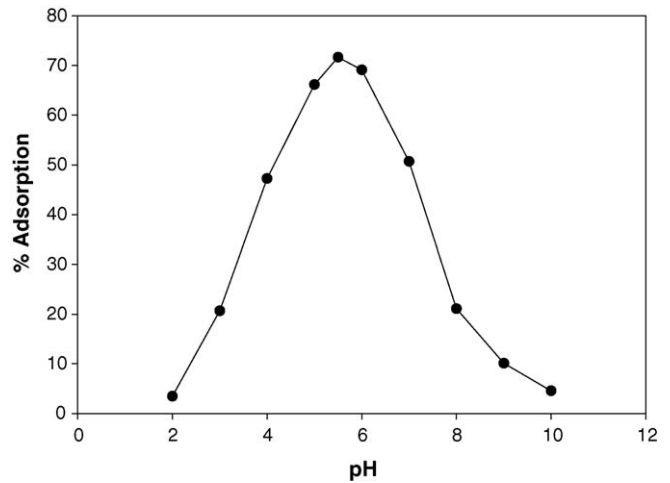


Fig. 3. Effect of pH on copper adsorption by *Tectona grandis* l.f. for 20 mg/L of metal and 0.1 g/30 mL of biomass concentration.

of free ionic copper(II) depends on pH, increasing with the increase in pH from 2.0 to 5.5 and then decreasing with increasing pH. At pH values lower than 3.0, copper(II) removal was inhibited, possibly as a result of the competition between hydrogen and copper(II) 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 *Tectona 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 adsorption onto the cell surface. Above pH 5.5, insoluble copper(II) hydroxide starts precipitating from the solution, so that adsorption rate was decreased. Elliot and Huang [8,9] investigated the hydrolysis products of copper(II) as a function of pH. Their result shows that the dominant species of copper(II) in the range 3–5.5 of pH are Cu and CuOH^+ , while the copper(II) at above 5.5 occurs as insoluble $\text{Cu}(\text{OH})_2$ (s). In this study, these copper(II) cation at around 5.5 would be expected to interact more strongly with the negatively charged binding sites in the adsorbent. As a result,

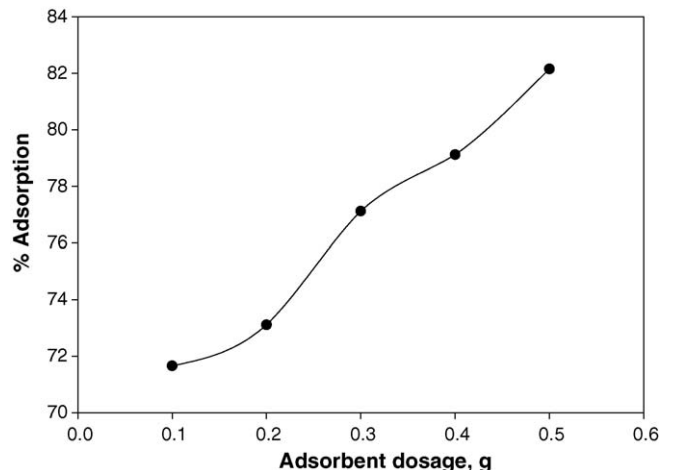


Fig. 4. Effect of *Tectona grandis* l.f. dosage on adsorption of copper for 20 mg/L of metal concentration.

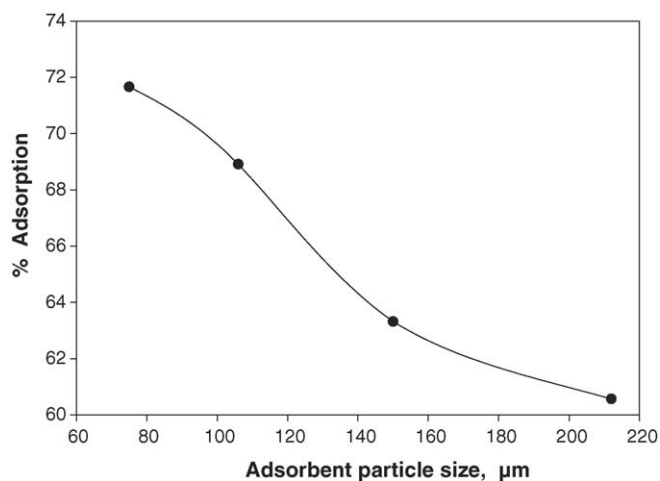


Fig. 5. Effect of *Tectona grandis* l.f. particle size on adsorption of copper for 20 mg/L of metal and 0.1 g/30 mL of biomass concentration.

the optimum pH for copper(II) adsorption was found as 5.5 and the other adsorption experiments were performed at this pH value.

3.4. Effect of adsorbent dosage

The influence of adsorbent dosage in removal of copper(II) is shown in Fig. 4. The increase in adsorbent dosage from 0.1 to 0.5 g resulted in an increase from 71.66 to 82.16% in adsorption of copper(II). This is because of the availability of more binding sites for complexation of copper(II) ions.

3.5. Effect of adsorbent particle size

The percentage of copper(II) adsorption on *Tectona grandis* l.f. was increased from 60.57 to 71.66 with decreasing particle size from 212 to 75 μm . The adsorption was increased due to increase in surface area of the particle as shown in Fig. 5.

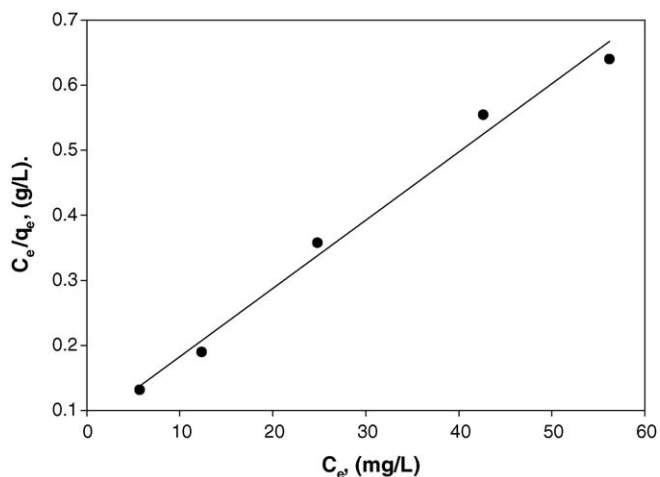


Fig. 6. Langmuir adsorption isotherm for copper at 0.1 mg/30 mL of biomass concentration.

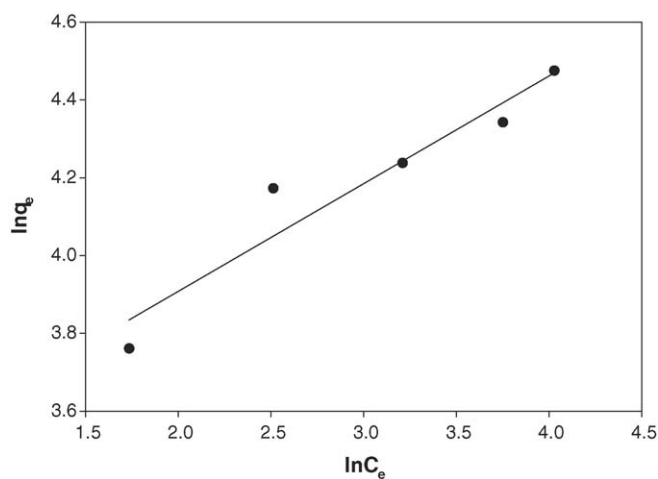


Fig. 7. Freundlich adsorption isotherm for copper at 0.1 mg/30 mL of biomass concentration.

3.5.1. Langmuir and Freundlich isotherm

The linearized Freundlich and Langmuir adsorption isotherms obtained at room temperature are shown in Figs. 6 and 7 and adsorption coefficients computed from these are given in Table 1. All the curves had good linearity (correlation coefficient) indicating strong binding of copper(II) ions to the surface of *Tectona grandis* l.f. particles.

From Langmuir isotherm, the adsorption affinity constant (b) and maximum capacity (q_{max}) of the ion copper(II) to form a complete monolayer on to the surface of the *Tectona grandis* l.f. biomass was estimated as 0.13 and 95.40 mg/g, respectively.

For Freundlich isotherm the constants related to the adsorption coefficients (K_f) and intensity (m) were 28.63 and 0.28, respectively.

The correlation coefficients obtained from the Langmuir model and Freundlich model were 0.988 and 0.920, respectively (Figs. 6 and 7). However as the solutions handled are very dilute in the present work, Langmuir equation was observed to be more suitable for the experimental data. A comparison of the maximum capacity, q_{max} , of *Tectona grandis* l.f. with other adsorbents reported in literature [10] is given in Table 2. The adsorbent capacity of *Tectona grandis* l.f. was relatively high when compared with other adsorbents. Differences of metal uptake are due to the properties of each adsorbent such as structure, functional groups and surface area.

3.6. Adsorption kinetics

The prediction of adsorption rate gives important information for designing batch adsorption systems. Information on

Table 1
Langmuir and Freundlich model parameters estimated from the fitting of experimental points of copper(II) adsorption

Langmuir model			Freundlich model		
q_{max} (mg/g)	b (L/mg)	R^2	K_f (mg/g)	m	R^2
95.40	0.1346	0.9881	28.63	0.2766	0.9203

Table 2
Comparison of maximum sorption capacity of *Tectona grandis* l.f. with other adsorbents for copper(II) ion

Adsorbent	q_{max}	Reference
Activated carbon from almond shell	8.85	[12]
Activated carbon from olive stone	9.21	[12]
Activated carbon from peach stone	7.21	[12]
Bagasse fly ash	2.26	[13]
Low rank Turkish coals	1.62	[14]
Coir pith carbon	39.70	[15]
Peanut bull carbon	65.57	[16]
Pinc bark	9.47	[17]
Saw dust	1.76	[2]
Washed sugar beet pulp	21.10	[18]
Activated sugar beet pulp	17.10	[19]
Activated carbon from sugar beet pulp	63.69	[20]
Sphagnum moss peat	12.40	[21]
Tree fern	10.60	[22]
<i>Padina</i> sp.	50.80	[23]
<i>M. spicatum</i>	10.37	[24]
Kaolinite	10.79	[25]
Dehydrated wheat bran	51.51	[10]
<i>Tectona grandis</i> l.f.	95.40	Present study

the kinetics of solute uptake is required for selecting optimum operating conditions for full-scale batch process. Fig. 8 shows the plot between metal uptake, q (mg/g) versus time, t (min) for initial solute concentration of 20 mg/L. From the figure it was observed that q value increased with increase in contact time. The kinetics of the adsorption data was analyzed using two kinetic models, pseudo-first-order and pseudo-second-order. These models correlate solute uptake, which are important in predicting the reactor volume. These models are explained as follows:

3.6.1. Pseudo-first-order model

The possibility of adsorption data following Lagergren pseudo-first-order kinetics is given by:

$$\frac{dq}{dt} = K_1(q_{eq} - q) \tag{11}$$

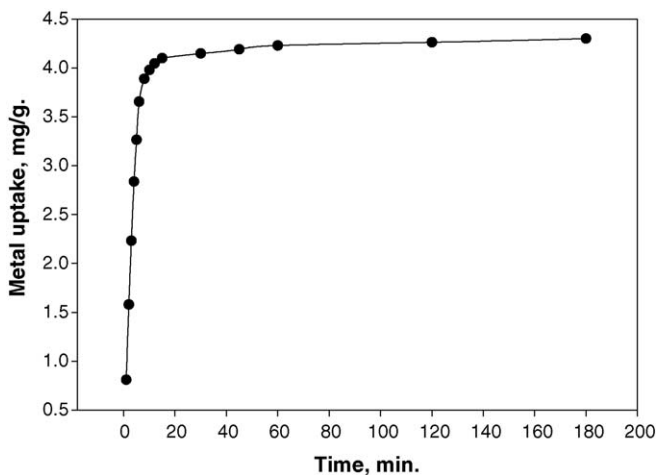


Fig. 8. Effect of contact time on copper uptake by *Tectona grandis* l.f. for 20 mg/L of metal and 0.1 g/30 mL of adsorbent concentration.

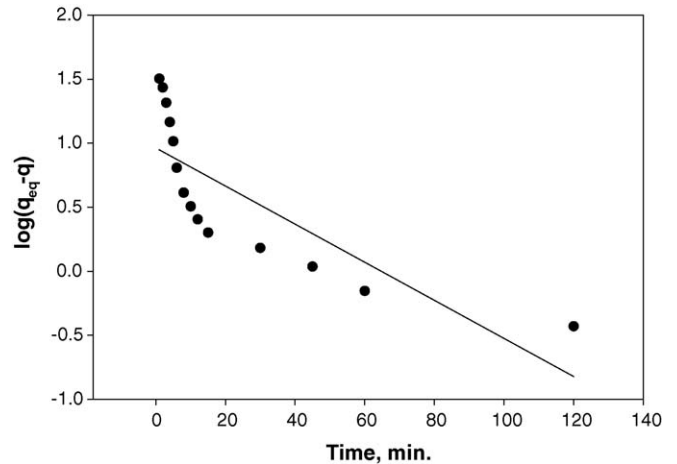


Fig. 9. Pseudo-first-order adsorption of copper by *Tectona grandis* l.f. for 20 mg/L of metal and 0.1 mg/30 mL of biomass concentration.

Integrating Eq. (11) with respect to integration conditions $q=0$ to $q=q$ at $t=0$ to $t=t$, the kinetic rate expression becomes:

$$\log(q_{eq} - q) = \log q_{eq} - \frac{K_1}{2.303}t \tag{12}$$

In order to obtain the rate constant, the straight-line plot (Fig. 9) of $\log(q_{eq} - q)$ versus time was made for *Tectona grandis* l.f. for initial copper(II) concentration, 20 mg/L. The intercept of the above plot should equal to $\log q_{eq}$. However, if q_{eq} from intercept does not equal to the equilibrium copper(II) uptake then the reaction is not likely to be first-order, even this plot has high correlation coefficient with the experimental data [11]. Correlation coefficient was found to be 0.939, but the calculated q_e is not equal to experimental q_{eq} , suggesting the insufficiency of pseudo-first-order model to fit the kinetic data for the initial copper(II) concentration examined.

3.6.2. Pseudo-second-order model

A pseudo-second-order model proposed by Ho and McKay [11] can be used to explain the sorption kinetics. This model

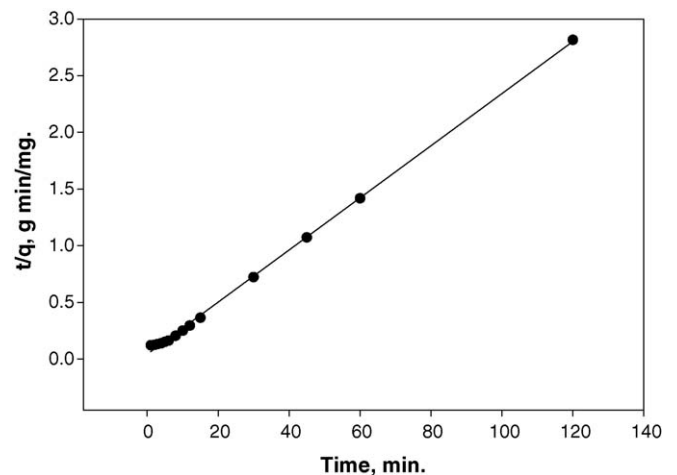


Fig. 10. Pseudo-second-order adsorption of copper by *Tectona grandis* l.f. for 20 mg/L of metal and 0.1 mg/30 mL of biomass concentration.

Table 3
Kinetic constants for copper(II) on *Tectona grandis* l.f.

Pseudo-first-order constants				Pseudo-second-order constants			
K	q_{eq} (calculated) (mg/g)	q_{eq} (experimental) (mg/g)	R^2	K	q_{eq} (calculated) (mg/g)	q_{eq} (experimental) (mg/g)	R^2
0.03	9.17	42.99	0.94	0.01	42.99	42.99	0.99

is based on the assumption that the adsorption follows second-order chemisorption. The pseudo-second-order model can be expressed as:

$$\frac{dq}{dt} = K_{\text{II}}(q_{\text{eq}} - q)^2 \quad (13)$$

Separating the variables in Eq. (13) gives:

$$\frac{dq}{(q_{\text{eq}} - q)^2} = K_{\text{II}} dt \quad (14)$$

Integrating Eq. (14) for the boundary conditions $q = 0$ to $q = q$ at $t = 0$ to $t = t$, Eq. (14) simplifies to:

$$\frac{t}{q} = \frac{1}{K_{\text{II}}q_{\text{eq}}^2} + \frac{1}{q_{\text{eq}}}t \quad (15)$$

where t is the contact time (min), q_{eq} (mg/g) and q (mg/g) are the amount of metal adsorbed at equilibrium and at any time, t . If second-order kinetics is applicable, the plot (Fig. 10) of t/q versus time of Eq. (15) should give a linear relationship from which the constants q_{eq} and K_{II} can be determined. The rate constants and the correlation coefficients for both tested models have been calculated and summarized in Table 3.

4. Conclusions

Based on the present study, the following conclusions were drawn. The adsorption performances are strongly affected by parameters such as initial concentration, pH, adsorbent dosage and adsorbent particle size. The equilibrium uptake was increased and percentage adsorption was decreased with increasing the initial concentration. The plot of pH versus percentage adsorption shows the significant adsorption takes place at 5.5. The percentage adsorption of copper(II) increases with increasing the adsorbent dosage. The percentage adsorption of copper(II) decreases with increasing particle size of adsorbent. The present work helped in identifying a new source of adsorbent for removal of metals from effluent wastes containing low concentrations of metals. The Langmuir model proved to be the best adjustment of the experimental data for *Tectona grandis* l.f. However, comparing the representative models of the adsorption between the adsorbents, a better adjustment of the equilibrium data was observed by the adsorbent *Tectona grandis* l.f. The

results obtained in these studies open perspectives with relation to the utilization of *Tectona grandis* l.f. in the ions copper(II) removal, in treatment of wastewater provided from industrial effluents. The kinetics of the adsorption of copper(II) on *Tectona grandis* l.f. can be better described with second-order kinetics.

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