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Removal of copper ions from aqueous solution by tree fern

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Abstract

Tree fern, an agricultural by-product, was used for the sorptive removal of copper ions from aqueous solution. The experimental data was analysed by Langmuir, Freundlich and Redlich-Peterson isotherms. The equilibrium sorption capacity of copper ions was determined from the Langmuir equation and found to be 11.7 mg/g. A batch sorption model, based on the assumption of the pseudo-second-order mechanism, was developed to predict the rate constant of sorption, the equilibrium sorption capacity and the initial sorption rate with the effect of initial copper ion concentration and the tree fern dose. Various thermodynamic parameters, such as ΔG^0 , ΔH^0 and ΔS^0 , have been calculated. The thermodynamics of copper ion/tree fern system indicates spontaneous and endothermic nature of the process.

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1. Introduction

Sorption has been an effective separation process for a wide variety of applications. Since activated carbon is expensive, an alternative inexpensive sorbent able to drastically reduce the cost of a sorption system has always been searched. The removal of copper ions from wastewaters has received considerable attention in recent years [1]. Extensive investigations have been carried out to identify suitable and relatively cheap biosorbents which are capable of removing significant quantities of copper ions. Table 1 shows a number of agricultural by-products as biosorbents available for copper ion sorption.

Tree fern is naturally and commercially available in Taiwan. This variety of tree fern is generally marketed for horticultural purposes because of its character of sorbability to keep water and manure for plants. Tree fern is a complex material containing lignin and cellulose as major constituents [2]. Chemical sorption can occur

by the polar functional groups of lignin, which include alcohols, aldehydes, ketones, acids phenolic hydroxides and ethers as chemical bonding agents [3]. It is, therefore, concluded that tree fern can be a suitable sorbate for sorption of metal cation because of its polar and acid characters.

In this study, the sorption capacity of tree fern for copper ions has been investigated by determining the equilibrium isotherm. In addition, kinetic studies have been carried out using an agitation batch sorber to study the effects of initial copper ion concentration and the tree fern dose. Kinetic analysis was performed to correlate the experimental data, based on the pseudo-second-order equation.

2. Materials and methods

2.1. Materials

Tree fern has been used commercially and could be easily obtained in Taiwan. The raw tree fern was dried in an oven at 100°C for a period of 24 h, and then grounded and screened through a set of sieves to get

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Table 1
A number of agricultural by-products available for sorption of copper ions

q_m (mg/g)	Material	Reference
38.7	Soybean hulls	[13]
19.1	Cottonseed hulls	[13]
16.4	Sphagnum moss peat	[14]
13.5	Banana pith	[15]
10.8	Apple wastes	[16]
1.98	Oil-palm fibre	[17]
1.74	Sawdust	[18]
11.7	Tree fern	This study

geometrical size 74–88 μm . This process was done to produce a uniform material for the complete set of sorption tests which was stored in an air-tight plastic container for all investigations. The stock solutions of copper(II) (2000 mg/dm^3) were prepared in distilled water using copper sulphate. All working solutions were prepared by diluting the stock solution with distilled water.

2.2. Methods

2.2.1. Equilibrium studies

A volume of 50 ml of copper(II) solution with a concentration in the range 30–150 mg/dm^3 was placed in a 125 ml conical flask. An accurately weighed tree fern sample 0.25 g with particle size 74–88 μm was then added to the solution. A series of such conical flasks was then shaken at a constant speed of 100 rpm in a shaking water bath with temperatures 2°C, 10°C, 20°C, 30°C and 40°C, respectively. After shaking the flasks for 5 h, the tree fern was separated by filtration through a membrane filter (0.45 μm). The filtrate was analysed for the remaining copper ion concentration by atomic absorption spectrophotometry (AAS).

2.2.2. Effect of tree fern dose

A range of copper(II) concentrations from 52.5 to 328 mg/dm^3 was used and agitation was carried out for 2 h. All contact investigations were executed to use a baffled, agitated 2 dm^3 sorber vessel. Samples (3 ml) were withdrawn at suitable time intervals, filtered through a 0.45 μm membrane filter and then analysed. A 6.8 g sample of tree fern (74–88 μm) was added to each 1.7 dm^3 volume of copper ion solution and an agitation speed of 300 rpm was used for all experiments. The temperature was controlled with a water bath at the temperature of 20°C for all studies.

2.2.3. Effect of initial concentration

A range of tree fern (74–88 μm) from 1 to 4 g/dm^3 was added to each 1.7 dm^3 volume of copper ion solution

with an initial concentration 150 mg/dm^3 and an agitation speed of 300 rpm was employed. The temperature was controlled with a water bath at the temperature of 20°C for all studies.

3. Results and discussion

3.1. Equilibrium studies

The analysis of the isotherm data is important to develop an equation which accurately represents the results and could be used for design purposes. In order to investigate the sorption isotherm, three equilibrium models were analysed: the Langmuir, the Freundlich and the Redlich-Peterson isotherm equations. The Langmuir sorption isotherm [4] is perhaps the best known of all isotherms describing sorption. The theoretical Langmuir isotherm is often used to describe sorption of a solute from a liquid solution as

$$q_e = \frac{q_m K_a C_e}{1 + K_a C_e} \quad (1)$$

The constants q_m and K_a are the characteristics of the Langmuir equation and can be determined from a linearised form of Eq. (1), represented by

$$\frac{C_e}{q_e} = \frac{1}{q_m K_a} + \frac{C_e}{q_m} \quad (2)$$

A plot of C_e/q_e versus C_e should indicate a straight line of slope $1/K_a q_m$ and an intercept of $1/q_m$.

The Freundlich isotherm [5] is the earliest known relationship describing the sorption equation. This fairly satisfactory empirical isotherm can be used for nonideal sorption that involves heterogeneous sorption and is expressed by the following equation:

$$q_e = K_F C_e^{1/n} \quad (3)$$

and the equation may be linearised by taking logarithms

$$\log(q_e) = 1/n \log(C_e) + \log(K_F), \quad (4)$$

where K_F and $1/n$ are empirical constants dependent on several environmental factors.

The Redlich-Peterson isotherm [6] contains three parameters and incorporates the features of the Langmuir and the Freundlich isotherms. It can be described as follows:

$$q_e = \frac{A C_e}{1 + B C_e^g} \quad (5)$$

It has three isotherm constants, namely, A , B and g ($0 < g < 1$). These can be evaluated from the linear plot represented by Eq. (6) using a trial and error optimisation method:

$$\ln\left(\frac{C_e}{q_e} - 1\right) = g \ln(C_e) + \ln(B). \quad (6)$$

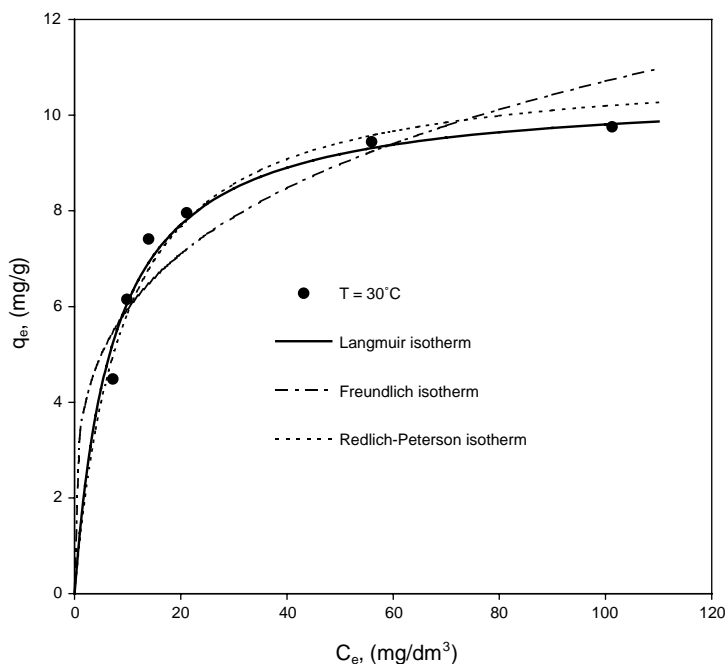


Fig. 1. Isotherms for the sorption of copper(II) using tree fern.

In order to assess different isotherms and their ability to correlate with experimental results, the theoretical plots from each isotherm have been shown with the experimental data for sorption of copper ions on tree fern at the temperature of 30°C in Fig. 1. The graph is plotted in the form of copper(II) sorbed per unit mass of tree fern, q_e , against the concentration of copper(II) remaining in solution, C_e . A comparison of coefficient of determination for three isotherms has been made and listed in Table 2. The coefficient of determination, r^2 , are greater than 0.997 and 0.980 for the Langmuir and the Redlich-Peterson isotherms, respectively. It is clear that the Langmuir and the Redlich-Peterson isotherms have best fitted for the sorption of copper on tree fern at various temperatures. The effect of temperature on the sorption isotherms is shown in Fig. 2. Results indicate that the capacity of tree fern for sorption of copper(II) increases with temperature which is typical for the biosorption of most metal ions from their solution [1,7]. When the system is in a state of equilibrium, the distribution of copper(II) between the tree fern and the copper(II) solution is of fundamental importance in determining the maximum sorption capacity of tree fern for the copper ion from the isotherm.

The Langmuir isotherm is applicable to homogeneous sorption where each copper ion/tree fern sorption process has equal sorption activation energy. The Langmuir constants K_a and q_m have been determined

with Eq. (2) and are shown in Table 3. The equilibrium sorption capacity, q_m , was found to increase from 8.98 to 11.7 mg/g for an increase in the solution temperatures from 2°C to 40°C. It is clear that the sorption of copper on tree fern is an endothermic process. However, the sorption constant, K_a , decreases from 0.197 to 0.100 dm³/mg, as temperatures vary from 2°C to 40°C. The Redlich-Peterson isotherm constants are also shown in Table 3. Both constants A and B were found to decrease for an increase in the solution temperature. In addition, it can be seen that in most cases the values of g tend to unity (>0.993), this means the isotherms are approaching the Langmuir form. An examination of Table 1 shows that the value for the maximum sorption capacity, q_m , is comparable with values reported previously. This table also shows the sorption capacities reported in earlier studies where q_m has not been derived specifically.

The effect of isotherm shape can be used to predict whether a sorption system is 'favourable' or 'unfavourable'. According to Hall et al. [8], the essential features of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter K_R which is defined by the following relationship:

$$K_R = \frac{1}{1 + K_a C_0} \quad (7)$$

This parameter indicates the shape of the isotherm accordingly

Values of K_R Type of isotherm

$K_R > 1$	Unfavourable
$K_R = 1$	Linear
$0 < K_R < 1$	Favourable
$K_R = 0$	Irreversible

The values of K_R at 2°C, 10°C, 20°C, 30°C and 40°C are given in Table 4. The K_R values indicate that sorption is more favourable for the higher initial copper concentrations than for the lower ones. It is apparent that the sorption of copper on tree fern is favourable with the conditions used in this study.

3.1.1. Thermodynamic parameters

The original concepts of thermodynamics assumed that in an isolated system, where energy cannot be

Table 2
A comparison of coefficient of determination for three isotherms

T (°C)	Langmuir	Freundlich	Redlich-Peterson
2	0.999	0.782	0.992
10	0.997	0.881	0.994
20	1.000	0.885	0.999
30	0.999	0.814	0.985
40	0.998	0.866	0.980

gained or lost, the entropy change is the driving force. In environmental engineering practice, both energy and entropy factors must be considered in order to determine what processes will occur spontaneously. The Gibbs free energy change, ΔG^0 , is the fundamental criterion of spontaneity. Reactions occur spontaneously at a given temperature if ΔG^0 is a negative quantity. The free energy of the sorption reaction, considering the sorption equilibrium constant, K_a , is given by the following equation:

$$\Delta G^0 = -RT \ln K_a, \tag{8}$$

where ΔG^0 is standard free energy change, J; R is universal gas constant, 8.314 J/mol K and T is absolute temperature, K.

Considering the relationship between free energy and the equilibrium constant, change in equilibrium constant with temperature can be obtained in the differential form as follows:

$$\frac{d \ln K_a}{dT} = \frac{\Delta H^0}{RT^2}. \tag{9}$$

After integration, the integrated form of Eq. (9) becomes:

$$\ln K_a = -\frac{\Delta H^0}{RT} + Y, \tag{10}$$

where Y is a constant. Eq. (10) can be rearranged to obtain

$$-RT \ln K_a = \Delta H^0 - TRY. \tag{11}$$

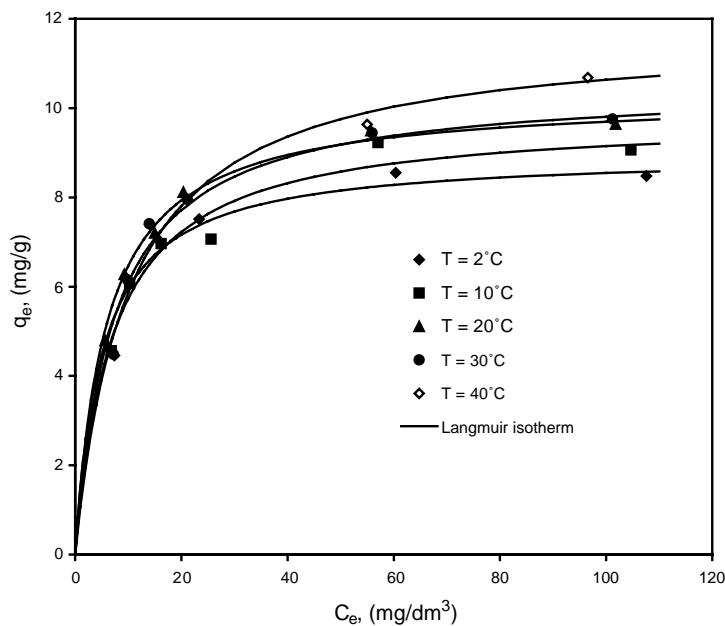


Fig. 2. Langmuir isotherms for the sorption of copper ions on tree fern.

Table 3
Isotherm constants for copper ions sorbed on tree fern

T (°C)	ΔG^0 kJ/mol	Langmuir		Redlich-Peterson		
		q_m , mg/g	K_a , dm ³ /mg	A , dm ³ /mg	B , (dm ³ /mg)	g
2	−0.0674	8.98	0.197	1.41	0.149	1.000
10	−0.193	9.80	0.141	1.32	0.133	1.000
20	−0.349	10.3	0.170	1.60	0.153	1.000
30	−0.506	10.5	0.137	1.25	0.112	1.000
40	−0.662	11.7	0.100	1.16	0.100	0.993

Table 4
 K_R values based on the langmuir isotherm

C_0 , (mg/dm ³)	2°C	10°C	20°C	30°C	40°C
29.7	0.146	0.193	0.166	0.197	0.251
40.6	0.111	0.149	0.127	0.152	0.197
51.0	0.0904	0.122	0.103	0.125	0.163
60.9	0.0768	0.104	0.0881	0.107	0.140
103	0.0468	0.064	0.0540	0.0659	0.0880
150	0.0327	0.0452	0.0378	0.0463	0.0622

Let

$$\Delta S^0 = RY. \quad (12)$$

Substituting Eqs. (8) and (12) into Eq. (11), the Gibbs free energy change, ΔG^0 , can be represented as follows:

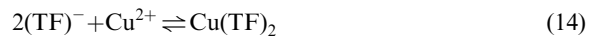
$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (13)$$

A plot of Gibbs free energy change, ΔG^0 , versus temperature, T , was found to be linear, Fig. 3. The values of ΔH^0 and ΔS^0 were determined from the slope and intercept of the plots. The thermodynamic parameters Gibbs free energy change, ΔG^0 , are shown in Table 3. The enthalpy change, ΔH^0 , and the entropy change, ΔS^0 , for the sorption processes are calculated to be 4.24 and 0.0156 J/mol K, respectively. The negative values of ΔG^0 Confirm the feasibility of the process and the spontaneous nature of sorption with a high preference of copper(II) on tree fern. The value of ΔH^0 is positive, indicating that the sorption reaction is endothermic. The positive value of ΔS^0 reflects the affinity of the tree fern for copper ions and suggests some structural changes in copper and tree fern [9]. In addition, positive value of ΔS^0 shows the increasing randomness at the solid/liquid interface during the sorption of copper ions on tree fern.

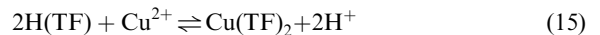
3.2. Kinetic studies

The rate at which sorption takes place is of most importance when designing batch sorption systems. Consequently, it is important to establish the time

dependence of such systems under various process conditions. The sorption of copper ions on tree fern may involve a chemical sorption which can control the reaction rate. Tree fern is a complex material containing mainly organic residues such as lignin and cellulose made of several polar functional groups [2]. These groups can be involved in chemical bonding and are responsible for the cation exchange capacity of the tree fern. Exchange sorption between the tree fern and copper reaction may be represented in two ways as shown in the following equations [10]:



and



where $(\text{TF})^-$ and (TF) are polar sites on the tree fern surface.

Rate expression for the sorption described by Eqs. (14) and (15) is

$$\frac{d(\text{TF})_t}{dt} = k_2[(\text{TF})_0 - (\text{TF})_t]^2, \quad (16)$$

or

$$\frac{d[\text{H}(\text{TF})]_t}{dt} = k_2[(\text{H}(\text{TF}))_0 - (\text{H}(\text{TF}))_t]^2, \quad (17)$$

where $(\text{TF})_t$ and $[\text{H}(\text{TF})]_t$ are the number of active sites occupied on the tree fern at time t , and $(\text{TF})_0$ and $[\text{H}(\text{TF})]_0$ are the number of equilibrium sites available on the tree fern.

The kinetic rate equations can be rewritten as follows:

$$\frac{dq_t}{dt} = k(q_e - q_t)^2, \tag{18}$$

where k is the pseudo-second-order rate constant of sorption, (g/mgmin), q_e is the amount of copper ion

sorbed at equilibrium, (mg/g), q_t is amount of copper ion on the surface of the sorbent at any time, t , (mg/g). Separating the variables in Eq. (18) gives

$$\frac{dq_t}{(q_e - q_t)^2} = k dt \tag{19}$$

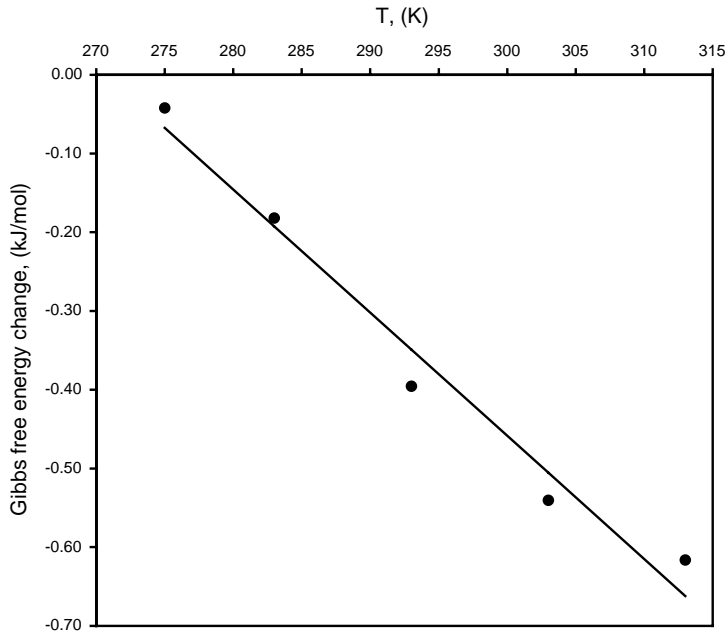


Fig. 3. Plot of Gibbs free energy change, ΔG° , versus temperature, T .

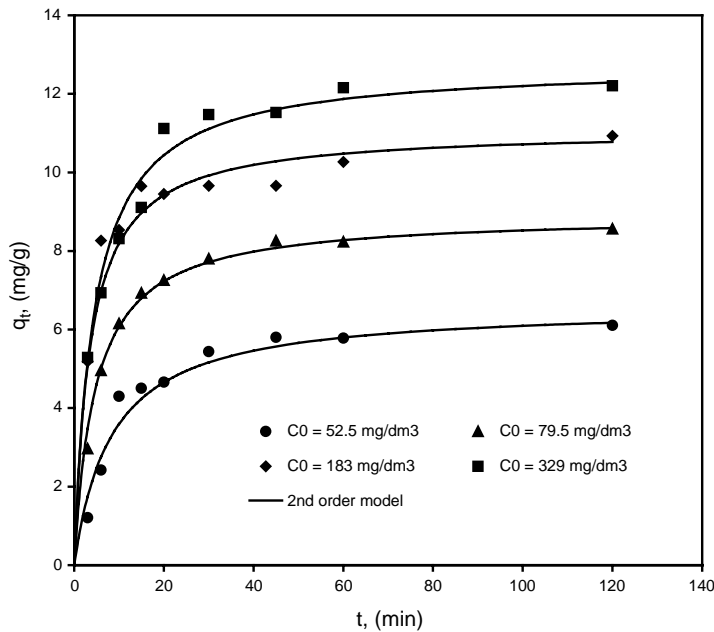


Fig. 4. Plot of sorbed amount versus time for copper(II) at various initial concentrations.

integrating this for the boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$, gives

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + kt \tag{20}$$

which is the integrated rate law for a pseudo-second-order reaction. Eq. (20) can be rearranged to obtain a linear form

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e}t. \tag{21}$$

This form of normalised plot has been first used by Ho [11] for the sorption of divalent metal ions onto peat.

Sorption rate can be obtained from Eq. (21):

$$\frac{q_t}{t} = \frac{1}{(1/kq_e^2) + (1/q_e)t}. \tag{22}$$

The initial sorption rate, h , as $t \rightarrow 0$ can be defined as $h = kq_e^2$.

The initial sorption rate, h , the equilibrium sorption capacity, q_e , and the pseudo-second-order rate constant,

k , can be determined experimentally from slop and intercept of plotting of t/q_t against t .

3.2.1. Effect of initial concentration

Sorption of copper ion from solution has been studied by using a baffled, agitated 2 dm³ sorber vessel. The rate of copper ion sorption on tree fern was determined as a function of the initial metal concentrations 52.5, 79.5, 183 and 328 mg/dm³. Fig. 4 illustrates a plot of the experimental data points for the sorption of copper ions on tree fern as a function of time. The sorption rate was rapid at the beginning of the reaction. Fig. 4 also shows excellent fits between the predicted curves and the experimental data points. It presents a good linearisation of the experimental data, thereby supporting the proposal that chemisorption is the rate-limiting step and that the mechanism follows a pseudo-second-order reaction model [12]. Table 5 presents the rate constant, k , the equilibrium sorption capacity, q_e , and the initial sorption rate, h , of sorption at various initial concentrations. They were calculated from the intercept and slope of the straight line plots of t/q_t versus t according to Eq. (15). Table 5 also shows a good compliance with the pseudo-second-order equation and the regression coefficients for the linear plots were higher than 0.995 for all the systems. The equilibrium sorption capacity, the initial sorption rate and the rate constants increased with an increase in initial copper ion concentration, respectively. The corresponding linear plot of the values of q_e against initial copper ion concentration C_0 , was

Table 5
Parameters for the effect of initial copper(II) concentration

C_0 , mg/dm ³	q_e , mg/g	k , g/mg min	h , mg/g min	r^2
52.5	6.60	0.0180	0.787	0.995
79.5	8.92	0.0238	1.90	1.000
183	11.1	0.0253	3.12	0.999
328	12.7	0.0178	2.89	0.998

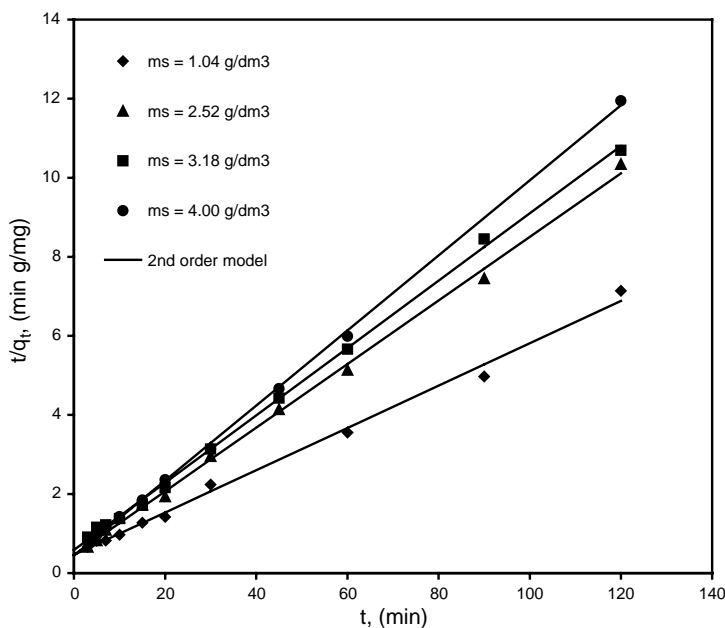


Fig. 5. Pseudo-second-order sorption kinetics of copper(II) on tree fern at various doses.

Table 6
Parameters for the effect of tree fern dose

m_s , g/dm ³	q_e , mg/g	k , g/mg min	h , mg/g min	r^2
1.04	18.7	0.00620	2.17	0.995
2.52	12.4	0.0141	2.18	0.998
3.18	11.7	0.0124	1.71	0.999
4.00	10.5	0.0204	2.26	0.999

regressed to obtain expressions for the value in terms of the initial copper concentration with high coefficient of determination ($r^2 = 0.998$). Therefore, it is further considered that q_e can be expressed as a function of C_0 as follows:

$$q_e = \frac{C_0}{4.16 + 6.60 \times 10^{-2} C_0} \quad (24)$$

3.2.2. Effect of tree fern dose

The effect of tree fern dose, M_s , was studied. The results are shown in Fig. 5 as a series of plot of t/q_t against time for sorption of copper(II) with tree fern dose varying from 1 to 4 g/dm³ for the pseudo-second-order model. The coefficient of determination, r^2 , the rate constant, k , the equilibrium sorption capacity, q_e , and the initial sorption rate, h , of sorption at various initial concentrations are shown in Table 6. The rate of the copper(II) sorption process appears to be controlled by the chemical process in this case in accordance with the pseudo-second-order reaction mechanism. Since the lignin component of the tree fern contains acid exchange groups due to fulvic and humic acids, it seems that these could exchange with the copper ions and thus lead to the chemical sorption mechanism predominating for the sorption system.

4. Conclusion

The sorption of copper ions on tree fern is of its spontaneous and endothermic natures. The copper ions binding capacity of biosorbent was shown as a function of initial metal ion concentration, temperature and tree fern dose. The equilibrium data was fitted very well to both the Redlich-Peterson and Langmuir sorption isotherms. The equilibrium sorption of copper ions was determined from the Langmuir equation and found to be 11.7 mg/g. The kinetics of copper ion sorption on tree fern was based on the assumption of the pseudo-second-order mechanism with the chemisorption being important.

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