

義守大學

教師資格審查書面資料

化學工程學系

送審人：何玉山教授

日期：96年8月

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個人資料

個人簡歷

主要學歷

畢／肄業學校	國別	主修學門系所	學位	起訖年月
伯明罕大學 (University of Birmingham)	英國	化學工程學系	博士 (Ph.D.)	1993/05 1995/12
雪菲爾大學 (University of Sheffield)	英國	化學系	哲學碩士 (M.Phil.)	1991/10 1993/06
私立中原大學	中華民國	化學工程學系	學士	1982/09 1986/06

現職

服務機關	服務部門／系所	職稱	起訖年月
北京大學大學	環境科學暨工程學系	長江學者講座教授	2006/04 起
台北市立萬芳醫院	研究發展委員會	執行長	2005/09 起

與專長相關之經歷

服務機關	服務部門／系所	職稱	起訖年月
北京大學	環境科學系	長江學者講座教授	2006/04 起
巴黎 Conservatoire National des Arts et Métiers	Laboratoire de Chimie Industrielle Génie des Procédés	訪問教授	2002/02 至 2004/03
臺北醫學大學	公共衛生學系	助理教授	2000/08 至 2006/12
大穎集團	研發部，企劃組	高級專員	1998/01 至 2000/04
香港科技大學	化學工程學系	博士後研究員	1996/12 至 1997/12
英國伯明罕大學	化學工程學系	博士後研究員	1995/12 至 1996/12

學經歷證明



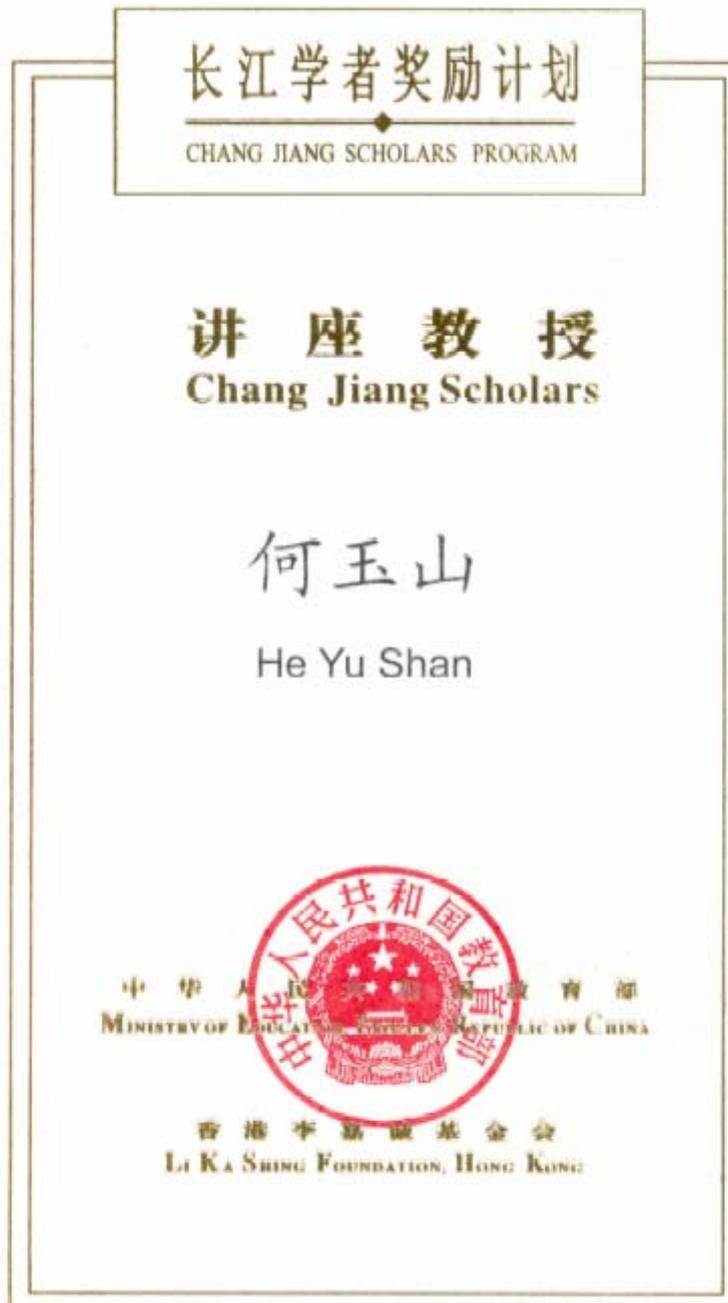
THE UNIVERSITY
OF BIRMINGHAM

It is hereby certified that
Yuh-Shan Ho
was admitted to the Degree of
Doctor of Philosophy
(*Chemical Engineering*)
on the fifteenth day of December 1995

VICE-CHANCELLOR AND PRINCIPAL

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248541





CERTIFICATE

March 24th 2005 in Paris

The Laboratoire de Chimie Industrielle Génie des Procédés
at Conservatoire National des Arts et Métiers in Paris is to
certify that Dr. Yuh-Shun HO was invited to be an
Instructional Professor from February 2004 to March 2005.
His major duty was to supervise PhD students of Paris VI
University.

Sincerely,


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Professor Alain Delacroix
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獎項證明

Ho, Y.S.* (2003), Removal of copper ions from aqueous solution by tree fern. *Water Research*, **37** (10), 2323-2330.

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Ho, Y.S.*, Chiu, W.T., Hsu, C.S. and Huang, C.T. (2004), Sorption of lead ions from aqueous solution using tree fern as a sorbent. *Hydrometallurgy*, **73** (1-2), 55-61.

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學術研究獎

何玉山助理教授於九十四年度學術研究表現卓著，經本校研究發展會議審慎評選，榮獲優良獎，特頒此狀以茲獎勵。

校長

許雪義

中華民國九十五年三月八日

Certificate of Award

The Bronze Research Award, TMU 2005
is presented to

Assistant Professor Ho, Yuh-Shan
for outstanding performance in research

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Chung Y. Hsu, MD, PhD. President

March 8, 2006



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卓著，經本校研究發展會議審慎評選，榮獲**最具
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優秀論文獎

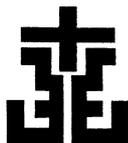
江若蓮、范揚智、何玉山#*、邱文達

Pseudo-Isotherms for the Sorption of Dyes on
Activated Clay

校長

許雪義

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Taipei Medical University

The Faculty Teaching Award

is presented to

Assistant Professor Yuh-Shan Ho

In recognition of excellence

in teaching.

9112

Chung Y. Hsu, MD, Ph.D.

President

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中華民國九十二年六月六日

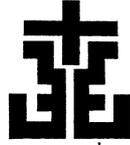
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何玉山助理教授 教學優異，生師評選榮獲
九十一學年度師鐸獎，特致送本狀。

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*The Bronze Research Award, TMU 2001
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For outstanding performance in research

*Chung-Hong Hu, MD, FACP
President
June 1, 2002*

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胡俊弘

狀以茲獎勵。

經本校學術研究委員會審慎評選榮獲優良獎特頒此

何玉山助理教授，於九十年學術研究表現卓著

學術研究獎

人研字9008號

代表論文

代表論文 (一)

Ho, Y.S.*, Huang, C.T. and Huang, H.W. (2002), Equilibrium sorption isotherm for metal ions on tree fern. *Process Biochemistry*, **37** (12), 1421-1430. (SCI)

Rank 1st in citation from 211 papers of *Process Biochemistry* (2002), Last data updates: 30 June 2007

Abstract: A new sorbent system for removing heavy metal ions, such as Zn(II), Cu(II) and Pb(II), from aqueous solutions has been investigated. This new sorbent is tree fern, an agriculture product. Variables of the system include solution temperature and sorbent particle size. The experimental results were fitted to the Langmuir, Freundlich and Redlich-Peterson isotherms to obtain the characteristic parameters of each model. Both the Langmuir and Redlich-Peterson isotherms were found to well represent the measured sorption data. According to the evaluation using the Langmuir equation, the maximum sorption capacities of metal ions onto tree fern were 7.58 mg/g for Zn(II), 10.6 mg/g for Cu(II) and 39.8 mg/g for Pb(II). It was noted that an increase in temperature resulted in a higher metal loading per unit weight of the sorbent. Decreasing the particle sizes of tree fern led in an increase in the metal uptake per unit weight of the sorbent.

Subject Categories:

Biochemistry & Molecular Biology: Impact Factor 2.008, 160/262 (2006)

Biotechnology & Applied Microbiology: Impact Factor 2.008, 66/140 (2006)

Engineering, Chemical: Impact Factor 2.008, 10/110 (2006)

Equilibrium sorption isotherm for metal ions on tree fern

Y.S. Ho*, C.T. Huang, H.W. Huang

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Received 8 January 2002; accepted 20 January 2002

Abstract

A new sorbent system for removing heavy metal ions, such as Zn(II), Cu(II) and Pb(II), from aqueous solutions has been investigated. This new sorbent is tree fern, an agriculture product. Variables of the system include solution temperature and sorbent particle size. The experimental results were fitted to the Langmuir, Freundlich and Redlich–Peterson isotherms to obtain the characteristic parameters of each model. Both the Langmuir and Redlich–Peterson isotherms were found to well represent the measured sorption data. According to the evaluation using the Langmuir equation, the maximum sorption capacities of metal ions onto tree fern were 7.58 mg/g for Zn(II), 10.6 mg/g for Cu(II) and 39.8 mg/g for Pb(II). It was noted that an increase in temperature resulted in a higher metal loading per unit weight of the sorbent. Decreasing the particle sizes of tree fern led in an increase in the metal uptake per unit weight of the sorbent. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Agriculture product; Sorption; Copper; Zinc; Lead; Tree fern

1. Introduction

Elements in every group of the periodic table have been found to be stimulatory to animals. Most metals in the fourth period are carcinogenic. It can be assumed that the carcinogenicity is related to the electronic structure of transition and inner transitional metals [1]. Since copper is an essential metal in a number of enzymes for all forms of life, problems arise when it is deficient or in excess. Excess copper accumulates in the liver and the most toxic form of copper is thought to be Cu^+ . Its toxicity is highly pH dependent and it has been reported to be more toxic to fish at lower pH values [2]. In some respect the intake of essential elements is more critical than for toxic elements. However, epidemiological evidence, such as a high incidence of cancer among coppersmiths, suggests a primary carcinogenic role for copper [1]. The cocarcinogenic character of copper is accepted. A higher incidence of stomach cancer in humans has been found in regions where the Zn:Cu ratio in the soil exceeded certain limits [1]. Lead is a typical toxic heavy metal with cumulative and nonde-

gradative characteristics. Lead is fairly widespread in our consumer society and probably is the most serious toxic metal. Evidence of harmful effects in adults is rarely seen at blood where lead levels are below 80 μg per 100 ml. Human exposure to lead occurs through air, water and food. The passage of lead into and between these media involves many complex environmental pathways. There is a long history of human exposure to abnormally elevated levels of lead in food and drink, due to practices such as cooking in lead-lined or lead-glazed pots and the supply of water through lead pipes [3].

The removal of metal ions from effluents is of importance to many countries of the world both environmentally and for water re-use. The application of low-cost sorbents including carbonaceous materials, agricultural products and waste by-products has been investigated [4]. In recent years, agricultural by-products have been widely studied for metal removal from water. These include peat [5], wood [6], pine bark [7], banana pith [8], rice bran, soybean and cottonseed hulls [9], peanut shells [10], hazelnut shell [11], rice husk [12], sawdust [13], wool [14], orange peel and compost [15] and leaves [16]. Most of this work has shown that natural products can be good sorbents for heavy metals. Indeed, it could be argued that many of these natural

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sorbents remove metals more by ion exchange than by adsorption. Nevertheless, many previous workers tend to base their analyses on sorption theories. These include: the acidic properties of carboxylic and phenolic functional groups present in humic substances [17] [18]. Some ion exchange reactions, e.g. proton release when metal cations bind to peat [17].

This work's goal was to study the possibility of the utilization of tree fern for the sorption of zinc, copper and lead ions from aqueous solutions. The system variables studied include sorbent particle size and temperature. In each system the isotherm constants for the Langmuir, Freundlich and Redlich–Peterson isotherms have been determined.

2. Materials and methods

The major interest of this study was to investigate sorption of heavy metals such as copper, zinc and lead by using tree fern naturally and commercially available in Taiwan. This variety of tree fern is generally marketed for horticultural purposes because of its character of sorb ability to keep water and manure for plants.

The raw tree fern was dried in an oven at 100 °C for a period of 24 h, and then ground and screened through a set of sieves to get different geometrical sizes such 38–43, 53–61, 74–88 and 104–124 µm. This produced a uniform material for the complete set of sorption tests which was stored in an air-tight plastic container for all investigations. Analytical grade reagents were used in all cases. The stock solutions of zinc(II), copper(II) and lead(II) (2000 mg/dm³) were prepared in distilled water using zinc sulphate, copper sulphate and lead nitrate, respectively. All working solutions were prepared by diluting the stock solution with distilled water.

Batch sorption experiments were performed at a constant temperature (20 °C) on a rotary shaker at 100 rpm using 125 ml capped conical flasks. In all sets of experiments, 0.25 g of tree fern (74–88 µm) was thoroughly mixed into 50 ml cation solution. After shaking the flasks for 5 h, the reaction mixtures were filtered through a 0.45 µm membrane filter to remove particulates and the filtrate was analyzed with an inductively coupled plasma atomic emission spectroscopy analyser (ICP-AES) for the concentration of cation.

2.1. Effect of particle size

Batch sorption tests were done at four different tests at particle sizes ranged 38–45, 53–61, 74–88 and 104–124 µm. Each used a range of initial metal ion concentrations from 30 to 150 mg/dm³.

2.2. Effect of temperature

Batch sorption experiments were carried out at the desired temperatures (2, 10, 30 and 40 °C) and each used a range of initial metal ion concentrations from 30 to 150 mg/dm³.

3. Result and discussion

The equilibrium sorption isotherm is fundamentally important in the design of sorption systems. Equilibrium studies in sorption give the capacity of the sorbent. It is described by sorption isotherm characterized by certain constants whose values express the surface properties and affinity of the sorbent. Equilibrium relationships between sorbent and sorbate are described by sorption isotherms, usually the ratio between the quantity sorbed and that remaining in the solution at a fixed temperature at equilibrium. In order to investigate the sorption isotherm, three equilibrium models were analyzed. These included the Langmuir, the Freundlich and the Redlich–Peterson isotherms.

3.1. Langmuir isotherm

The Langmuir sorption isotherm [19] has been successfully applied to many pollutants sorption processes and has been the most widely used sorption isotherm for the sorption of a solute from a liquid solution. A basic assumption of the Langmuir theory is that sorption takes place at specific homogeneous sites within the sorbent. It is then assumed that once a metal ion occupies a site, no further sorption can take place at that site. The rate of sorption 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 ϕ , the rate per unit of surface is:

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

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

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

where k_a and k_d are rate coefficients, r_a is sorption rate, r_d is desorption rate, C is concentration in the solution, and ϕ is fraction of the surface covered.

At equilibrium, the two rates are equal, and:

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

and

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

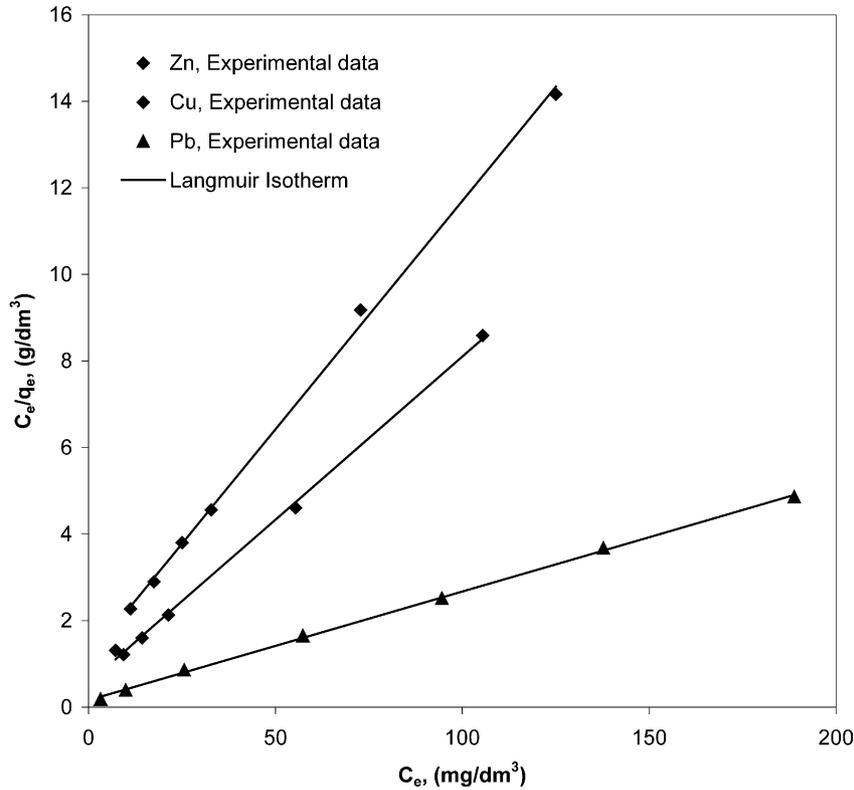


Fig. 1. Langmuir isotherms of metal ions sorbed on tree fern.

Since q_e is proportional to ϕ :

$$\phi = \frac{q_e}{q_m} \quad (5)$$

The saturated monolayer sorption capacity, q_m , can be obtained. When ϕ approaches 1, then $q_e = q_m$.

The saturated monolayer isotherm can be represented as:

$$q_e = \frac{q_m K_a C_e}{1 + K_a C_e} \quad (6)$$

The above equation can be rearranged to the following linear form:

$$\frac{C_e}{q_e} = \frac{1}{K_a q_m} + \frac{1}{q_m} C_e \quad (7)$$

where C_e is the equilibrium concentration (mg/dm³); q_e is the amount of metal ion sorbed (mg/g); q_m is q_e for a complete monolayer (mg/g); K_a is sorption equilibrium constant (dm³/mg). A plot of C_e/q_e versus C_e should indicate a straight line of slope $1/q_m$ and an intercept of $1/K_a q_m$.

3.2. Freundlich isotherm

In 1906, Freundlich studied the sorption of a material onto animal charcoal [20]. He found that if the

concentration of solute in the solution at equilibrium, C_e , was raised to the power $1/n$, the amount of solute sorbed being q_e , then $C_e^{1/n}/q_e$ was a constant at a given temperature.

This fairly satisfactory empirical isotherm can be used for nonideal sorption and is expressed by the following equation:

$$q_e = K_F C_e^{1/n} \quad (8)$$

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

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (9)$$

3.3. Redlich–Peterson isotherm

The Redlich–Peterson isotherm [21] contains three parameters and incorporates the features of the Langmuir and the Freundlich isotherms. The Redlich–Peterson isotherm has a linear dependence on concentration in the numerator and an exponential function in the denominator. It can be described as follows:

$$q_e = \frac{AC_e}{1 + BC_e^g} \quad (10)$$

It has three isotherm constants, namely, A , B and g

Table 1
Isotherm constants for metal ions sorption onto tree fern

	Zn	Cu	Pb
Langmuir			
q_m , (mg/g)	7.58	10.6	39.8
K_a , (dm ³ /mg)	0.0926	0.134	0.156
r^2	0.998	0.998	0.999
Freundlich			
K_F , (mg/g)(dm ³ /mg) ^{1/n}	2.49	3.24	15.5
1/n	0.222	0.261	0.222
r^2	0.940	0.818	0.953
Redlich–Peterson			
g , (dm ³ /mg) ^{1/n}	0.932	0.929	0.907
A , (dm ³ /g)	0.995	1.53	15.6
B	0.185	0.190	0.636
r^2	0.999	0.980	1.000

($0 < g < 1$), which characterize the isotherm. Its limiting behavior is summarized: where $g = 1$

$$q_e = \frac{AC_e}{1 + BC_e} \quad (11)$$

i.e. the Langmuir form results. Where $g = 0$

$$q_e = \frac{AC_e}{1 + B} \quad (12)$$

i.e. the Henry's Law form results.

Eq. (10) can be converted to a linear form by taking logarithms:

$$\ln\left(A\frac{C_e}{q_e} - 1\right) = g \ln(C_e) + \ln(B) \quad (13)$$

Three isotherm constants, A , B and g can be evaluated from the linear plot represented by Eq. (13) using a trial and error optimization method.

A general trial and error procedure which is applicable to computer operation was developed to determine the correlation coefficient, r^2 , for a series of values of A for the linear regression of $\ln(C_e)$ on $\ln(A(C_e/q_e) - 1)$ and to obtain the best value of A which yields a maximum 'optimized' value of r^2 .

The structure of tree fern is cellulose based, and the surface of cellulose in contact with water is negatively charged. Metal compounds used in this study will dissolve to give the cationic metal and this will undergo attraction on approaching the anionic tree fern structure. On this basis, it is expected that a metal cation will have a strong sorption affinity for tree fern.

3.4. Effect of metal ion

Fig. 1 shows the linear plot of C_e/q_e versus C_e gives a straight line of slope $1/q_m$ and intercept $1/K_a q_m$. The values of the Langmuir constants q_m and K_a are presented in Table 1 for the three metal/tree fern sorption systems. These values of the correlation

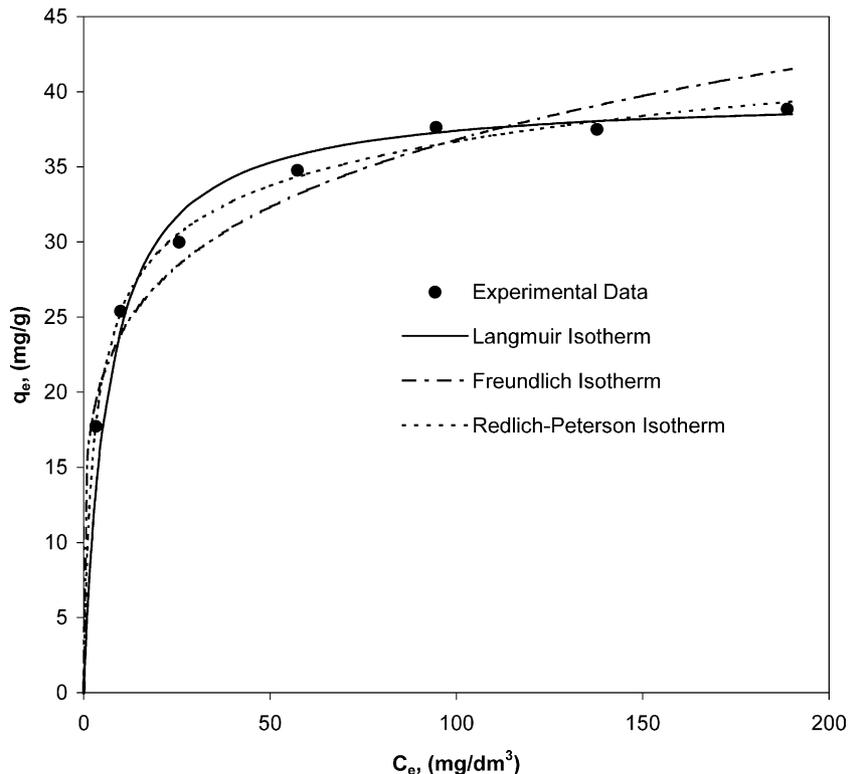


Fig. 2. Isotherms of lead ions sorbed on tree fern.

coefficients indicate that there is a strong positive relationship for the data and that the metal/tree fern sorption data follows the Langmuir sorption isotherm. The monolayer saturation capacities, q_m , for the three metal ions are 7.58, 10.6 and 39.8 mg/g tree fern for zinc, copper and lead, respectively.

The applicability of the Freundlich sorption isotherm is also analyzed by plotting $\log(q_e)$ versus $\log(C_e)$, but data are not found in good agreement as that case of the Langmuir. Table 1 shows the Freundlich sorption isotherm constants and the correlation coefficients.

The sorption behaviour of the zinc, copper and lead on tree fern can be described by the Redlich–Peterson sorption isotherm. Examination of the data shows that the Redlich–Peterson isotherm is an appropriate description of the data for metal ion sorption over the concentration ranges studied. Table 1 shows the Redlich–Peterson isotherm constants A , B and g as well as the correlation coefficients for the metal sorption systems using tree fern. In all cases the Redlich–Peterson isotherm exhibits a high correlation coefficient as the case of the Langmuir, which is a considerably better fit compared with the Freundlich isotherm. In addition, it can be seen that in most cases the values of g tend to unity (>0.907), that is the isotherms are approaching the Langmuir form. Fig. 2 shows plots comparing the theoretical Langmuir isotherm, the empirical Freundlich isotherm and the Redlich–Peterson isotherm with experimental data. The equation shows an excellent fit with the experimental data for the Redlich–Peterson and the Langmuir isotherms.

The solubility of a metal is an essential property to enable the metal to penetrate into the porous structure of tree fern. The concentrations of metal species (i.e. MOH^+ , M(OH)_2 , M(OH)_3^- , and M(OH)_4^{2-}) are too small to affect the concentrations of M^{2+} in this study. Although many metal species can be viewed as potential sorbates in the uptake of M^{2+} from solution, the data presented in this study suggest that, under experimental conditions ($\text{pH} < 6$), the species responsible for the sorptive removal of M^{2+} is the predominant one in the species distribution, namely the M^{2+} . Thus, sorption can be explained by elucidating the mechanism whereby the M^{2+} molecules are accommodated by tree fern surface.

The plateau on each isotherm corresponds to monolayer coverage of the surface by the metal ions and this value is the ultimate sorptive capacity at high concentrations can be used to estimate the specific surface area, S , of tree fern using the following equation and the results are shown in Table 2.

$$S = \frac{q_m N A}{M} \quad (14)$$

where S is the specific surface area, m^2/g tree fern; q_m is

Table 2
Specific surface areas for Zn^{2+} , Cu^{2+} and Pb^{2+}

Metal	q_m (mg metal/g tree fern)	S (m^2/g tree fern)
Zn^{2+}	7.58	1.20
Cu^{2+}	10.6	1.59
Pb^{2+}	39.8	6.43

monolayer sorption capacity, gram metal per gram tree fern; N is Avogadro number, 6.02×10^{23} ; A is the cross sectional area of metal ion, m^2 ; M is molecular weight of metal. For Zn^{2+} , Cu^{2+} and Pb^{2+} ions, the molecular weights are 65.4, 63.5 and 207 and the cross sectional areas of Zn^{2+} , Cu^{2+} and Pb^{2+} have been determined to be 1.72 \AA^2 , 1.58 \AA^2 and 5.56 \AA^2 (Zn^{2+} , Cu^{2+} and Pb^{2+} radius is 0.74 \AA , 0.71 \AA , and 1.33 \AA , Cotton and Wilkinson, 1988) in a close packed monolayer. Therefore, the specific surface areas can be calculated for Zn^{2+} , Cu^{2+} and Pb^{2+} (Table 2). The maximum specific surface area of tree fern towards Zn^{2+} binding is $1.20 \text{ m}^2/\text{g}$; Cu^{2+} binding is $1.59 \text{ m}^2/\text{g}$; Pb^{2+} binding is $6.43 \text{ m}^2/\text{g}$.

The effect of isotherm shape can be used to predict whether a sorption system is ‘favourable’ or ‘unfavourable’ both in fixed-bed systems [22] as well as in batch processes [6]. According to Hall et al. [23], 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:

$$K_R = \frac{1}{1 + K_a C_0} \quad (15)$$

where K_R is a dimensionless separation factor, C_0 is initial concentration (mg/dm^3) and K_a is Langmuir constant (dm^3/mg). The parameter K_R 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 for zinc, copper and lead are given in Fig. 3. The K_R values indicate that sorption is more favourable for the higher initial metal ion concentrations than for the lower ones. The sorption is very favourable for lead and favourable for copper and zinc. Referring to Fig. 3, it is obvious that tree fern is a good sorbent for zinc, copper and lead. According to this classification, system favor ability tends to be in the order of $\text{Pb} > \text{Cu} > \text{Zn}$.

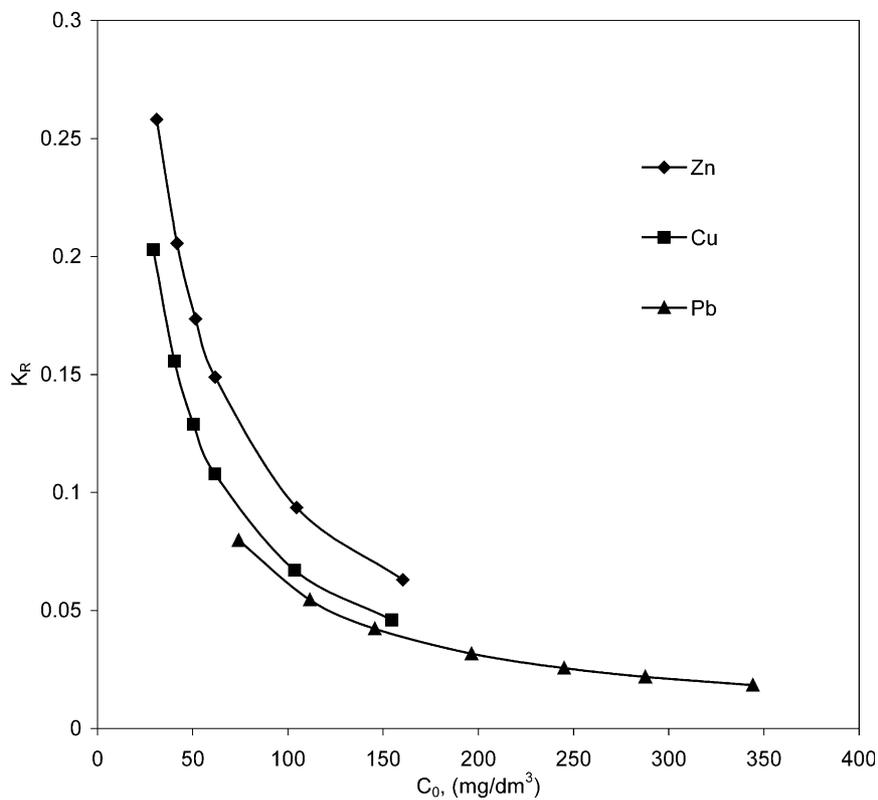


Fig. 3. Plot of K_R against initial metal concentration of Zn(II), Cu(II) and Pb(II).

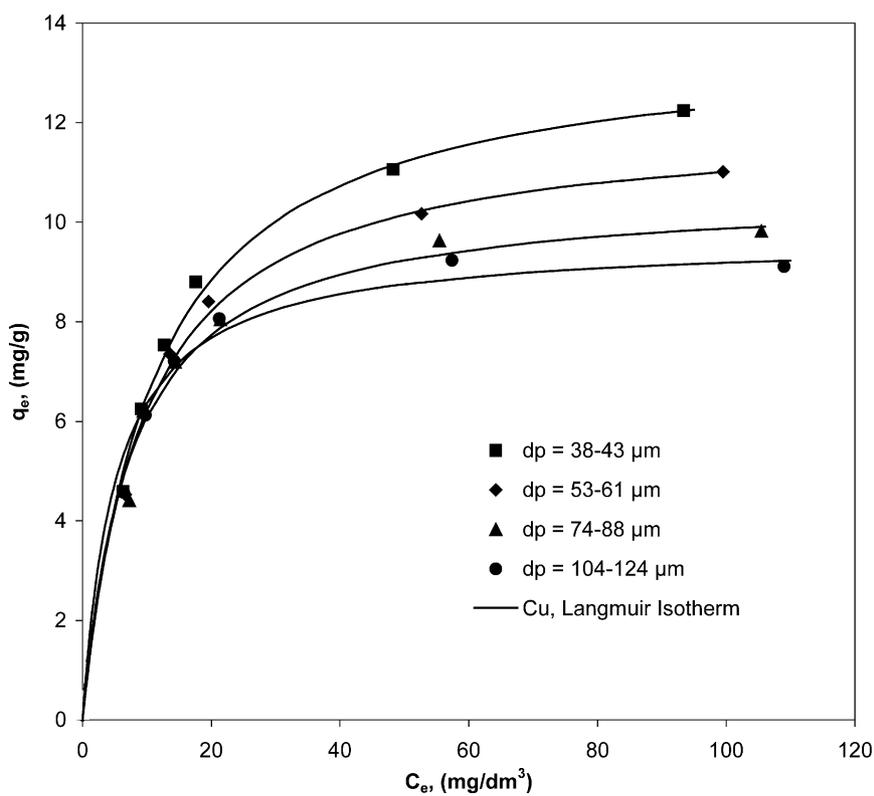


Fig. 4. Langmuir isotherms for the sorption of copper ions using tree fern at various particle sizes.

Table 3
Langmuir sorption isotherm constants at different particle sizes

d_p (μm)	R^2	q_m (mg/g)	K_a (dm^3/mg)	S (m^2/g tree fern)
40.5	0.999	13.7	0.0912	2.05
57	0.999	12.0	0.107	1.81
81	0.998	10.6	0.134	1.59
114	0.998	9.66	0.193	1.45

3.5. Effect of particle size

Sorption isotherms of copper ions at various particle sizes of tree fern are shown in Fig. 4. A Type I sorption curve, as defined by the classification [24], is evident at all particle sizes, indicating a strong uptake of copper(II) from aqueous solution. The amount of copper ion sorbed increased under the condition that the particle size of the sorbent decreased. Langmuir parameters q_m and K_a for each of the four isotherms have been calculated and are listed in Table 3. It is clear that q_m , the monolayer coverage for each particle size, increased from 9.66 to 13.7 mg/g with decreasing particle size from 104–124 to 38–43 μm . This may be attributed to the larger external surface available with smaller particles at a constant total mass of tree fern in the system. The value of monolayer sorption capacity, q_m , can be used to estimate the specific surface area, S , of tree fern using Eq. (14) and the results are shown in Table 3. The mean diameter of the tree fern, d_p , the Langmuir sorption

constant, K_a , and the monolayer coverage, q_m , from Table 3 can be used to derive a mathematical relationship. The relationship has a correlation coefficient as high as 0.999 are:

$$q_m = \frac{d_p}{0.121d_p - 2.06} \tag{16}$$

$$K_a = \exp(1.02 \times 10^{-2}d_p - 2.81) \tag{17}$$

The values of K_R for copper at different particle sizes are given in Fig. 5. Again, the K_R values indicate that sorption is more favourable for the higher initial copper concentrations than for the lower ones. However, the sorption process becomes more favourable with increasing particle size of tree fern.

3.6. Effect of temperature

Sorption isotherms of copper ions at various temperatures of solution are shown in Fig. 6. The sorption process conforms the Langmuir sorption isotherm to high correlation coefficient (> 0.997). Values of Langmuir parameters, q_m and K_a for different temperatures have been calculated from Eq. (7) and the results are given in Table 4. It is clear that monolayer coverage for each temperature increased with increasing temperature. Increasing the temperature may produce a swelling effect within the internal structure of tree fern enabling metal ions to penetrate further [25]. The value of q_m obtained

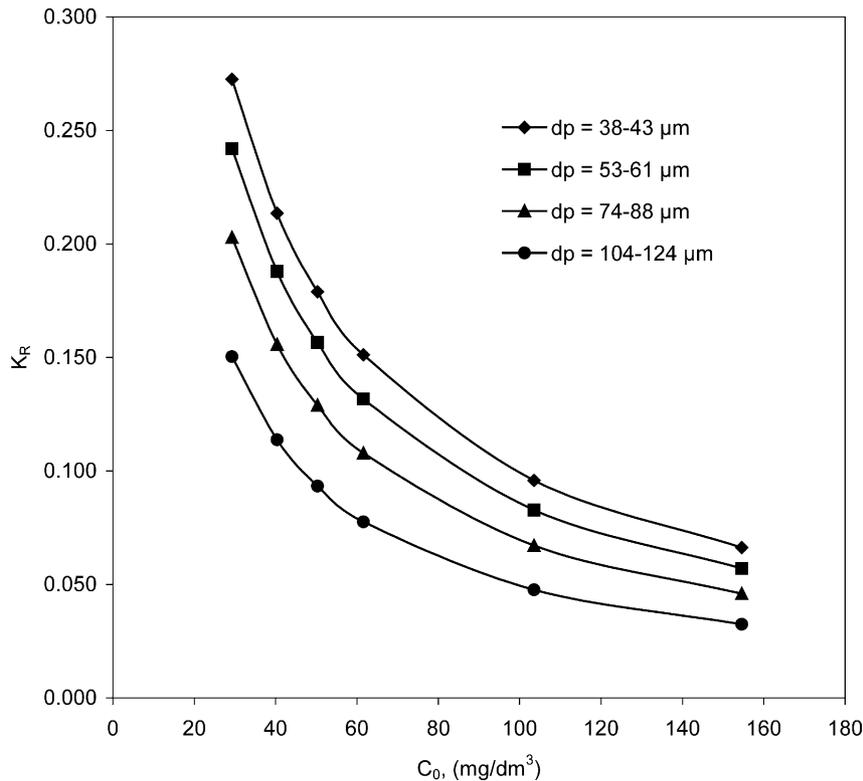


Fig. 5. Plot of K_R against initial copper ion concentration of various particle sizes.

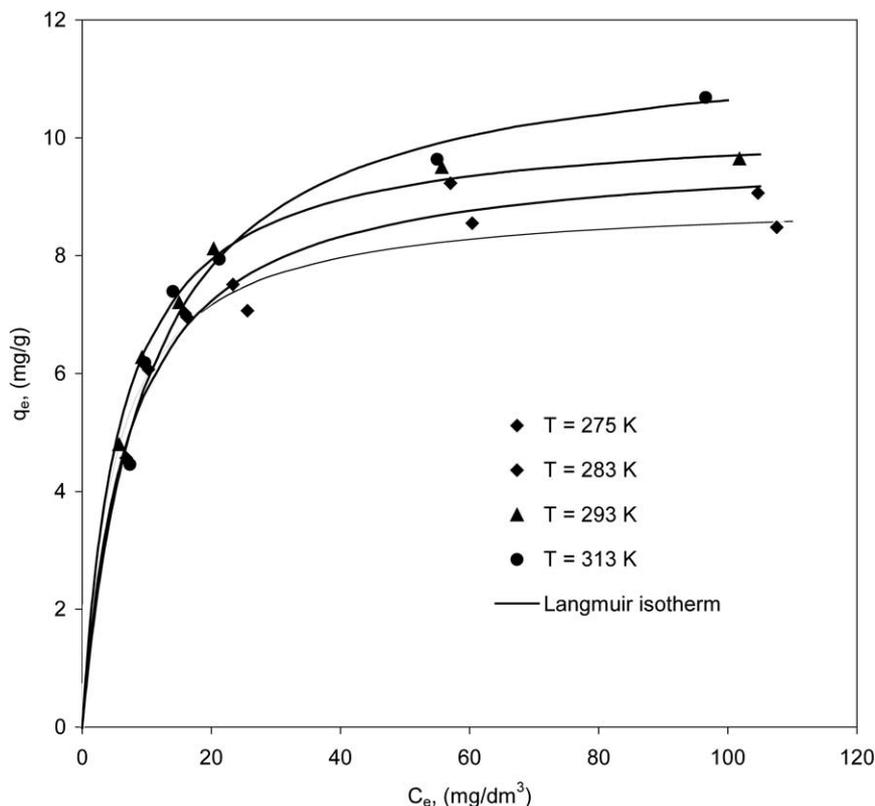


Fig. 6. Langmuir isotherms for the sorption of copper ions using tree fern at various temperatures.

Table 4
Langmuir sorption isotherm constants at different temperatures

T (K)	r^2	q_m (mg/g)	K_a (dm ³ /mg)
275	0.999	8.98	0.197
283	0.997	9.80	0.141
293	1.000	10.3	0.170
313	0.998	11.7	0.100

at 40 °C appears to be higher in comparison with the uptakes obtained at the other temperatures.

The values of K_R for copper at different temperatures are shown in Fig. 7. All calculated K_R values indicate that sorption of copper(II) on tree fern is favourable at all concentrations and temperatures studied. The K_R values indicate that sorption is more favourable for the higher initial copper ion concentrations and temperatures than for the lower ones. Referring to Fig. 7, it is obvious that tree fern is a good sorbent for removing copper from solution.

4. Conclusion

Tree fern is able to sorb zinc, copper and lead ions from aqueous solutions. It was noted that an increase in the temperature resulted in a higher metal loading per unit weight of the sorbent. Decrease in the particle size of tree fern resulted in an increase in the metals uptake per unit weight of the sorbent. Metal/tree fern isotherms have been developed and analyzed according to three isotherm equations. The experimental results were analyzed by using the Langmuir, Freundlich and Redlich–Peterson equations and the correlation coefficients for fitting the Langmuir and Redlich–Peterson equations were significantly better than the coefficients for the Freundlich equation. The results from this study are extremely well described by the theoretical Langmuir isotherm and the three-parameter Redlich–Peterson isotherm. The metal ion binding capacity of biosorbent was a function of particle size, temperature and type of metal ion. Sorption capacity increases with increasing temperature, but decreases with increasing tree fern particle size. The results showed that tree fern can be used for the sorption of the Zn^{2+} , Cu^{2+} and Pb^{2+} .

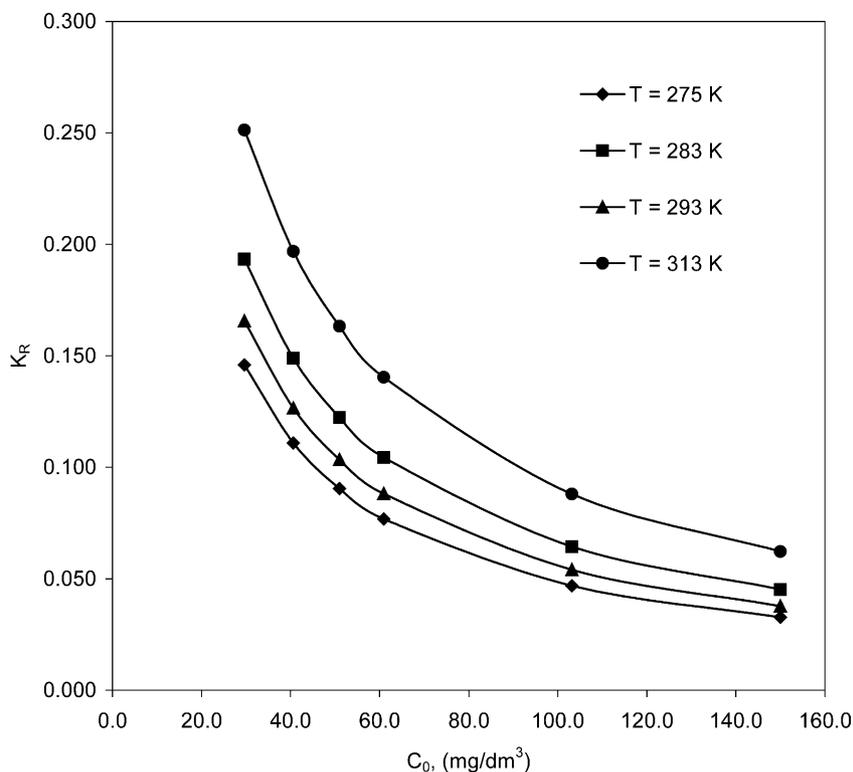


Fig. 7. Plot of K_R against initial copper ion concentration of various temperatures.

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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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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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Keywords: Isotherm; Kinetics; Copper; Tree fern; Pseudo-second-order sorption kinetics; Thermodynamic

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:

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

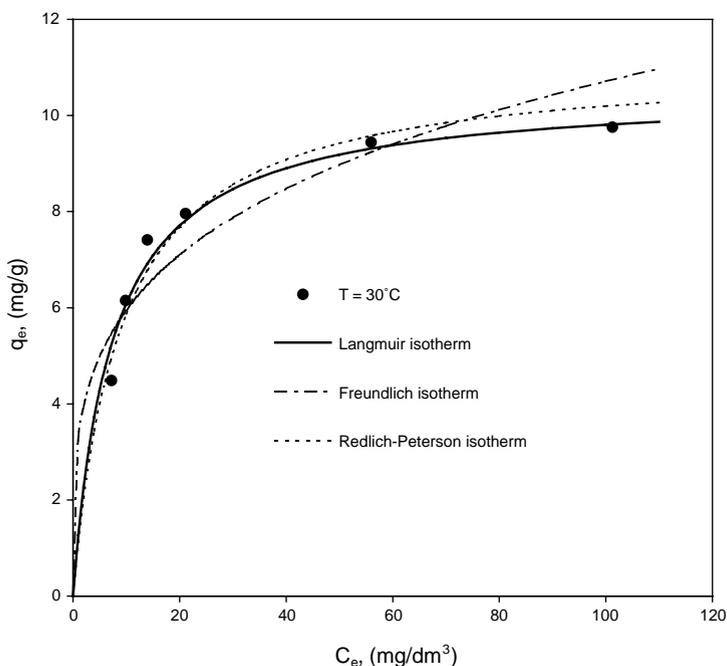


Fig. 1. Isotherms for the sorption of copper(II) using tree fern.

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

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

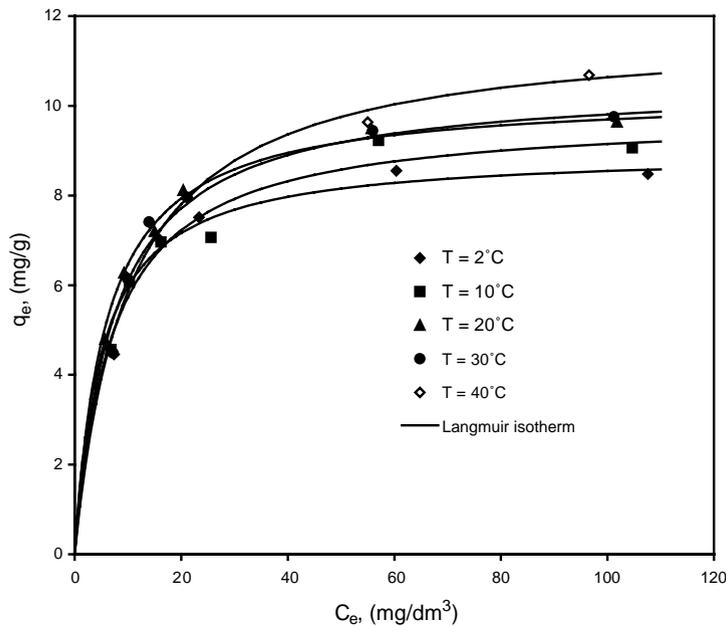


Fig. 2. Langmuir isotherms for the sorption of copper ions on tree fern.

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.

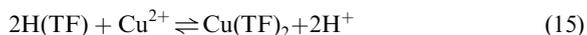
3.2. Kinetic studies

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

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

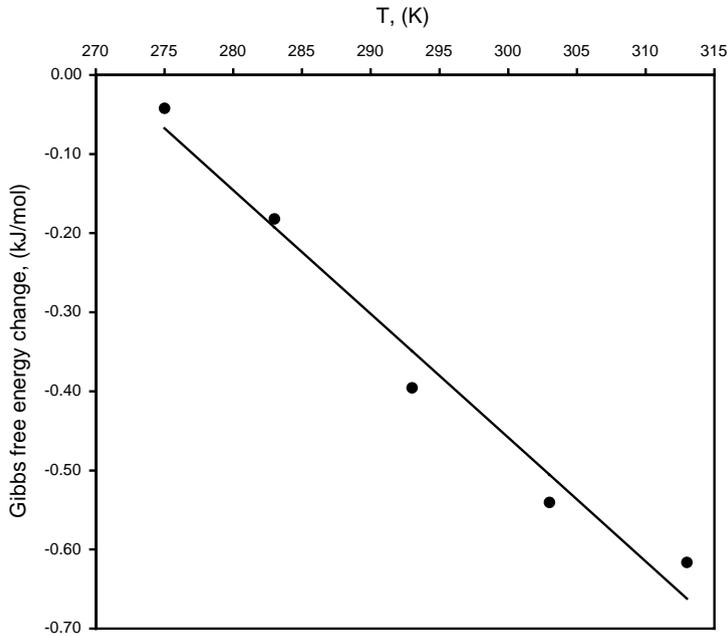


Fig. 3. Plot of Gibbs free energy change, ΔG° , versus temperature, T .

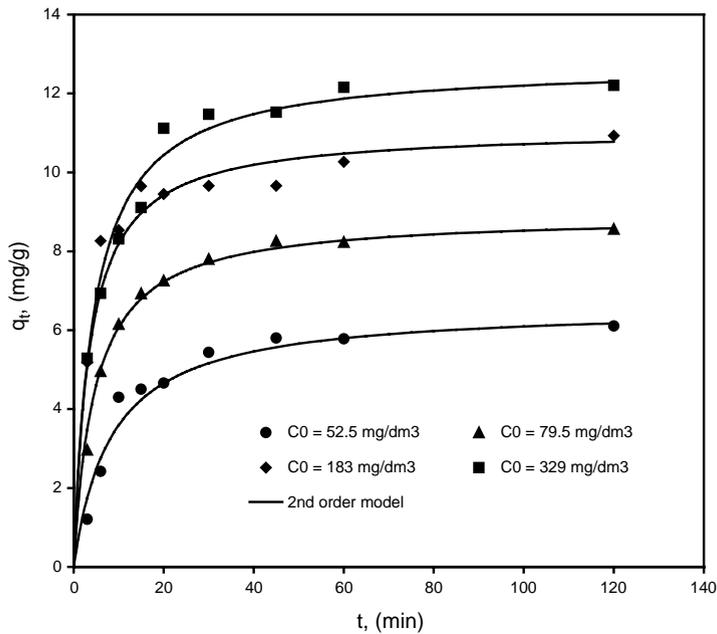


Fig. 4. Plot of sorbed amount versus time for copper(II) at various initial concentrations.

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

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

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

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

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):

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

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 slope 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

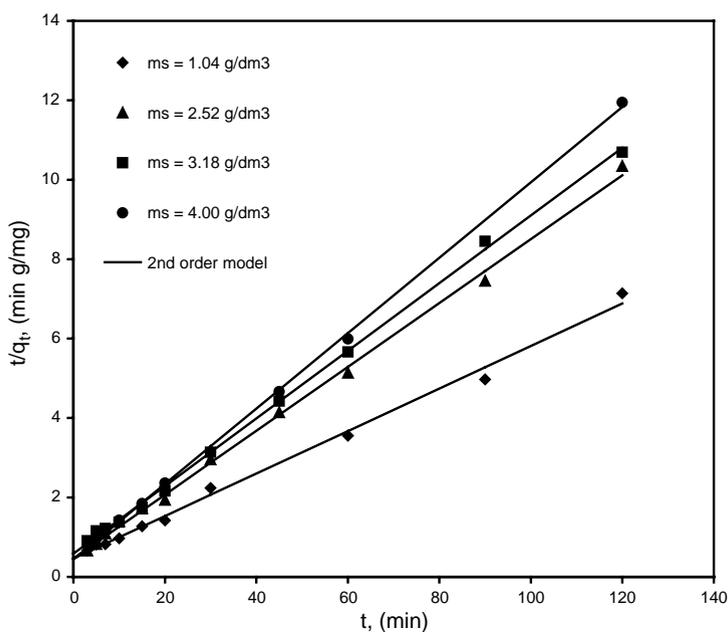


Fig. 5. Pseudo-second-order sorption kinetics of copper(II) on tree fern at various doses.

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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代表論文 (三)

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Abstract: The batch kinetic sorption of copper ions and dyes onto two low-cost biosorbents, peat and pith, has been studied. A model, based on the assumption of a pseudo-second-order mechanism, has been developed to predict the rate constant of sorption, the equilibrium capacity and initial sorption rate with the effect of initial concentration, particle size, temperature and sorbent concentration dose. An activation energy of sorption has also been evaluated as 7.13 kJ/mol for the sorption of BB69 onto pith.

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Sorption of dyes and copper ions onto biosorbents

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Abstract

The batch kinetic sorption of copper ions and dyes onto two low-cost biosorbents, peat and pith, has been studied. A model, based on the assumption of a pseudo-second-order mechanism, has been developed to predict the rate constant of sorption, the equilibrium capacity and initial sorption rate with the effect of initial concentration, particle size, temperature and sorbent concentration dose. An activation energy of sorption has also been evaluated as 7.13 kJ/mol for the sorption of BB69 onto pith. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Biosorbent; Copper; Dye; Kinetics and sorption

1. Introduction

Increasing limits imposed by Environmental Legislation on the concentrations of pollutants in aqueous effluents make treatment imperative. Adsorption is an attractive method for the removal of solutes from effluents since if the adsorption system is designed correctly it will produce a high-quality treated effluent [1,2]. The sorption process, in comparison with the other listed processes for the treatment of polluted aqueous effluents, allows flexibility in design and operation, and produces aesthetically superior effluent suitable for re-use, free of pollutant. In addition, because adsorption is sometimes reversible, the regeneration of the sorbent with resultant economy of operation may be possible. Adsorption is a physiochemical wastewater treatment process, which has gained prominence as a means of producing quality treated effluents from effluents, which contained low concentrations of dissolved organic compounds and metal ions. Dissolved molecules are attracted to the surface of the adsorbent and this interaction may be expressed both in terms of adsorptive characteristics and physical properties. The most widely used adsorbent is activated carbon but it is expensive and if lower cost adsorbents could be found it would

reduce adsorption process costs. Several of the alternatives which have been investigated are activated silica, activated alumina, peat, wood, lignite, bagasse pith, waste red mud and fly ash. Consequently in the present paper, two low-cost adsorbents, namely peat and pith have been used to treat two common effluents—a copper ion containing effluent and two dye containing effluents.

Peanut hull has been used to sorb copper ions [3] and agricultural waste has been used for the same purpose [4]. Over 100 sorption systems for copper uptake onto plants, fungi, algae and several other sorbents have been reported [5–7]. Activated silica has been shown to be useful in treating textile mill effluent [8] and to remove basic dyes using a fluidised bed system [9] and its economic viability is enhanced by the possibility of its regeneration and re-use. Activated alumina has also been investigated for removing phosphates from wastewaters [10]. Peat has been used to sorb heavy metal ions [11,12]. A considerable amount of research work has been done recently on the adsorption of dyes on both peat and wood [13–19]. In search for cheaper adsorbents, it was decided to undertake a study to assess the potential of bagasse pith as an adsorbent for dyestuffs and sphagnum moss peat for metal ion removal. Bagasse pith is a waste product from the sugarcane industry. Waste banana pith [20] has been used for colour removal from wastewaters, and waste red mud [21] has been used to adsorb Congo Red dye.

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Table 1
Chemical analysis of the bagasse pith

Determination	%
α -Cellulose	53.7
Pentosan	27.9
Lignin	20.2
Alcohol/benzene solubility	7.5
Ash	6.6

In order to design sorption treatment systems, a knowledge of kinetic/diffusion processes is essential. The simpler the model, the easier and more economic becomes the design procedure but accuracy should not be sacrificed. This paper uses two models—one reaction kinetic-based and another intraparticle diffusion-based models to analyse sorption data for three systems. The three systems studied are copper onto peat, Acid Blue 25 (AB25) dye and Basic Blue 69 (BB69) dye onto pith.

2. Materials and methods

2.1. Materials

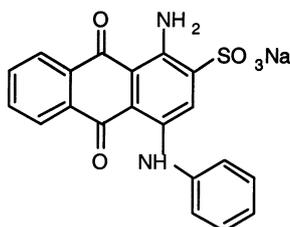
The sphagnum moss peat used in this study, which was from northern Ireland, was obtained from a local Garden Centre. It was dried at 105 °C for 24 h and then screened through a 14-mesh sieve (B.S. 410/43) before being used. The Egyptian bagasse pith was provided by Abou-Korkas sugar mill (El-Minia, Egypt). The pith particles were sieved in the laboratory into various particle size ranges.

The bagasse pith had the compositions based on a chemical analysis, as shown in Table 1.

2.1.1. Sorbates

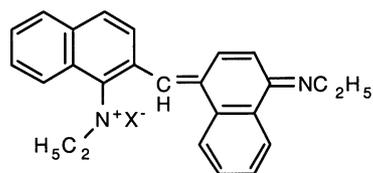
The sorbates used in the experiments and their structures are listed below. The dyestuffs were used as the commercial salts.

Acid Blue 25 (Telon Blue ANL) CI 62055 was supplied by Bayer:



Basic Blue 69 (Astrazone Blue FRR) was supplied by Bayer. No structure is available for this dye. It belongs to the methine class, of which the chromophore is a conjugate chain of carbon atoms terminated by an

equivalent unsaturated group. A general structure for the methine class is:



2.2. Methods

The sorption of copper ions onto peat and BB69 and AB25 dyes onto pith were carried out by batch sorption and the variables studied were initial sorbate concentration, particle size and temperature. Samples were withdrawn at suitable time intervals and were filtered and their concentrations determined by spectrophotometry for the dyes and an atomic absorption spectrophotometer for copper. The effect of concentration of dye solution on the sorption was studied by contacting a fixed mass of pith (1.7 g for BB69 and 3.4 g for AB25) at a fixed particle size (500–710 μm) with 1.7 dm^3 of solution in a range of concentration (200–300 mg/dm^3 for BB69 and 100–166 mg/dm^3 for AB25) using a fixed impeller speed (400 rpm) at a fixed temperature (20 °C).

The effect of concentration of copper solution on the sorption was studied in capped conical flasks (500 ml), by suspending the peat in the copper ion solution, adjusting the pH to a value of 5 with either sulphuric acid or sodium hydroxide solution and mixing on a shaker with a constant speed of 100 rpm.

The effect of particle size on sorption was studied by contacting a fixed mass of pith (1.7 g for BB69 and 3.4 g for AB25) at a range of particle sizes (500–710, 355–500, 500–710 and 710–1000 μm) with 1.7 dm^3 of a dye solution of a fixed initial concentration (200 mg/dm^3 for BB69 and 100 mg/dm^3 for AB25) using a fixed impeller speed (400 rpm) at a fixed temperature (20 °C).

The effect of temperature on dye sorption was studied by contacting a fixed mass of pith (1.7 g for BB69 and 3.4 g for AB25) at a fixed particle size (500–710 μm) with 1.71 dm^3 of a dye solution of a fixed concentration (200 mg/dm^3 for BB69 and 170 mg/dm^3 for AB25) using a fixed impeller speed (400 rpm) at a range of temperatures (20, 40, 60 and 80 °C).

The effect of pith dose on sorption was studied by contacting a fixed particle size (500–700 μm) at a range of pith dosages (0.25–0.75 g/dm^3 for BB69 and 0.5–1 g/dm^3 for AB25) with 1.7 dm^3 of a dye solution of a fixed initial concentration (200 mg/dm^3 for BB69 and 100 mg/dm^3 for AB25) using a fixed impeller speed (400 rpm) at a fixed temperature (20 °C).

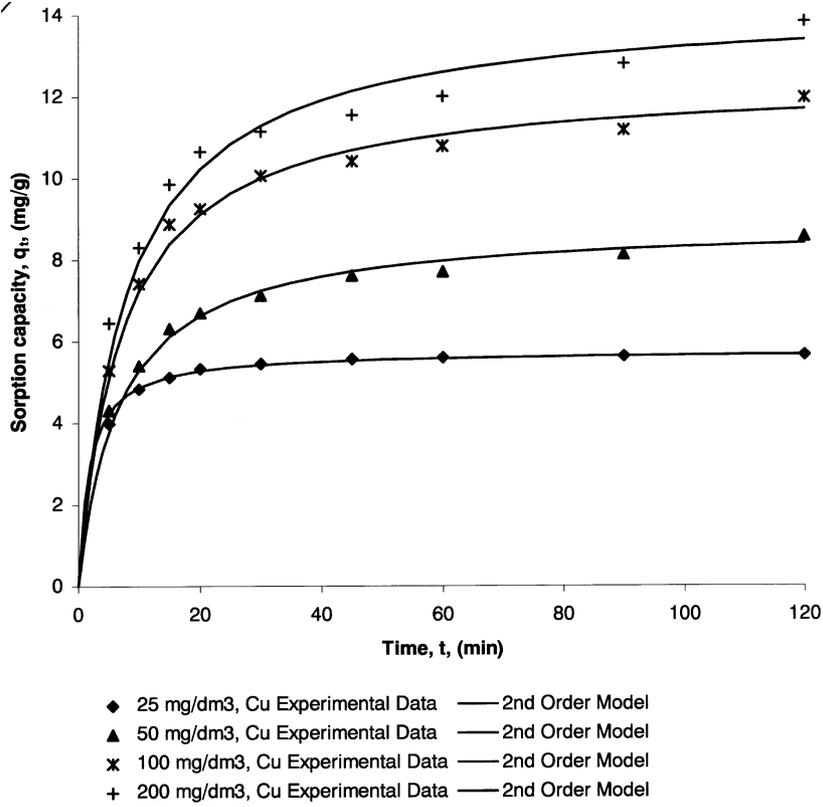


Fig. 1. Effect of initial concentration on the sorption of copper onto peat.

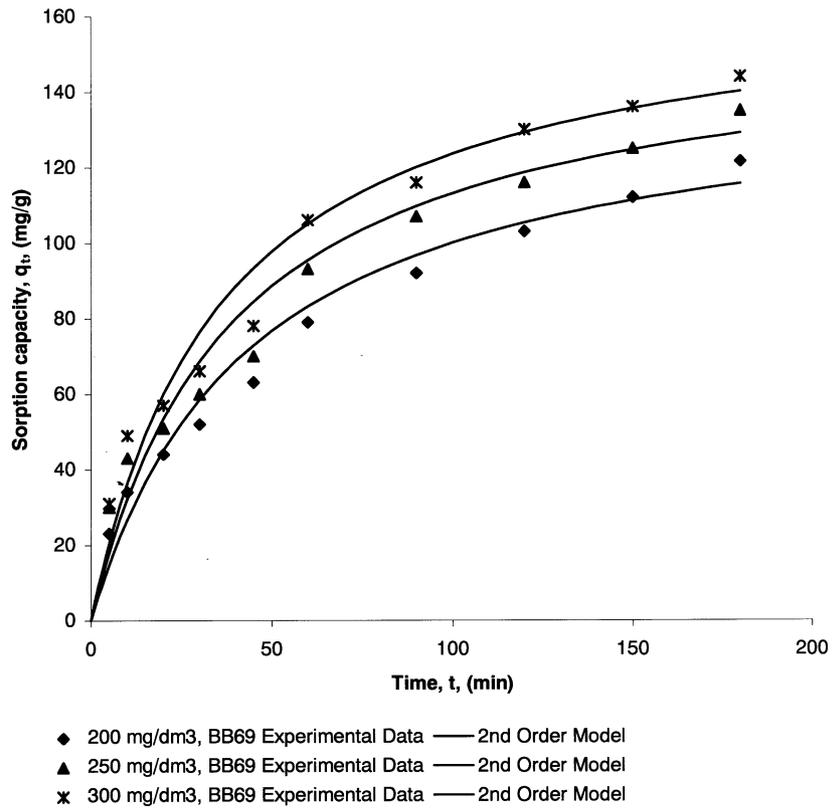


Fig. 2. Effect of initial concentration on the sorption of BB69 onto pith.

Table 2
Effect of initial concentration of copper, AB25 and BB69

	C_0 (mg/dm ³)	r^2	q_e (mg/g)	k (g/(mg min))	h (mg/(g min))	R_c (%)	r_i^2	k_i (mg/(g min ^{0.5}))
Cu	25	1.00	5.75	9.64×10^{-2}	3.19	92.0	0.630	0.147
	50	0.999	8.87	1.68×10^{-2}	1.32	70.9	0.865	0.429
	100	0.998	12.4	1.13×10^{-2}	1.73	49.5	0.818	0.634
	200	0.996	14.3	8.91×10^{-3}	1.81	28.5	0.874	0.720
BB69	200	0.974	1.44×10^2	1.59×10^{-4}	3.29	71.8	0.995	8.86
	250	0.972	1.57×10^2	1.66×10^{-4}	4.07	62.7	0.986	9.55
	300	0.978	1.68×10^2	1.65×10^{-4}	4.67	56.0	0.976	10.3
AB25	100	0.979	11.2	1.83×10^{-3}	0.232	22.5	0.986	0.700
	129	0.963	12.1	1.86×10^{-3}	0.270	18.7	0.978	0.744
	166	0.954	14.4	1.19×10^{-3}	0.246	17.3	0.983	0.881

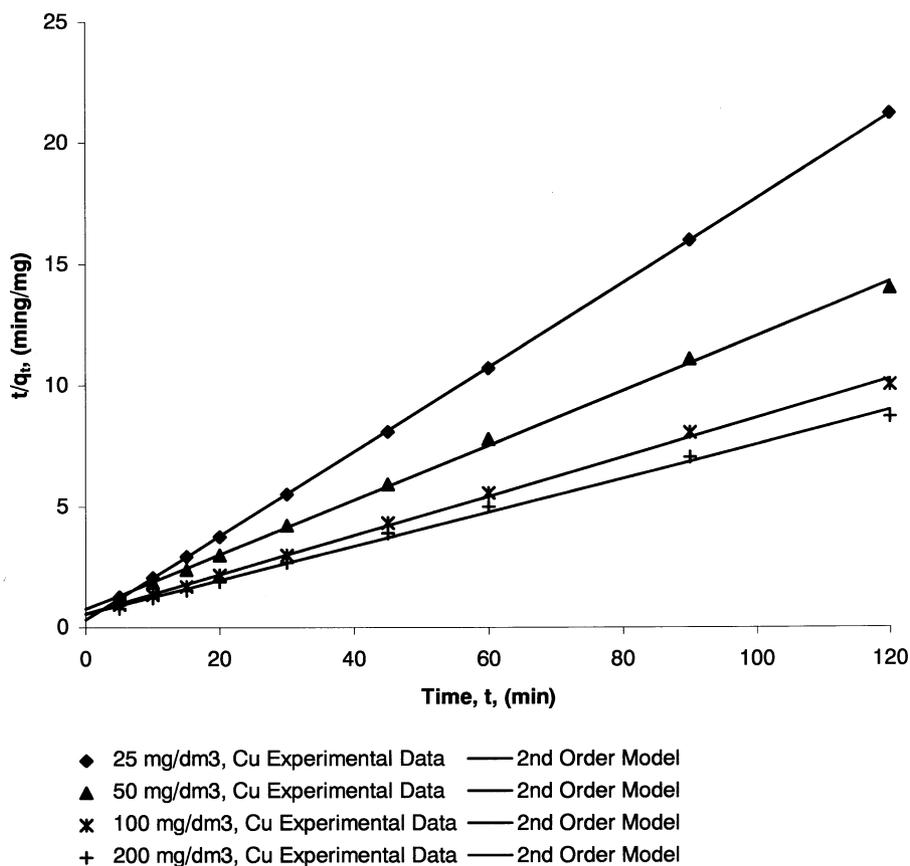


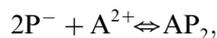
Fig. 3. Plot of amount of sorption versus time for copper sorption onto peat at various initial concentrations.

3. Results and discussion

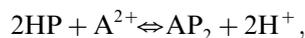
The sorption of pollutants from aqueous solutions plays a significant role in water pollution control. It is therefore important to be able to predict the rate at which contamination is removed from aqueous solutions in order to design an appropriate adsorption treatment plant.

Pith is the name commonly given to parenchyma cells which have the character of fibres and peat contains polar functional groups such as aldehydes, ketones,

acids, and phenolics. These characters of biomaterials can be involved in chemical bonding and are responsible for the cation exchange capacity. Thus, the reaction may be expressed by the following two relationships:



and



where P^- and HP are polar sites on the biosorbent surface and A^{2+} is soluted sorbates.

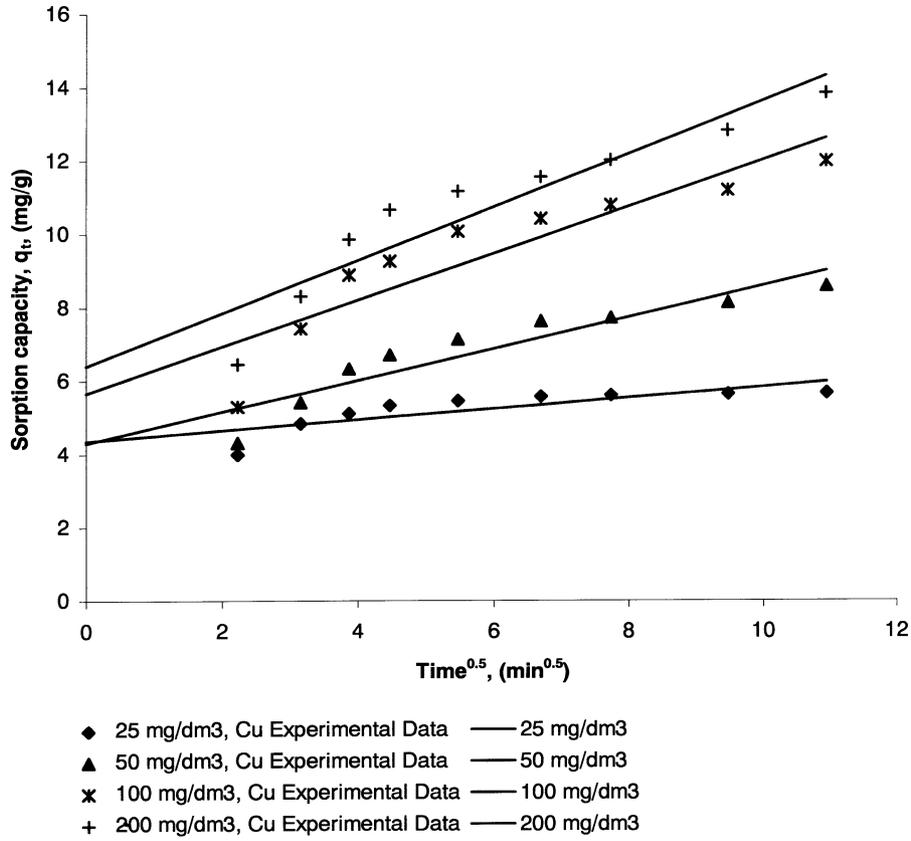


Fig. 4. Plot of sorption capacity versus square root of time for copper sorption onto peat.

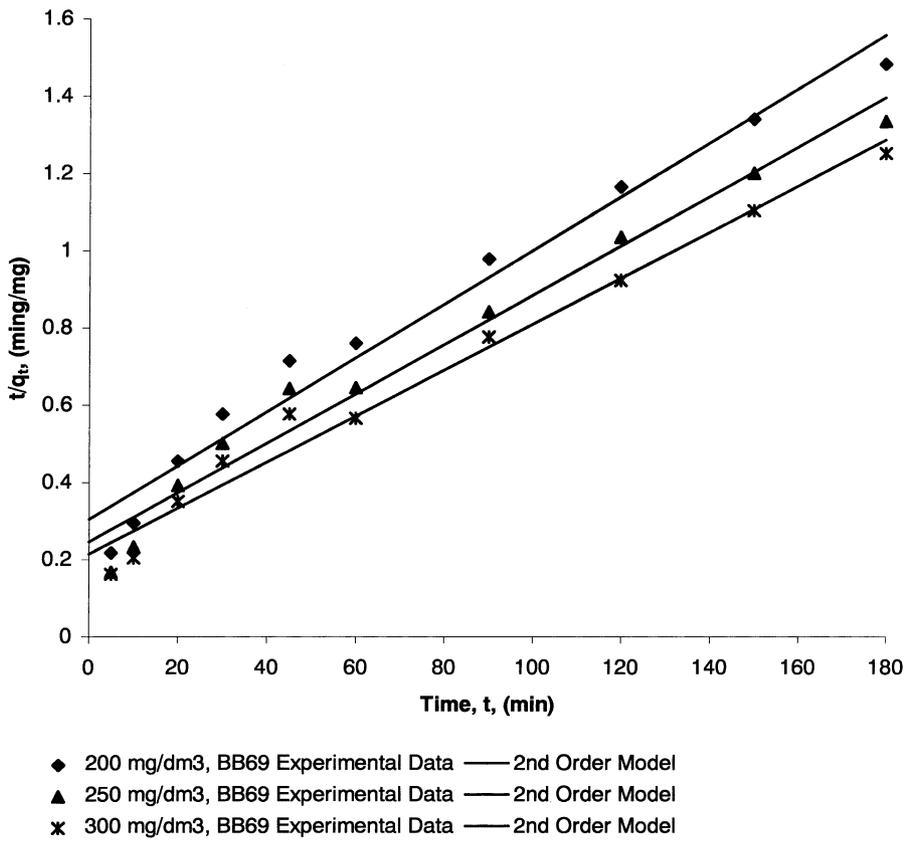


Fig. 5. Plot of amount of sorption versus time for BB69 sorption onto pith at various initial concentrations.

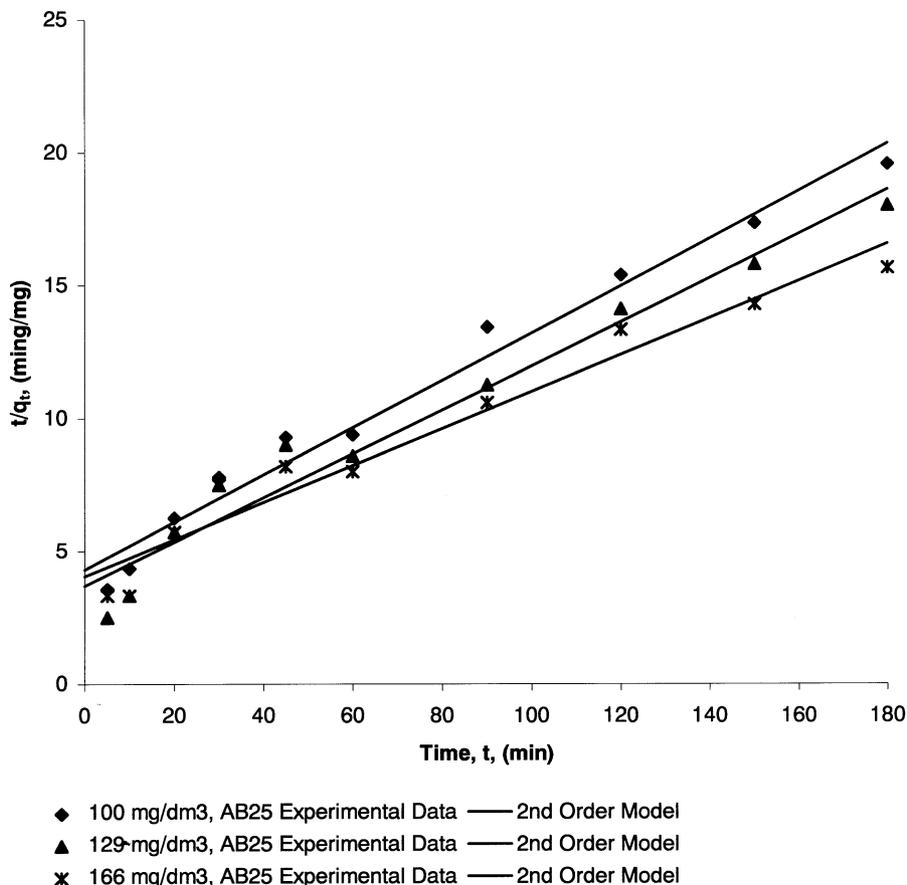


Fig. 6. Plot of amount of sorption versus time for AB25 sorption onto pith at various initial concentrations.

The rate of pseudo-second-order reaction may be dependent on the amount of solute sorbed on the surface of biosorbent and the amount sorbed at equilibrium. The sorption equilibrium, q_e , is a function of, e.g., the temperature, the initial metal ion concentration, the biosorbent dose, particle size and the nature of solute–sorbent interaction.

The rate expression for the sorption described is

$$\frac{d(P)_t}{dt} = k[(P)_0 - (P)_t]^2,$$

or

$$\frac{d(HP)_t}{dt} = k[(HP)_0 - (HP)_t]^2,$$

where $(P)_t$ and $(HP)_t$ are the number of active sites occupied on the biosorbent at time t and $(P)_0$ and $(HP)_0$ are the number of equilibrium sites available on the biosorbent.

The kinetic rate equations can be rewritten as follows:

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

where k is the rate constant of sorption ($g/(mg \text{ min})$), q_e the amount of soluted sorbate at equilibrium (mg/g) and q_t the amount of soluted sorbate on the surface of the biosorbent at any time t (mg/g).

Separating the variables in the equation above gives

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

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

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + kt, \quad (1)$$

which is the integrated rate law for a pseudo-second-order reaction.

The kinetics of sorption of copper, BB69 and AB25 on biosorbents (peat and pith) were studied on the basis of the pseudo-second-order rate equation (1) and

$$h = kq_e^2, \quad (2)$$

where h is the initial sorption rate ($mg/(g \text{ min})$).

Eq. (1) can be rearranged to Eq. (3) which provides a linearised form for plotting as q_t/t versus time t :

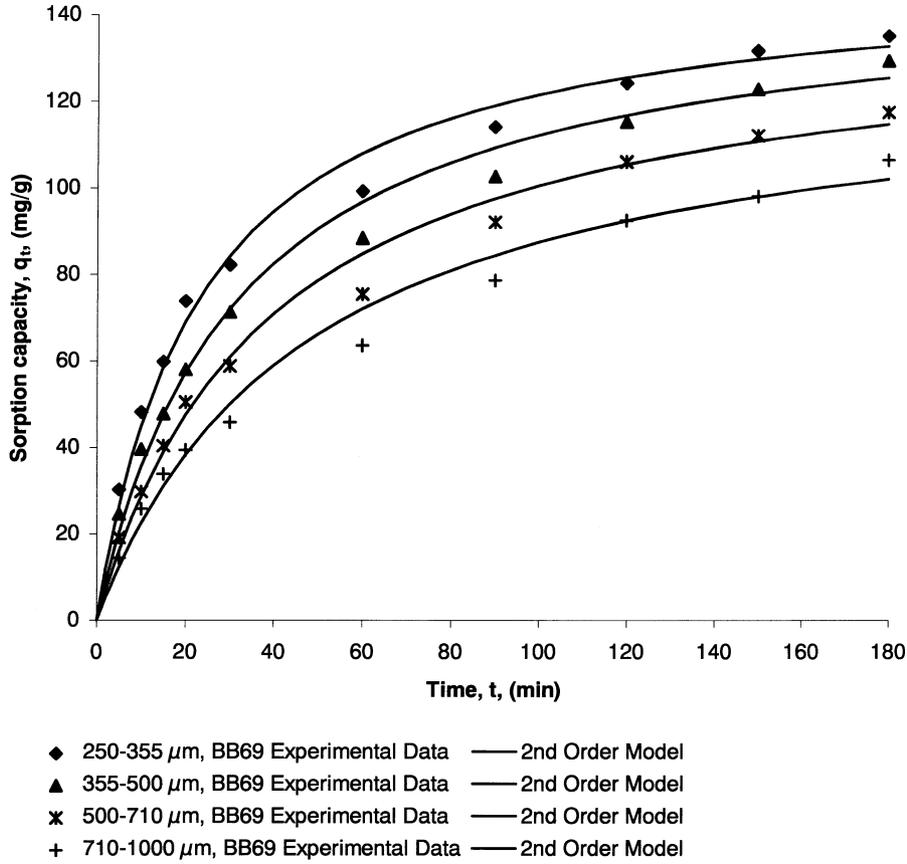


Fig. 7. Effect of pith particle size on the sorption of BB69 onto pith.

Table 3
Effect of particle size of BB69 and AB25

	d_p (μm)	r^2	q_c (mg/g)	k (g/(mg min))	h (mg/(g min))	R_c (%)	r_i^2	k_i (mg/(g min ^{0.5}))
BB69	250–355	0.997	1.50×10^2	2.86×10^{-4}	6.43	74.9	0.956	8.91
	355–500	0.993	1.47×10^2	2.17×10^{-4}	4.70	73.6	0.980	9.12
	500–710	0.991	1.39×10^2	1.87×10^{-4}	3.61	69.6	0.985	8.77
	710–1000	0.984	1.29×10^2	1.65×10^{-4}	2.73	64.3	0.995	8.07
AB25	250–355	0.999	14.3	3.78×10^{-3}	0.769	28.0	0.926	0.820
	355–500	0.997	12.8	3.64×10^{-3}	0.599	25.2	0.926	0.745
	500–710	0.998	11.6	3.13×10^{-3}	0.419	22.7	0.934	0.722
	710–1000	0.995	10.0	2.57×10^{-3}	0.259	19.7	0.968	0.636

$$\frac{t}{q_t} = \frac{1}{kq_c^2} + \frac{1}{q_c} t. \tag{3}$$

3.1. Effect of contact time and initial concentration

Figs. 1 and 2 show the effect of agitation time on the removal of copper ions by peat and BB69 by pith. The results show that an increase in the initial copper and dye concentrations produces a reduction in the percentage removal of copper ions and dyestuff from the

water. The removal of copper decreases from 92.0 to 28.5% with the increase of initial copper ion concentration from 25 to 200 mg/dm³ at pH 5, showing the process to be highly dependent on the initial concentration. The percentage removal of BB69 and AB25 also decreases with an increase in the initial dye concentrations. The removal of BB69 decreases from 71.8 to 56.0% with the increase of initial concentration from 200 to 300 mg/dm³ and for AB25 from 22.5 to 17.3% with the increase of initial dye concentration from 100 to 166 mg/dm³. However, it may be shown that the adsorption capacity varies from 5.75 to 14.3 mg/g, as C_0 varies from

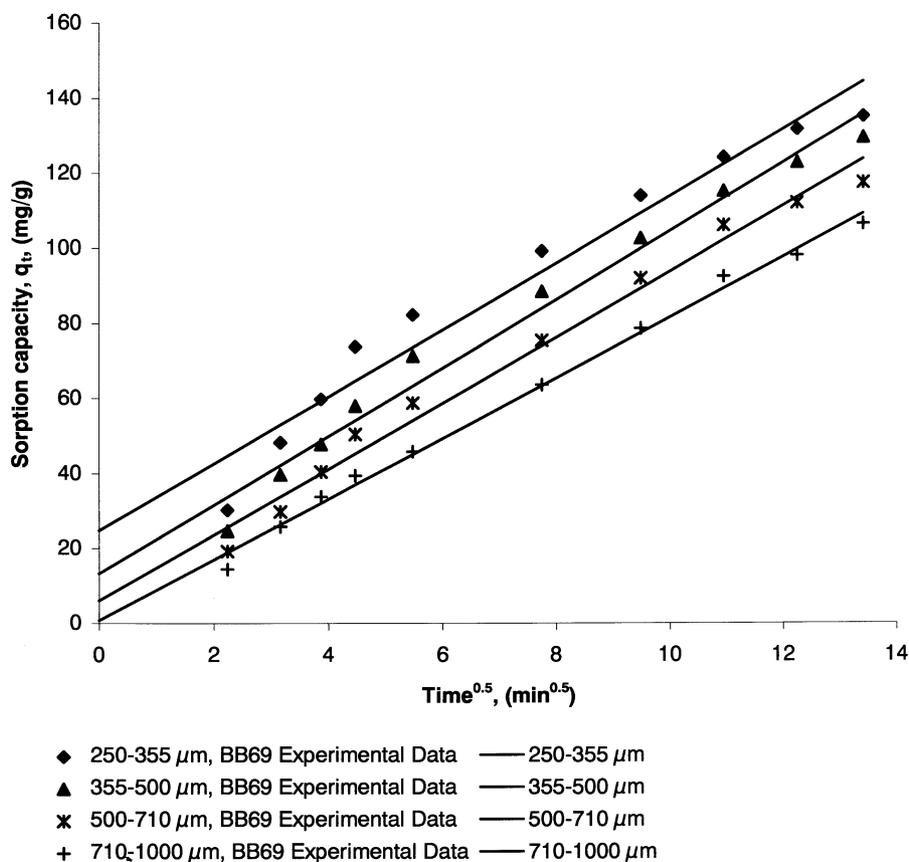


Fig. 8. Plot of sorption capacity versus square root of time for BB69 sorption onto pith.

25 to 200 mg/dm³ for copper; from 144 to 168 mg/g, as C_0 varies from 200 to 300 mg/dm³ for BB69 and from 11.2 to 14.4 mg/g, as C_0 varies from 100 to 166 mg/dm³ for AB25. It is clear that the sorption capacity of basic dye is always much higher than acid dye in the pith sorption system. The rate constants, k , obtained from the plots of Eq. (3), are shown in Table 2. Fig. 3 shows a plot of the linearised form of the model in Eq. (3) for the sorption of copper ions onto peat at different initial copper ion concentrations. Table 2 also indicates that the regression coefficients for the linear plots from the pseudo-second-order equation are better than 0.954 for all systems. The correlation coefficient of the two dye/pith sorption systems are lower than the copper/peat system as shown from data in Table 2.

The nature of the rate-limiting step in a batch system can be assessed from the properties of the solute and sorbent. Weber and Morris [22] stated that if intraparticle diffusion is the rate-controlling factor, uptake of the sorbate varies with the square root of time. Thus, rates of sorption are usually measured by determining the change in concentrations of sorbate with the sorbent as a function of the square root of time. Fig. 4 shows the amount of sorption against square root of time and the straight lines do not pass through the origin; therefore,

intraparticle diffusion also may not be the sole rate-limiting factor [14]. Poots et al. [13] proposed that during the early stages of sorption, some boundary layer resistance was involved. However, for the sorption of copper ions onto peat, the linearised plots of Eq. (3) have a good correlation of the data as shown in Fig. 3. The correlation coefficients, r^2 , for the pseudo-second-order kinetic model are much greater than the intraparticle diffusion coefficients for the sorption/reaction of copper ions onto peat, strongly suggesting a chemical reaction mechanism. In the case of the sorption of the two dyes on pith, the reaction correlation coefficients and the intraparticle diffusion coefficients are all high (>0.95) with most of the r_i^2 -values being slightly higher. This suggests that for dye sorption onto pith, the mechanism is predominantly intraparticle diffusion but the distinction is not completely clear. The overall rate of the sorption process appears to be controlled by the chemical process in the case of copper in accordance with the pseudo-second-order reaction mechanism. For the two dyes, there could be a combination of mechanisms. Eq. (3) has been plotted to show the effect of initial dye concentration for the sorption of BB69 and AB25 in Figs. 5 and 6 respectively.

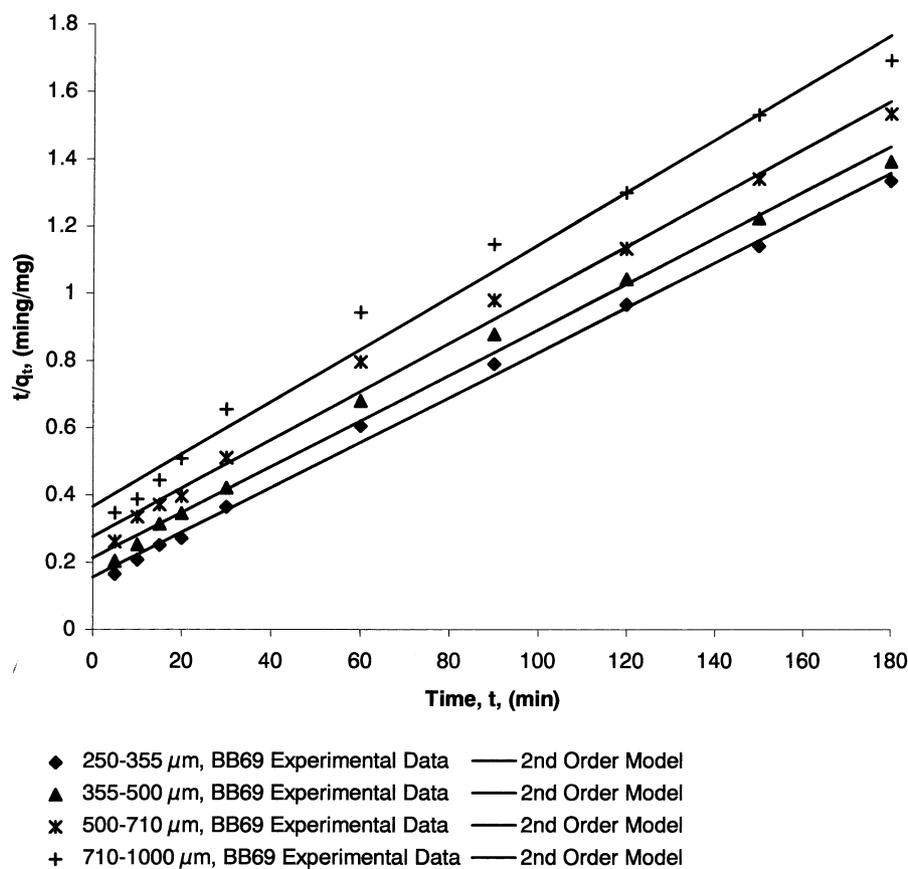


Fig. 9. Plot of amount of sorption versus time for BB69 sorption onto pith at various particle sizes.

3.2. Effect of contact time and particle size of BB69 and AB25

Fig. 7 shows a series of contact time curves with sorbent size ranging from 250–355 to 710–1000 μm of BB69. The removal of BB69 increases from 64.3 to 74.9% and for AB25 the increase in sorption capacity is from 19.7 to 28.0% with the decrease of the pith particle size ranging from 250–355 to 710–1000 μm . This indicates that the smaller the sorbent particle size, then for a given mass pith, more surface area is made available and therefore the number of sites increases. The results are shown in Table 3 for BB69 and AB25. The correlation coefficients, r^2 , and the pseudo-second-order rate parameters, k , are shown and compared with r_i^2 and k_i -values for the intraparticle diffusion-based model. The data show a good compliance with the pseudo-second-order equation and the regression coefficients for the linear plots were higher than 0.984 for all the systems in these studies. The correlation coefficients of the intraparticle diffusion model are given in Table 3 for the effect of contact time and particle size of BB69 and AB25 also and although they are all greater than 0.926, they are significantly lower than the coefficients obtained for the second-order kinetic model.

Fig. 8 shows that plotting the amount sorbed per unit weight of sorbent against square root of time generates best-fit straight lines that do not pass through the origin again indicating that there is an initial boundary layer resistance which decreases as the available external surface area also decreases. Fig. 9 shows a plot of t/q_t against time, t , for the sorption of BB69 onto pith based on the assumption of a pseudo-second-order mechanism. In Table 3, all correlation coefficients are extremely high. The second-order r^2 are decreasing with increasing particle size and the intraparticle correlation coefficients r_i^2 are increasing with increasing particle size. This suggests that if the sorption is a combination of reaction and diffusion-controlled processes, there is a trend towards diffusion control with increasing d_p . This would be expected since the amount of external surface area available for rapid reaction decreases with increasing particle size for constant sorbent mass. Therefore, the reaction has to wait longer for diffusion into the less accessible pores within the particle bonding as the pith particle size increases. A similar, although less pronounced trend can be observed for the effect of increasing particle size on r^2 and r_i^2 for the sorption of AB25 onto pith. The intraparticle diffusion is more likely to be affected by larger dye ions than copper ions, which in size are smaller and more mobile than dye ions.

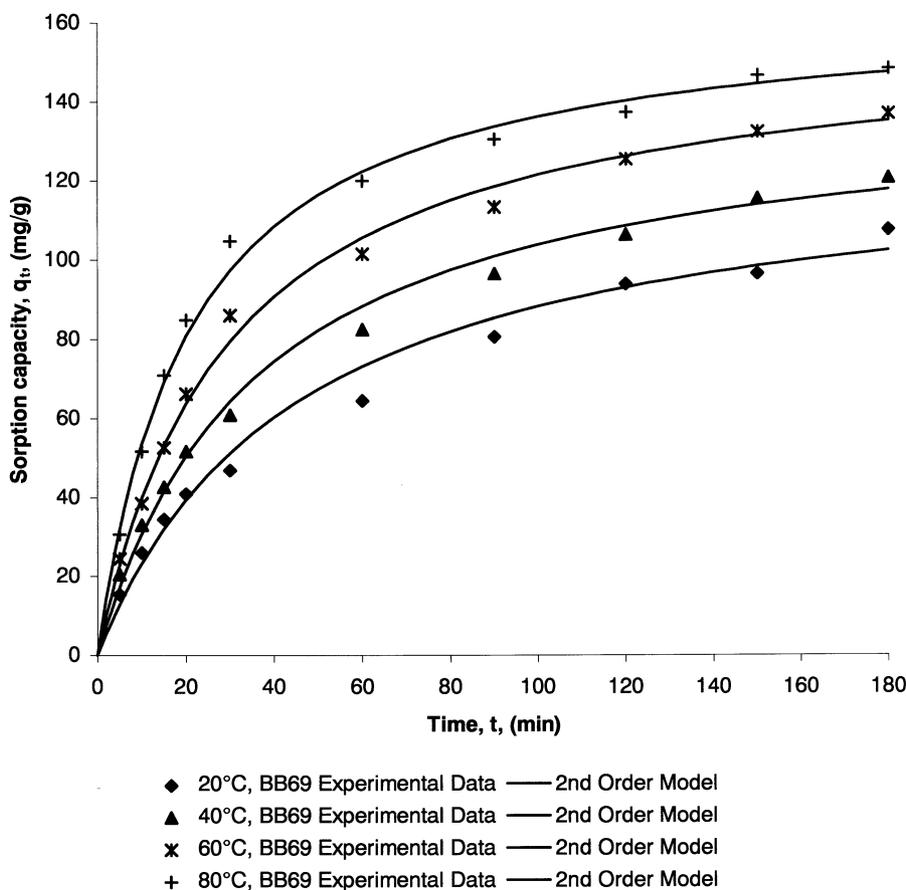


Fig. 10. Effect of temperature on the sorption of BB69 onto pith.

The correlation coefficients of the relation between time/amount sorption and time as defined by Eq. (3) is high for the effect of particle size for the sorption of the two dyes on pith. The sorption process may involve a chemical reaction process and demonstrates that the pseudo-second-order rate constant, k , is a function of surface area of the sorbent.

3.3. Effect of temperature of BB69 and AB25

A series of contact time experiments has been carried out with a constant initial dye concentration of 200 mg/dm³, pith dose 1 g/dm³ with various temperatures of reaction sorption. The increase in the equilibrium sorption of dye with temperature indicates that a high temperature favours dye removal by adsorption on pith. This effect is shown in Figs. 10 and 11. Obviously, the exothermic nature of the reaction in the present process can be explained by this behaviour of the system [23,24]. The sorption of dye by pith may involve not only physical but also chemical adsorption. This effect may be due to the fact that at higher temperatures, an increase in free volume occurs due to increased movement of the solute [25]. This may be due to a relative increase in the tendency of dye molecules to escape from

the solid phase to the bulk phase with increasing temperature of the solution [26]. It may also be due to the dissolution of the sorbing species, changes in the size of the pores, and enhanced rate of intraparticle diffusion of adsorbent [27]. This effect could be explained by assuming that at higher values of temperature, the total energy of the sorbate molecules is increased and consequently their escaping tendency is also increased; therefore, the sorption of lead species is lowered [28]. Thus, on increasing the temperature of the reaction from 20 to 80 °C, the removal of the dye increased from 64.0 to 82.2% for BB69 and 19.7 to 28.7% for AB25. Consequently, it is clear that adsorption equilibrium is temperature-dependent.

Figs. 10 and 11 show a good compliance with the pseudo-second-order equation. The experimental points are shown together with the theoretically generated curves. The agreement between the sets of data reflects the extremely high correlation coefficients obtained and are shown in Table 4.

The results in Table 4 also show the sorption rate constant, k , initial sorption rate, h , and equilibrium sorption capacity, q_e , as a function of solution temperature. Thus, on increasing the temperature from 20 to 80 °C, the specific sorption at equilibrium, q_e , increased

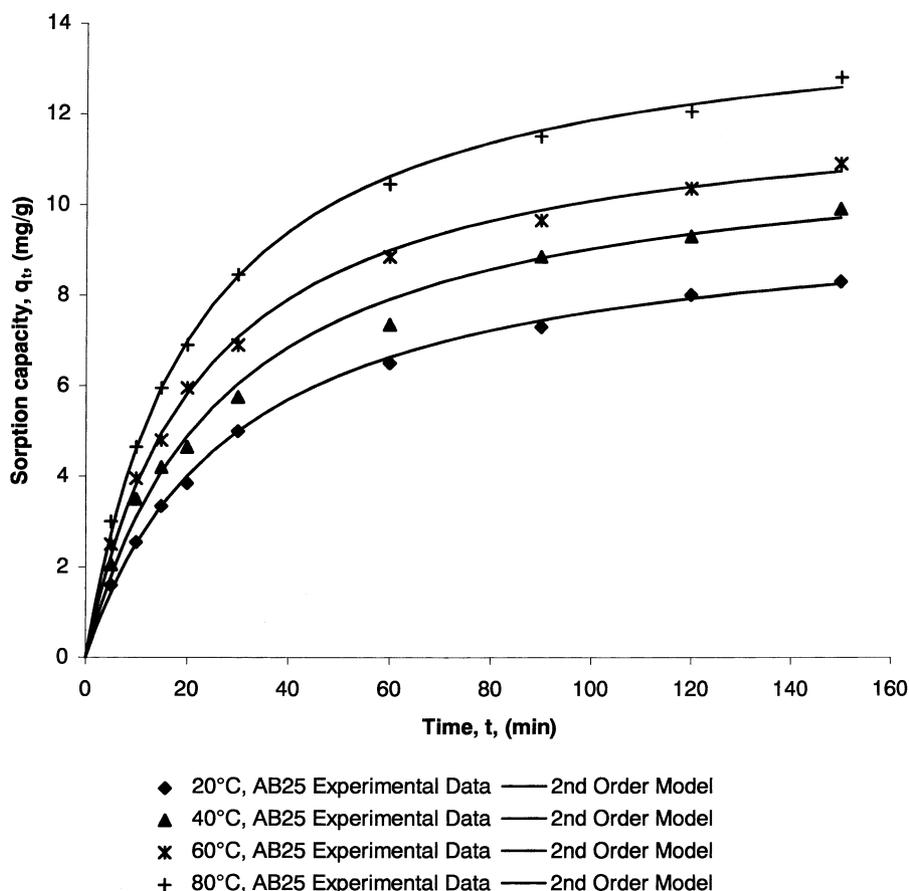


Fig. 11. Effect of temperature on the sorption of AB25 onto pith.

Table 4
Effect of temperature of BB69 and AB25

	T (°C)	r^2	q_e (mg/g)	k (g/(mg min))	h (mg/(g min))	R_e (%)	r_i^2	k_i (mg/(g min ^{0.5}))
BB69	20	0.984	1.28×10^2	1.74×10^{-4}	2.84	64.0	0.992	8.05
	40	0.995	1.41×10^2	1.97×10^{-4}	3.93	70.7	0.984	8.90
	60	0.998	1.57×10^2	2.17×10^{-4}	5.37	78.6	0.946	9.81
	80	0.999	1.64×10^2	2.94×10^{-4}	7.96	82.2	0.900	9.76
AB25	20	0.999	9.84	3.50×10^{-3}	0.339	19.7	0.966	0.671
	40	0.995	11.4	3.27×10^{-3}	0.427	22.9	0.976	0.765
	60	0.999	12.3	3.65×10^{-3}	0.554	24.6	0.952	0.811
	80	0.999	14.4	3.31×10^{-3}	0.682	28.7	0.943	0.940

Table 5
Empirical parameters for predicted q_e and h from T

	A_q	B_q (mg/(g K ^(A_q)))	r^2	A_h	B_h (mg/(g min K ^(A_h)))	r^2
BB69	1.39	4.89×10^{-2}	0.981	5.47	9.07×10^{-14}	0.994
AB25	1.94	1.61×10^{-4}	0.983	3.80	1.46×10^{-10}	0.999

from 128 to 164 mg/g for BB69 and 9.84 to 14.4 mg/g for AB25. The initial sorption rate increases with an increase in the temperature. Table 4 shows that h varies from 2.84 to 7.96 mg/(g min) for BB69 and h varies from

0.339 to 0.682 mg/(g min) for AB25, respectively, for a temperature variation from 20 to 80 °C. Both dye/pith systems show extremely high reaction correlation coefficients, r^2 , which are all greater than 0.995. The

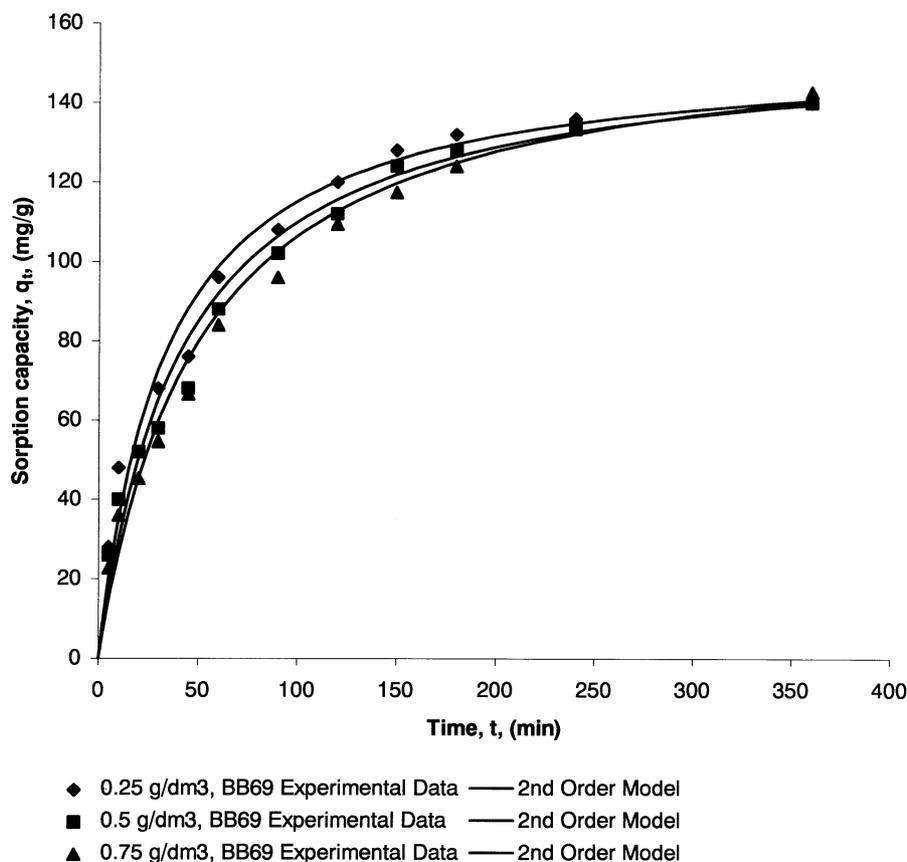


Fig. 12. Effect of pith dose on the sorption of BB69 onto pith.

intraparticle coefficients, r_i^2 , are also high, being greater than 0.900 in all cases, but they are all consistently decreasing with increasing temperature. This trend would tend to indicate that a chemisorption reaction or an activated process was becoming more predominant in the rate-controlling step. The pseudo-second-order rate constants for the BB69 on pith system show a steady increase with temperature whereas the k -values for AB25 on pith are constant and equal to 3.45 ± 0.20 g/(mg min). Despite the high r^2 -values, this suggests that the AB25/pith system may not be an activated or chemisorption process.

An examination of the effect of temperature on both the equilibrium capacity, q_e , and initial sorption rate, h , produces best-fit correlation of the types shown by Eqs. (4) and (5) with high correlation coefficients shown in Table 5.

$$q_e = B_q T^{A_q}, \quad (4)$$

and

$$h = B_h T^{A_h}. \quad (5)$$

Substituting the values of q_e and h from Table 5 into Eqs. (4) and (5) and then into Eq. (1), the rate law for a

pseudo-second-order and the relationship of q_t , T and t can be represented as follows:

for BB69:

$$q_t = \frac{t}{9.07 \times 10^{14} T^{-5.47} + (4.89 \times 10^2 T^{-1.39})t}, \quad (6)$$

for AB25:

$$q_t = \frac{t}{1.46 \times 10^{10} T^{-3.80} + (1.61 \times 10^4 T^{-1.94})t}. \quad (7)$$

These equations can then be used to derive the amount of dye sorbed at any given temperature and the reaction time.

The values of rate constant, k , were found to increase from 1.74×10^{-4} to 2.94×10^{-4} g/(mg min), for an increase in the solution temperature from 293 to 353 K for the sorption of BB69. There is a linear relationship between the pseudo-rate constant and temperature with correlation coefficient of 0.903. The sorption rate constant is usually expressed as a function solution of temperature by the following relationship:

$$k = k_0 \exp\left(\frac{-E}{RT}\right), \quad (8)$$

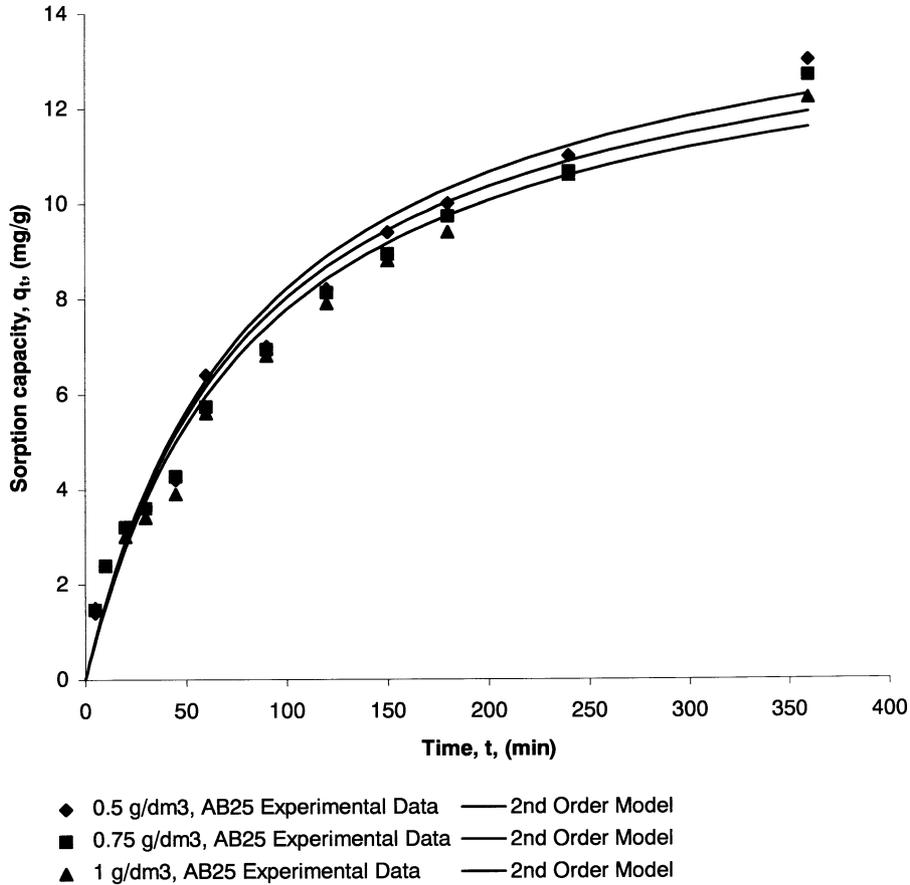


Fig. 13. Effect of pith dose on the sorption of AB25 onto pith.

Table 6
 Effect of pith dose of BB69 and AB25

	m_s (g/dm ³)	r^2	q_c (mg/g)	k (g/(mg min))	h (mg/(g min))	R_c (%)	r_i^2	k_i (mg/(g min ^{0.5}))
BB69	0.25	0.996	1.54×10^2	1.96×10^{-4}	4.61	19.2	0.903	7.13
	0.5	0.993	1.56×10^2	1.55×10^{-4}	3.75	38.9	0.933	7.38
	0.75	0.992	1.60×10^2	1.25×10^{-4}	3.19	59.9	0.955	7.65
AB25	0.5	0.962	15.2	7.81×10^{-4}	0.179	7.58	0.985	0.716
	0.75	0.963	14.6	8.33×10^{-4}	0.178	11.0	0.991	0.690
	1.0	0.959	14.3	8.37×10^{-4}	0.171	14.3	0.987	0.674

where k is the rate constant of sorption (g/(mg min)), k_0 the temperature-independent factor (g/(mg min)), E the activation energy of sorption (kJ/mol), R the gas constant (8.314 J/(mol K)) and T the solution temperature (K).

Therefore, the relationship between k and T can be represented in an Arrhenius form as

$$k = 3.12 \times 10^{-3} \exp\left(\frac{-7.13 \times 10^3}{8.314T}\right).$$

From this equation, the rate constant of sorption, k_0 , is 3.12×10^{-3} g/(mg min) and activation energy of sorption, E , is 7.13 kJ/mol for the sorption system of BB69/pith. Since sorption is an exothermic process, it would be expected that an increased solution temperature would result in decreased sorption capacity. However, Weber [29] has stated that, since diffusion is an endothermic process, the rate of sorption will increase with increased solution temperature when intraparticle transport (pore diffusion) is the rate-limiting step. The results of this study on the effect of temperature indicate

that for the sorption of BB69 dye on pith involves some chemical sorption. The values of k at different temperatures for the sorption of AB25 onto pith are shown in Table 5 and for a temperature range of 60 K, the values may be considered as relatively constant. This suggests a non-activated sorption process such as physical sorption for AB25 sorption on pith. It is possible that this pseudo-second-order model could act as a methodology for discriminating between sorption mechanisms on this basis.

3.4. Effect of pith dose of BB69 and AB25

Figs. 12 and 13 show a series of contact time curves with sorbent dose ranging from 0.25 to 0.75 g/dm³ of BB69 and 0.5 to 1 g/dm³ of AB25. The removal of BB69 increases from 19.2 to 59.9% and for AB25 the increase in removal is from 7.58 to 14.3% with the increase of the pith dose ranging from 0.25 to 0.75 g/dm³ for BB69 and 0.5 to 1 g/dm³ for AB25, respectively. However, the sorption capacity increases slightly and varies from 154 to 160 mg/g, as m_s varies from 0.25 to 0.75 g/dm³ for BB69 and from 15.2 to 14.3 mg/g, as m_s varies from 0.5 to 1 g/dm³ for AB25, respectively. The correlation coefficients, r^2 , and the pseudo-second-order rate parameters, k , are shown and compared with r_1^2 - and k_1 -values for the intraparticle diffusion-based model (Table 6). The data show a good compliance with the pseudo-second-order equation and the regression coefficients for the linear plots were higher than 0.959 for all the systems in these studies. However, in the case of AB25, the effect of contact time and pith dose the r_1^2 values are all greater than 0.985 and are significantly greater than the coefficients obtained for the second-order kinetic model.

4. Conclusion

The kinetics of sorption of copper, BB69 and AB25 on biosorbents (peat and pith) were studied on the basis of the pseudo-second-order rate mechanism. The sorption of capacity of basic dye (BB69) is much higher than acid dye (AB25) because of the ionic charges on the dyes and the character of the biomaterials. The activation energy of sorption can be evaluated with the pseudo-second-order rate constants. The sorption of BB69 by pith is an exothermic, activated process whereas the sorption of AB25 on pith appears to be a non-activated process. For both dye/pith systems, intraparticle diffusion and chemical reactions seem significant in the rate-controlling step but for the sorption of copper ions onto peat the pseudo-second-order chemical reaction kinetics provide the best correlation of the data.

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代表論文 (四)

Ho, Y.S.*, Chiu, W.T., Hsu, C.S. and Huang, C.T. (2004), Sorption of lead ions from aqueous solution using tree fern as a sorbent. *Hydrometallurgy*, **73** (1-2), 55-61. (SCI) Rank 1st in citation from 128 papers of *Hydrometallurgy* (2004), Last data updates: 30 June 2007

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Abstract: This study is on sorption of lead ions on an agricultural by-product, tree fern. Equilibrium isotherms have been measured and modeled. The equilibrium sorption capacity of lead(II) was determined from the Langmuir isotherm and found to be 40.0 mg/g. Based on the assumption of the pseudo-second order mechanism, a batch sorption model was developed to predict the rate constant of sorption, the equilibrium sorption capacity and the initial sorption rate with the effect of initial lead(II) concentration and temperature. The sorption rate was found to increase with temperature, and an activation energy of approximately 87 kJ/mol was determined from the pseudo-second order rate constants. The findings of this investigation suggest that chemical sorption plays a role in controlling the sorption rate.

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Sorption of lead ions from aqueous solution using tree fern as a sorbent

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Abstract

This study is on sorption of lead ions on an agricultural by-product, tree fern. Equilibrium isotherms have been measured and modeled. The equilibrium sorption capacity of lead(II) was determined from the Langmuir isotherm and found to be 40.0 mg/g. Based on the assumption of the pseudo-second order mechanism, a batch sorption model was developed to predict the rate constant of sorption, the equilibrium sorption capacity and the initial sorption rate with the effect of initial lead(II) concentration and temperature. The sorption rate was found to increase with temperature, and an activation energy of approximately 87 kJ/mol was determined from the pseudo-second order rate constants. The findings of this investigation suggest that chemical sorption plays a role in controlling the sorption rate.

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Keywords: Isotherm; Kinetics; Pseudo-second order mechanism; Lead; Tree fern

1. Introduction

Understanding the sorption of metal ions from aqueous solution is important in water pollution control. In recent years, there has been considerable interest in the use of agricultural by-products as sorbents. Table 1 is a list of the agricultural by-products available for removing lead ion from wastewaters. Investigations have been carried out to identify

suitable agricultural sorbents to remove significant quantities of lead ions.

The tree fern, which is commercially available in Taiwan, is used as a sorbent for lead ions. It sorbs water easily and is marketed for horticultural uses as soil for plants. Being dark brown in colour, the tree fern constitutes mainly of lignin and cellulose (Newman, 1997). All chemical sorbents have polar functional groups (alcohols, aldehydes, ketones, acids, phenolic hydroxides and ethers) for chemical bindings (Adler and Lundquist, 1963). The tree fern, which is highly polar, is used as a specific sorbent to remove dissolved solids (transition metals and polar organic molecules).

This study investigates whether the tree fern can be used as a sorbent to remove lead ions from

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Table 1

A list of agricultural sorption by-products available to remove lead ions

Capacities, q_m (mg/g)	Materials	References
78.7	Tea leaves	Tan and Abd. Rahman, 1988
46.6	Sago	Quek et al., 1998
39.4	Groundnut husks	Okieimen et al., 1991
35.5	Grain	Low et al., 2000
30.7	Sphagnum moss peat	Ho et al., 1996a
40.0	Tree fern	This study

aqueous solutions and whether the corresponding equilibrium isotherm can be determined kinetically.

2. Materials and methods

2.1. Materials

The raw tree fern was dried in an oven at 100 °C for a period of 24 h, and then ground and screened through a set of sieves to get particles of geometrical size 53–61 µm. The materials were stored in an airtight plastic container before all investigations. The stock solutions of lead(II) (2000 mg/L) were prepared in distilled water using lead nitrate. All working solutions were prepared by diluting the stock solution with distilled water.

2.2. Equilibrium studies

A lead(II) solution (50 mL) with a concentration of 74.1–344 mg/L was placed in a 125 mL conical flask. A tree fern sample 0.25 g was added to the solution. A series of conical flasks was then agitated at a constant speed of 100 rpm in a shaking water bath at 20 °C. After shaking the flasks for 5 h, the tree fern was separated by filtering the liquid content through a Nylon membrane filter (0.45 µm). Then the filtrate was analysed for the remaining lead(II) concentration with atomic absorption spectrophotometry (AAS).

2.3. Effect of initial concentration

A range of lead(II) concentrations (74.1–350 mg/L) was used and the flasks were agitated for 1 h. All

contact investigations were performed by using a baffled, agitated 2-L vessel. A 6.8-g sample of tree fern was added to each 1.7 L volume of lead(II) solution and agitated at 300 rpm for all experiments. The temperature was set at 20 °C with a water bath for all studies. Samples (3 mL) were withdrawn at suitable time intervals by having them filtered through a 0.45-µm membrane filter.

2.4. Effect of temperature

Agitation was carried out for 1 h at temperatures ranging from 278 to 318 K. A 6.8-g sample of tree fern was added to each 1.7 L volume of lead(II) solution with an initial concentration 200 mg/L and agitated at 300 rpm.

3. Theory

3.1. Equilibrium studies

Analysing the results of the isotherm data is important to develop an equation, which can be used for design purposes. To investigate the sorption isotherm, three equilibrium models, the Langmuir, the Freundlich and the Redlich-Peterson isotherm equations, were analysed. The theoretical Langmuir sorption isotherm (Langmuir, 1916), which is the best known of all isotherms describing sorption, is often used to describe sorption of a solute from a liquid solution as:

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

where q_e is the equilibrium sorption capacity (mg/g), C_e the equilibrium liquid phase concentration (mg/L), q_m the q_e for a complete monolayer (mg/g) and K_a the sorption equilibrium constant (L/mg).

The Freundlich isotherm (Freundlich, 1906), which is the earliest known relationship describing the sorption isotherm, can be used in sorption from dilute solutions. Its sorption isotherm is expressed by the following equation:

$$q_e = K_F C_e^{1/n} \quad (2)$$

where C_e and q_e have the same meaning as noted above. K_F and $1/n$ stand for empirical constants. K_F is the sorption value, the amount sorbed at unit concentration at 1 mg/L; it is characteristic for the sorbent and the specific sorbate.

The Redlich-Peterson isotherm (Redlich and Peterson, 1959), which contains three parameters incorporating the features of the Langmuir and the Freundlich isotherms, can be described as:

$$q_e = \frac{AC_e}{1 + BC_e^g} \quad (3)$$

where C_e and q_e have the same meaning as in the previous section on the Langmuir isotherm. It has three isotherm constants: A , B and g ($0 < g < 1$). All of them can be evaluated from the linear plot represented by Eq. (4) using a trial-and-error optimisation method:

$$\ln\left(A\frac{C_e}{q_e} - 1\right) = g\ln(C_e) + \ln(B) \quad (4)$$

3.2. Kinetic studies

Several models are used to express the mechanism of solute sorption onto a sorbent. The characteristic constants of sorption were determined by using a pseudo-first order equation (Lagergren, 1898), a pseudo-second order equation (Ho, 1995) and a chemical phenomenon model (Boyd et al., 1947).

3.2.1. The pseudo-first order model

The Lagergren (1898) rate equation, which is the first rate equation developed for sorption in liquid/solid systems, is based on solid capacity. The Lagergren rate equation is the most widely used rate equation for assessing the sorption of a solute from a liquid solution. The pseudo-first order equation is represented as:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_L}{2.303}t \quad (5)$$

or

$$\log(1 - F) = -\frac{k_L}{2.303}t \quad (6)$$

where q_e is the amount of lead(II) sorbed at equilibrium (mg/g), q_t amount of lead(II) sorbed at time t (mg/g), k_L the rate constant of pseudo-first order sorption (1/min) and F the fractional attainment of equilibrium (q_t/q_e).

3.2.2. The pseudo-second order model

The sorption of lead(II) onto tree fern may involve a chemical sorption. Ho (1995) developed a pseudo-second order kinetic expression for the sorption system of divalent metal ions using sphagnum moss peat. This model has since been widely applied also to a number of metal/sorbent sorption systems (Ho et al., 1996b; Ho and McKay, 1998). To investigate the mechanism of sorption, the rate constants for the sorption of lead(II) were used to determine the equation of a pseudo-second order mechanism:

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e}t \quad (7)$$

where q_e , q_t and t have the same meaning as in the previous sections on pseudo-first order model. The symbol k is the rate constant of pseudo-second order sorption (g/mg min).

The initial sorption rate can be obtained as q_t/t approaches zero:

$$h_o = kq_e^2 \quad (8)$$

where h_o is the initial sorption rate (mg/g min).

3.2.3. The chemical phenomenon model

Boyd et al. (1947) developed a rate equation incorporating the rates of ion-exchange from aqueous solutions by organic zeolites. The rates of exchange sorption are governed either by diffusion through a thin liquid film, or by the chemical exchange. Based on diffusion through a boundary liquid film and sorption kinetics as a chemical phenomenon, the rate equation is obtained as expressed in Eq. (9):

$$\log(1 - F) = \frac{K_D}{2.303}t \quad (9)$$

where F and t have the same meaning as in the previous sections on pseudo-first order model, and K_D is a constant.

A rate equation for diffusion through a boundary liquid film (Eq. (10)) is derived from the pseudo-first order rate equation of Lagergren:

$$\log(1 - F) = -\frac{K_R}{2.303}t \quad (10)$$

where F and t have the same meaning as in the previous sections on pseudo-first order model, and K_R is a constant. If the sorption is due to ion exchange, the constant of the equation will depend only on the concentrations of the ions in solution and the temperature.

4. Results and discussion

4.1. Equilibrium studies

The equilibrium distribution of lead between the sorbent and the solution is important in determining the maximum sorption capacity of the tree fern for lead(II). To assess the different isotherms and their ability to correlate experimental results, the theoretical plots from each isotherm have been presented with the experimental data for sorption of lead(II) on tree fern at 20 °C (Fig. 1). The graph is plotted in the form of lead(II) sorbed per unit mass of tree fern q_e , against the concentration of lead(II) remaining in solution C_e . The correlation coefficients are 1.000, 0.999 and

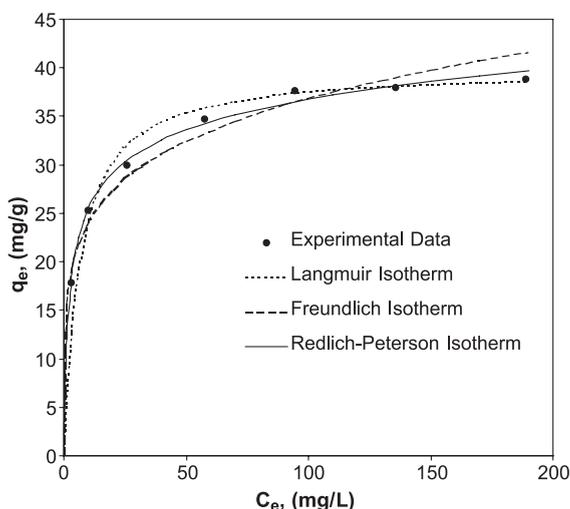


Fig. 1. Isotherms for the sorption of lead using tree fern.

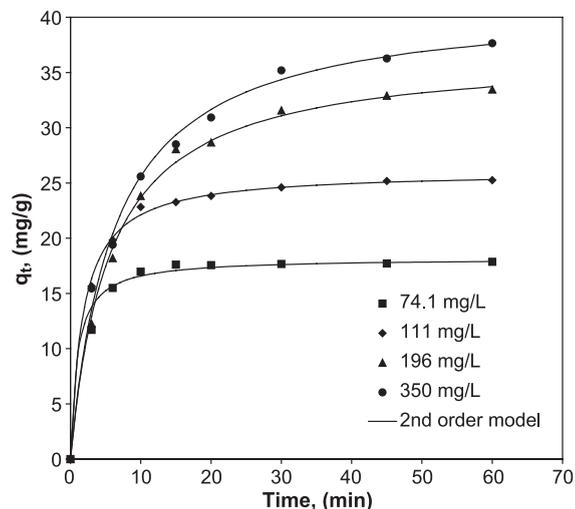


Fig. 2. Effect of time on sorbed lead concentrations for various initial Pb(II) concentrations.

0.964 for the Redlich-Peterson, the Langmuir and the Freundlich sorption isotherms, respectively. The monolayer sorption saturation capacity of lead(II) q_m , and sorption constant K_a , were determined from the slope and intercept of the Langmuir equation, and was found to be 40.0 mg/g and 0.157 L/mg, respectively. The Freundlich sorption isotherm constant K_F is 15.7 mg^{0.814} L^{0.186}/g and $1/n$ 0.186. The Redlich-Peterson isotherm constant A is 20.0 L/g, B 0.878 L^{0.892}/mg^{0.892} and g 0.892.

Many agricultural sorbents have been tested for their capacity of sorbing lead(II), but their results vary with various sorbents and sources as shown in Table 1. An examination of Table 1 shows that the value for the monolayer sorption saturation capacity q_m , is comparable with values reported in the literature. This table also shows the sorption capacities reported in earlier studies where q_m had not been derived specifically.

4.2. Effect of initial lead concentration

Fig. 2 shows that the rate of lead(II) sorption on tree fern as a function of the initial lead(II) concentration. The initial rapid sorption of lead(II) is due to ion exchange with surface cations on the tree fern. The later slow sorption of lead(II) represents a gradual uptake of cation exchange at the inner surface

Table 2
Rate constants for effect of initial Pb(II) concentration

C_0 (mg/L)	Pseudo-second order				Pseudo-first order		
	r^2	q_e (mg/g)	k (g/mg min)	h_0 (mg/g min)	r^2	q_e (mg/g)	k_L (1/min)
74.1	1.000	18.2	5.68×10^{-2}	18.8	0.867	6.80	0.140
111	1.000	26.1	2.14×10^{-2}	14.5	0.880	10.8	0.0871
196	0.999	36.8	4.87×10^{-3}	6.62	0.946	27.8	0.0675
350	0.999	41.5	3.90×10^{-3}	6.70	0.980	29.6	0.0538

(Low and Lee, 1990). The results have been analysed by using the pseudo-second order model. As shown in Table 2, the correlation coefficients r^2 , rate constant k , initial sorption rate h_0 and equilibrium sorption capacity q_e , are obtained from the slope and intercept of Eq. (7). The rate constants and the initial sorption rate decreased with an increase in initial lead(II) concentration. Nevertheless, the equilibrium sorption capacity increases from 18.2 to 41.5 mg/g, as initial lead(II) concentrations vary from 74.1 to 350 mg/L. The solid line curves in Fig. 2 are the theoretical plots indicating high values of r^2 (>0.999). This finding suggests that this sorption system is not a pseudo-first order reaction. The pseudo-second order model can describe the sorption of lead(II) on tree fern. The possibility of chemical sorption involving valency forces through sharing or exchange of electrons between sorbent and sorbate, correlates the data best if the rate-limiting step is assumed. The corresponding linear plots of the values of q_e , k and h_0 against C_0 were regressed to obtain expressions for these values in terms of the initial lead(II) concentration with high correlation coefficients (>0.984). Therefore, q_e , k and h_0 can be expressed as a function of C_0 for lead(II) as:

$$q_e = \exp\left(3.98 + \frac{79.4}{C_0}\right) \quad (11)$$

$$k = \frac{C_0}{333C_0 - 2.69 \times 10^4} \quad (12)$$

$$h_0 = \frac{C_0}{0.181C_0 - 9.71} \quad (13)$$

4.3. Effect of temperature

The rate of uptake of lead(II) by tree fern in these studies was controlled by a chemical sorption phe-

nomenon. Moreover, a pseudo-second order model is applied in sorption of lead(II) on tree fern. As shown in Fig. 3, the variation in temperatures influenced the time required to reach saturation with excellent agreement between the experimental data and predicted theoretical curves. The data listed in Table 3 shows that the initial sorption rate correlates positively with the temperature. The initial sorption rate varied from 1.24 to 140 mg/g min when the temperatures changed from 278 to 318 K. The values of the rate constants were found to increase from 9.18×10^{-4} to 0.103 g/mg min with an increase in the solution temperatures from 278 to 318 K. However, the equilibrium sorption capacity was little effected by increased temperature. In conventional physisorption systems, increasing temperature usually increases the rate of approach to equilibrium, but decreases the equilibrium capacity (McKay et al., 1997).

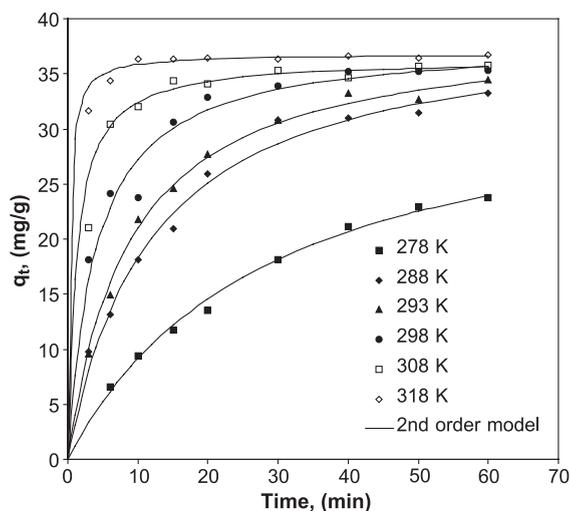


Fig. 3. Effect of time on sorbed lead concentrations for various temperatures.

Table 3
Pseudo-second order rate constant for effect of temperature

T (K)	Pseudo-second order				Pseudo-first order		
	r^2	q_e (mg/g)	k (g/mg min)	h_0 (mg/g min)	r^2	q_e (mg/g)	k_L (1/min)
278	0.989	35.5	9.81×10^{-4}	1.24	0.993	32.0	0.0193
288	0.994	39.9	2.13×10^{-3}	3.38	0.988	34.6	0.0438
293	0.998	39.4	2.90×10^{-3}	4.50	0.976	33.5	0.0546
298	0.998	38.0	6.60×10^{-3}	9.55	0.946	25.1	0.0776
308	1.000	36.4	2.24×10^{-2}	29.7	0.838	14.7	0.109
318	1.000	36.8	1.03×10^{-1}	140	0.789	5.38	0.158

The increase in the pseudo-second order rate constants with increasing temperature may be described by the equation:

$$k = k_0 \exp\left(\frac{-E}{RT}\right) \quad (14)$$

where k is the rate constant of sorption (g/mg min), k_0 the temperature-independent factor (g/mg min), E the activation energy of sorption (kJ/mol), R the gas constant (8.314 J/mol K) and T the solution temperature (K).

There is a linear relationship between the pseudo-second order rate constant and the reciprocal absolute temperature with a correlation coefficient of 0.976. The values of k were plotted as a function of the reciprocal of the Kelvin temperature and the linear variation is shown in Fig. 4. Hence, the relationship

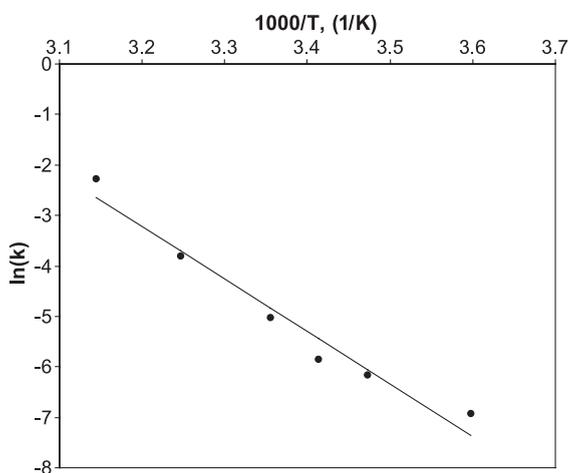


Fig. 4. The relationship between T and k .

between k and T can be represented in an Arrhenius form as:

$$k = 1.19 \times 10^{13} \exp\left(\frac{-87}{8.314T}\right) \quad (15)$$

From Eq. (15), the rate constant of sorption k_0 is 1.19×10^{13} g/mg min and the activation energy for sorption E is 87 kJ/mol, which is out of the range (8–22 kJ/mol) of diffusion-controlled processes (Glasston et al., 1941). Ho and McKay (1998) reported that the activation energy for the sorption of lead(II) on peat is 29.8 kJ/mol. In addition, McKay et al. (1981) reported that the activation energy for the sorption of Telon Blue dye on peat is 26.6 kJ/mol. Again, this value of the activation energy is higher than the normal range of 8–22 kJ/mol typical of physical adsorption process. The results of this study on the effect of temperature suggest that the sorption rate-controlling step is likely chemical in nature for the sorption of lead(II) on tree fern.

Fig. 5 shows a plot of the linearized form of the pseudo-first order model in Eq. (5) for the sorption of lead(II) onto tree fern at various initial lead(II) concentrations for the initial 20 min. As indicated in Fig. 5, the experimental points and theoretical lines deviate rapidly after this short period. The rate of sorption was thought to be proportional to the difference between the sorption capacity q_e at equi-

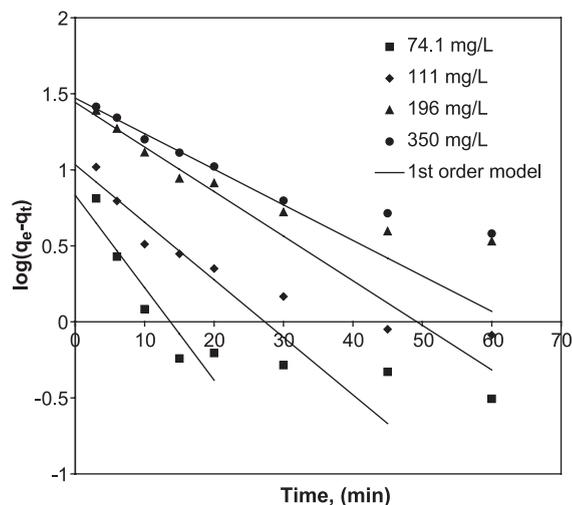


Fig. 5. Pseudo-first order sorption kinetics of lead onto tree fern at various initial Pb(II) concentrations.

librium and the capacity at any time t of the sorbed in a pseudo-first order at the initial reaction stage. Table 2 indicates that values of pseudo-first order rate constants ranged from 0.140 to 0.0538 1/min when the initial lead(II) concentrations were increased from 74.1 to 350 mg/L. As listed in Table 3, the pseudo-first order rate constant k_L and the equilibrium sorption capacity q_e at different temperatures were calculated from the intercept and slope of the straight line plots of $\log(q_e - q_t)$ versus t in accordance with Eq. (5). The values of the rate constants were found to increase from 0.0193 to 0.158 1/min as the temperature increased from 278 to 318 K.

5. Conclusion

The biosorption of lead ions on tree fern was investigated. Tree fern is a suitable sorbent for the removal of lead(II) from aqueous solution. The lead(II) removal was a function of initial lead ion concentration and temperature. The Redlich-Peterson and the Langmuir isotherms have higher correlation coefficients than those of Freundlich isotherm for the sorption of lead(II) onto tree fern. The pseudo-second order kinetic model was successfully applied to the experimental data, confirming that biosorption was chemically controlled. In addition, an activation energy consistent with chemisorption was determined, based on the pseudo-second order rate constants.

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Abstract: The kinetics of four sorption systems, Cu/tree fern, Pb/tree fern, AB9/activated clay and BR18/activated clay have been studied based on the assumption of a pseudo-second order rate law. Pseudo-isotherms using the pseudo-second order kinetic expression constant have been developed to describe the four liquid-solid sorption systems. The experimental results have been analyzed using a pseudo-Langmuir and a pseudo-Redlich-Peterson isotherm. Both isotherms were found to represent the measured sorption data well. According to the evaluation using the pseudo-Langmuir equation, the monolayer sorption capacities were obtained to be 13.9, 46.6, 124 and 105 mg g⁻¹ for copper, lead, AB9 and BR18 respectively.

Subject Categories:

Chemistry, Physical: Impact Factor 0.590, 91/108 (2006)

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Pseudo-Isotherms Using a Second Order Kinetic Expression Constant

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Abstract. The kinetics of four sorption systems, Cu/tree fern, Pb/tree fern, AB9/activated clay and BR18/activated clay have been studied based on the assumption of a pseudo-second order rate law. Pseudo-isotherms using the pseudo-second order kinetic expression constant have been developed to describe the four liquid-solid sorption systems. The experimental results have been analyzed using a pseudo-Langmuir and a pseudo-Redlich-Peterson isotherm. Both isotherms were found to represent the measured sorption data well. According to the evaluation using the pseudo-Langmuir equation, the monolayer sorption capacities were obtained to be 13.9, 46.6, 124 and 105 mg g⁻¹ for copper, lead, AB9 and BR18 respectively.

Keywords: pseudo-isotherm, pseudo-second order, kinetics, equilibrium, adsorption

Introduction

The equilibrium sorption isotherm is fundamentally important in the design of sorption systems. Equilibrium relationships between sorbent and sorbate are described by sorption isotherms, usually the ratio between the quantity sorbed and the remaining of the solution at a fixed temperature at equilibrium. In many cases, the equilibrium sorption capacity is unknown and when chemisorption tends to become unmeasurably slow, the amount sorbed is still significantly smaller than the equilibrium amount (Ungarish and Aharoni, 1981). On the other hand, equilibrium takes a long time to obtain in some sorption systems. For example, sorption of naphthalene on solid coal tar particles takes more than 60 h to reach equilibrium (Bayard et al., 2000). In 1995, Ho developed a pseudo-second order expression for solid-liquid sorption systems. The pseudo-second order equation has the following advantages: it does not have the problem of assigning an effective sorption capacity; the sorption capacity, rate constant of pseudo-second order and the initial sorption rate all can be determined from the equation without knowing any parameter beforehand. An earlier and yet important

discussion of the use of this model in bi-metal/solutions has been given by Ho et al. (1996). Several applications to metal (Manohar et al., 2002; Reddad et al., 2002); dye (Aksu and Tezer, 2000; Fu and Viraraghavan, 2001) and organic (Kelleher et al., 2001) sorption systems have also been reported. More recently, Ho and Chiang (2001) have published extensively on the use of the model in mixed sorbents.

Tree fern is a complex material containing lignin and cellulose as major constituents (Newman, 1997). 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 (Adler and Lundquist, 1963). It is, therefore, concluded that tree fern can be a suitable sorbate for sorption of metal cations because of its polar and acid characters. The removal of divalent metal ions, such as Zn(II), Cu(II), Pb(II) by using tree fern was first reported by Ho et al. (2002, 2004) and Cd(II) (Ho and Wang, 2004).

This paper studies four sorption systems: Cu/tree fern, Pb/tree fern, Acid Blue 9/activated clay, and Basic Red 18/activated clay, where a batch sorption pseudo-isotherm was also developed. Pseudo-isotherms were

derived from a pseudo-second order kinetic expression constant and were used to predict the monolayer sorption capacities and sorption constants. A comparison of the reaction order rate parameter is also discussed.

Materials and Methods

Metal/Tree Fern Sorption Systems

A range of copper(II) concentrations from 52.5 to 328 mg dm⁻³ and lead(II) concentrations from 74.1 to 350 mg dm⁻³ were used and agitation was carried out for 2 h. All contact investigations were executed in a baffled agitated 2 dm³ sorber vessel. Samples (3 mL) were withdrawn at suitable time intervals and 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 dm³ of metal ion solution and an agitation speed of 300 rpm was used for all experiments. The temperature was controlled with a water bath of 20°C for all studies.

Dye/Activated Clay Sorption Systems

In this study, the experimental data of Acid Blue 9 and Basic Red 18 are analyzed through the use of a pseudo-second order kinetic mechanism had been reported previously in the literature by Ho et al. (2001).

Kinetics Model

Adsorption kinetics deals with the rate at which sorption occurs, where the rate is defined as the change of a given quantity over specific period of time. Nevertheless, after a period of time the sorption is reversible when enough sorbate had been sorbed and desorption had become more active. At this point, the concentration of the sorbate depends on the rate differences between the sorption and desorption reactions. If one neglects the desorption reaction, then the reaction rate will depend only on the concentrations of the sorbate.

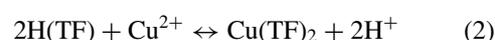
Reaction rate of a chemical reaction is defined as the change in concentration of a reactant or product per unit time. The concentrations of the products do not appear in the rate law because the reaction rate is being studied under the conditions where the reverse reactions do not contribute to the overall rate. The reaction order and rate constant must be determined by

experiments. In 1995, Ho presented a pseudo-second order rate law expression, which demonstrated how the rate depended on the sorption equilibrium capacity but not the concentration of the sorbate.

Tree fern contains polar functional groups such as aldehydes, ketones, acids, and phenolics. These groups can be involved in chemical bonding and are responsible for the cation exchange capacity of the tree fern (Ho, 2003). Thus, the tree fern-copper reaction may be represented in two ways:



and



where (TF)⁻ and (TF) are polar sites on the tree fern surface.

Rate expression for the sorption described by Eqs. (1) and (2) is

$$\frac{d(\text{TF})_t}{dt} = k_2[(\text{TF})_0 - (\text{TF})_t]^2 \quad (3)$$

or

$$\frac{d[\text{H}(\text{TF})]_t}{dt} = k_2[(\text{H}(\text{TF}))_0 - (\text{H}(\text{TF}))_t]^2 \quad (4)$$

where (TF)_t and [H(TF)]_t are the number of active sites occupied on the tree fern at time *t*, and (TF)₀ and [H(TF)]₀ are the number of equilibrium sites available on the tree fern.

The kinetic rate equations can be rewritten as follows:

$$\frac{dq_t}{dt} = k(q_e - q_t)^2 \quad (5)$$

An integrated pseudo-second order rate law can be obtained from Eq. (5) for the boundary conditions *t* = 0 to *t* = *t* and *q_t* = 0 to *q_t* = *q_t*, and is given by:

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + kt \quad (6)$$

Equation (6) can be rearranged to obtain a linear form:

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e}t \quad (7)$$

where *q_e* is the amount of sorbate sorbed at equilibrium (mg g⁻¹); *t* is the reaction time (min); *q_t* is the amount

of sorbate sorbed at time t (mg g^{-1}); k is the equilibrium rate constant of pseudo-second order sorption ($\text{g mg}^{-1} \text{min}^{-1}$).

The pseudo-second order rate law equation shows how the sorption capacity of sorbate depends on time. If the equilibrium sorption capacity of sorbate and the rate constant k are known, then the sorption capacity of sorbate at any time can be calculated. Using the linear form equation, Eq. (7), and plotting t/q_t versus t , will give a straight line with slope $1/q_e$ and intercept $1/kq_e^2$.

Isotherm Models

Langmuir Isotherm

The Langmuir sorption isotherm has been successfully applied to many pollutant sorption processes and it is the most commonly used sorption isotherm for the sorption of a solute from a liquid solution (Langmuir, 1916). The saturated monolayer isotherm can be represented as:

$$q_e = \frac{q_m K_a C_e}{1 + K_a C_e} \quad (8)$$

The above equation can be rearranged to the following linear form:

$$\frac{C_e}{q_e} = \frac{1}{K_a q_m} + \frac{1}{q_m} C_e \quad (9)$$

where C_e is the equilibrium concentration (mg dm^{-3}); q_e is the amount of metal ion sorbed (mg g^{-1}); q_m is q_e for a complete monolayer (mg g^{-1}); K_a is sorption equilibrium constant ($\text{dm}^3 \text{mg}^{-1}$). A plot of C_e/q_e versus C_e should give a straight line with slope of $1/q_m$ and an intercept of $1/K_a q_m$.

Redlich-Peterson Isotherm

The Redlich-Peterson isotherm contains three parameters and incorporates the features of the Langmuir and the Freundlich isotherms (Redlich and Peterson, 1959). The Redlich-Peterson isotherm has a linear dependence on concentration in the numerator and an exponential function in the denominator. It can be described as follows:

$$q_e = \frac{AC_e}{1 + BC_e^g} \quad (10)$$

It has three isotherm constants, namely, A , B and g ($0 < g < 1$), which characterize the isotherm. Equation (10) can be converted to a linear form by taking natural logarithms:

$$\ln\left(A \frac{C_e}{q_e} - 1\right) = g \ln(C_e) + \ln(B) \quad (11)$$

Three isotherm constants, A , B and g can be evaluated from the linear plot represented by Eq. (11) using a trial and error optimization method. A general trial and error procedure which is applicable to computer operation was developed to determine the coefficients of determination, r^2 , for a series of values of A for the linear regression of $\ln(C_e)$ on $\ln[A(C_e/q_e) - 1]$ and to obtain the best value of A which yields a maximum 'optimized' value of r^2 .

Results and Discussions

The experimental data were analysed according to the pseudo-second order equation. Figure 1 shows linear variation of t/q_t with time, t , for the sorption system of Pb/tree fern at various initial concentrations. Good linearization of the experimental data was observed from the graph, thereby implying that a pseudo-second order reaction is involved. Figure 2 shows the sorption of copper(II) onto tree fern with various initial copper(II) concentration. The solid curves in the figure were the theoretical plots of the pseudo-second order equation. Table 1 listed all four sorption systems included the pseudo-second order rate constant, k , the equilibrium sorption capacity, q_e , and the coefficient of determination, r^2 , at various initial concentration of sorbate, C_0 . These data were calculated from the intercept and the slope of a straight line according to Eq. (7). The data illustrated good compliance with the pseudo-second order rate law based on sorption capacity because the coefficients of determination were higher than 0.995 for all the systems in this study.

Generally true equilibrium conditions are not reflected in many sorption systems so the equilibrium sorption capacity, q_e , is unknown (Bayard et al., 2000; Ungarish and Aharoni, 1981). Equilibrium takes a long time to obtain in some sorption systems. For instance, sorption of acid dyes onto activated carbon such as Acid Red 114, Polar Yellow and Polar Blue RAWL, will take 21 days to achieve equilibrium (Choy et al., 1999). In the proposed pseudo-second order equation, by fitting Eq. (7) to the experimental data, q_e can be obtained

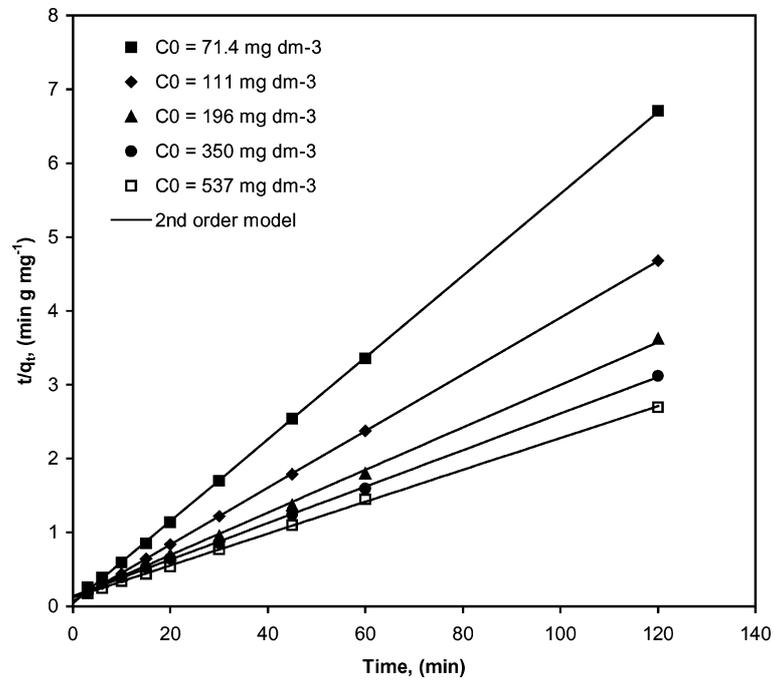


Figure 1. Pseudo-second order sorption kinetics of lead onto tree fern at various initial concentrations.

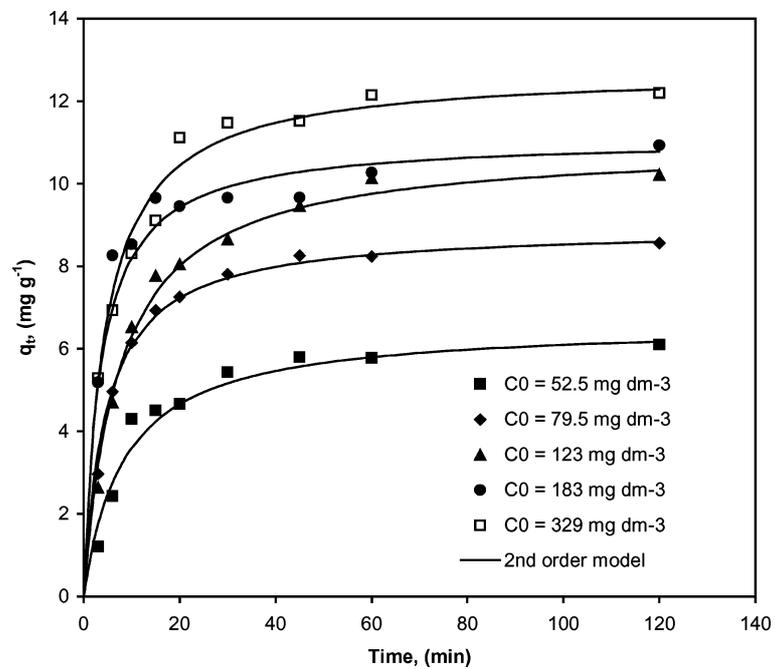


Figure 2. Plot of sorbed amount versus time for copper at various initial concentrations.

Table 1. Kinetic parameters for four sorption systems.

System	C_0 (mg dm ⁻³)	C_e (mg dm ⁻³)	q_e (mg g)	k (g mg ⁻¹ min ⁻¹)	r^2
AB9/Activated clay	59.7	0.583	14.8	0.660	1.000
	114	1.78	28.0	0.272	1.000
	356	22.8	83.3	0.0329	1.000
	475	45.7	107	0.0138	1.000
	552	86.9	116	0.0110	1.000
BR18/Activated clay	111	1.91	27.2	3.48	1.000
	213	2.37	52.7	0.238	1.000
	326	13.1	78.3	0.0439	1.000
	443	72.5	92.7	0.0300	1.000
	520	104	104	0.0338	1.000
Cu/Tree fern	52.5	26.1	6.60	0.0180	0.995
	79.5	43.8	8.92	0.0238	1.000
	123	78.9	11.0	0.0124	0.999
	183	138	11.1	0.0253	0.998
	328	278	12.7	0.0178	0.999
Pb/Tree fern	74.1	1.9	18.0	0.0681	1.000
	111	7.3	26.0	0.0219	1.000
	196	57.6	34.7	0.0070	0.999
	350	188.3	40.5	0.0044	1.000
	537	351.3	46.3	0.0039	1.000

from the slope of the plot of t/q_t against t in a shorter time than the traditional method. For this reason, it is reasonable to use pseudo-second order parameters to obtain the equilibrium sorbate concentration, C_e , to analyse the pseudo-isotherms.

Four sorption systems, Cu/tree fern, Pb/tree fern, AB9/activated clay and BR18/activated clay were tested by applying the pseudo-Langmuir and pseudo-Redlich-Peterson isotherms using a pseudo-second order kinetic expression constant. The amount of sorbate sorbed at equilibrium can be obtained from the pseudo-second order equation and the equilibrium liquid phase sorbate concentration can be calculated from the equation below:

$$C_e = C_0 - \frac{q_e m_s}{V} \quad (12)$$

where C_e is the equilibrium liquid phase sorbate concentration, mg dm⁻³; C_0 is the initial liquid phase sorbate concentration, mg dm⁻³; q_e is the equilibrium sorption capacity, mg g⁻¹; V is solution volume, dm³, and m_s is the mass of mixed sorbent, g.

Figure 3 shows the linear plot of C_e/q_e versus C_e . The result was a straight line with slope of $1/q_m$ and intercept of $1/K_a q_m$ for dye/activated clay sorption systems. The values of the pseudo-Langmuir constants q_m and K_a are presented in Table 2 for the four sorption systems. These values of the coefficients of determination, r^2 , indicated a strong positive relationship between the data and the linear equation where the solid-liquid sorption data followed the pseudo-Langmuir sorption isotherm. Figure 4 shows pseudo-Langmuir and pseudo-Redlich-Peterson isotherms for

Table 2. Pseudo-Langmuir isotherm constants for four sorption systems.

System	q_m (mg g ⁻¹)	K_a (dm ³ mg ⁻¹)	r^2
AB9/Activated clay	124	0.147	0.995
BR18/Activated clay	105	0.215	0.995
Cu/Tree fern	13.9	0.0378	0.997
Pb/Tree fern	46.6	0.0857	0.994

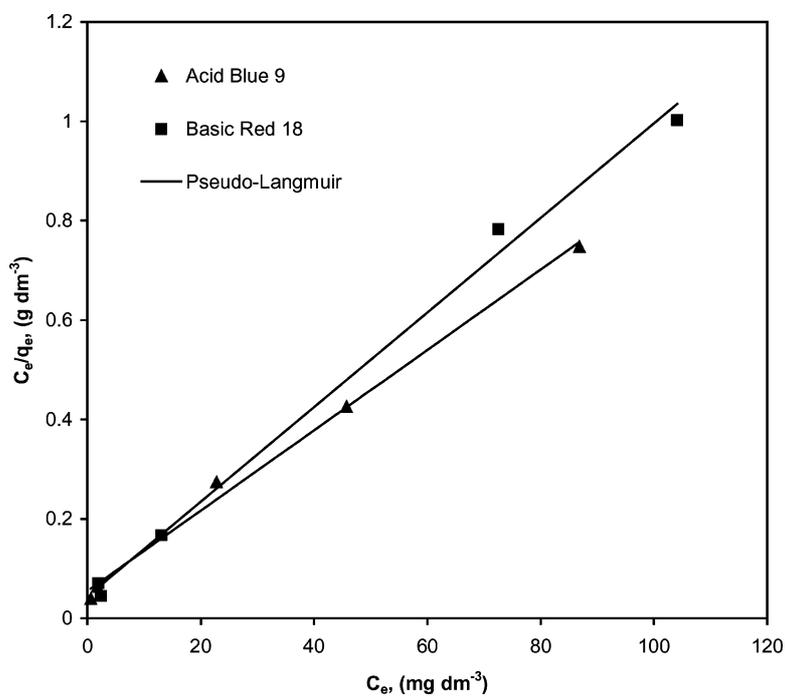


Figure 3. Pseudo-Langmuir isotherm for sorption of dyes onto activated clay.

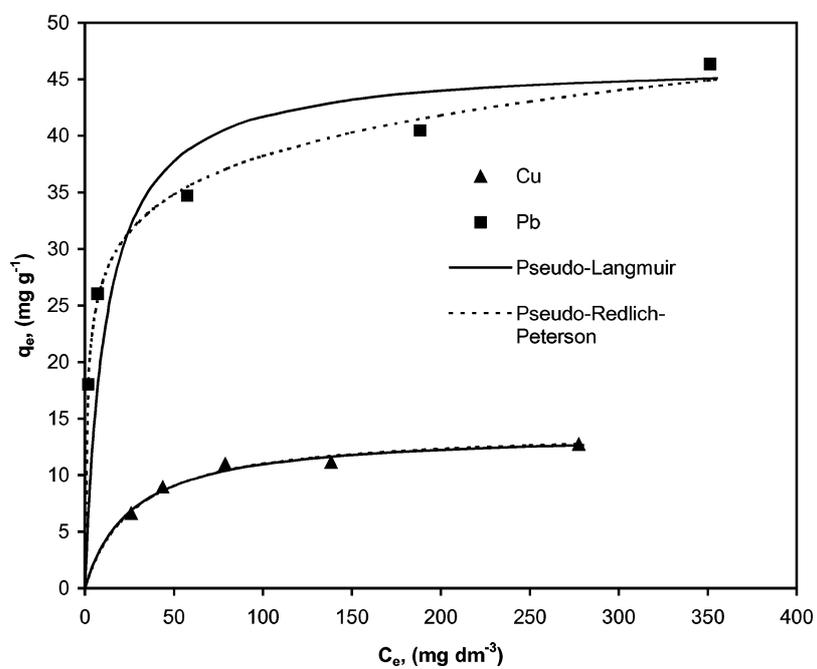


Figure 4. Pseudo-Langmuir and Pseudo-Redlich-Peterson isotherm for sorption of metal ions onto tree fern.

Table 3. Pseudo-Redlich-Peterson isotherm constants for four sorption systems.

System	A (dm ³ g ⁻¹)	B (dm ³ mg ⁻¹) ^g	g	r ²
AB9/Activated clay	45.6	1.20	0.729	0.999
BR18/Activated clay	1.23 × 10 ⁹	3.81 × 10 ⁷	0.739	0.969
Cu/Tree fern	0.510	0.0363	1.000	0.995
Pb/Tree fern	40.2	1.84	0.877	1.000

the metal/tree fern sorption systems. The monolayer saturation capacities, q_m , and sorption constants, K_a , were determined from the slope and intercept of the pseudo-Langmuir equation listed in Table 2. The monolayer saturation capacities, q_m , for the four sorption systems were determined to be 13.9, 46.6, 124 and 105 mg g⁻¹ for copper/tree fern, lead/tree fern, AB9/activated clay and BR18/activated clay respectively.

Experimental results also showed that the pseudo-Redlich-Peterson isotherm was an appropriate description of the data for both metal/tree fern and dye/activated clay sorption over the concentration ranges studied. Table 3 shows the pseudo-Redlich-Peterson isotherm constants A , B and g as well as the coefficients of determination, r^2 , for four sorption systems. In all cases, the pseudo-Redlich-Peterson isotherm exhibited a high coefficient of determination.

Conclusion

This investigation was based on the assumption of a pseudo-second order mechanism in relation to four sorption systems, Cu/tree fern, Pb/tree fern, AB9/activated clay and BR18/activated clay. The results from the study showed high coefficients of determination. Pseudo-Langmuir and pseudo-Redlich-Peterson isotherm were derived from the pseudo-second order kinetic expression constant and were used to describe the liquid-solid sorption systems. The results also showed an excellent fit with the experimental data for both pseudo-isotherms. According to the evaluation using the pseudo-Langmuir equation, the monolayer sorption capacities were obtained to be 13.9 mg g⁻¹ for Cu/tree fern, 46.6 mg g⁻¹ for Pb/tree fern, 124 mg g⁻¹ for AB9/activated clay and 105 mg g⁻¹ for BR18/activated clay.

Nomenclature

(TF) ⁻ and (TF)	Polar sites on the tree fern surface
(TF) ₀ and [H(TF)] ₀	The number of equilibrium sites available on the tree fern
(TF) _t and [H(TF)] _t	The number of active sites occupied on the tree fern at time t
A	Redlich-Peterson isotherm constant (dm ³ g ⁻¹)
B	Redlich-Peterson isotherm constant (dm ³ mg ⁻¹) ^g
C_0	Initial liquid phase sorbate concentration (mg dm ⁻³)
C_e	Equilibrium concentration (mg dm ⁻³)
g	Redlich-Peterson isotherm constant ($0 < g < 1$)
k	Pseudo-second order rate constant (g mg ⁻¹ min ⁻¹)
K_a	Sorption equilibrium constant (dm ³ mg ⁻¹)
m_s	Mass of mixed sorbent (g)
q_e	Amount of sorbate sorbed at equilibrium (mg g ⁻¹)
q_m	q_e for a complete monolayer (mg g ⁻¹)
q_t	Amount of sorbate sorbed at time t (mg g ⁻¹)
r^2	Coefficient of determination
t	Reaction time (min)
V	Solution volume (dm ³)

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代表論文 (六)

Ho, Y.S.*, Chiang, T.H. and Hsueh, Y.M. (2005), Removal of basic dye from aqueous solution using tree fern as a biosorbent. *Process Biochemistry*, **40** (1), 119-124. (SCI) Rank 1st in citation from 473 articles of *Process Biochemistry* (2005), Last data updates: 25 August 2007

Abstract: A batch sorption system using tree fern as biosorbent was investigated to remove Basic Red 13 from aqueous solutions. The system variables studied include sorbent particle size and temperature and results revealed the potential of tree fern, an agriculture product, as a low-cost sorbent. The Langmuir isotherm was found to represent the measured sorption data well. The dye sorption capacity of tree fern increased as the sorbent particle size decreased. Maximum saturated monolayer sorption capacity of tree fern for Basic Red 13 was 408 mg/g. Various thermodynamic parameters such as ΔG° , ΔH° and ΔS° were calculated indicating that this system was a spontaneous and endothermic process. (C) 2003 Elsevier Ltd. All rights reserved.

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Removal of basic dye from aqueous solution using tree fern as a biosorbent

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Abstract

A batch sorption system using tree fern as biosorbent was investigated to remove Basic Red 13 from aqueous solutions. The system variables studied include sorbent particle size and temperature and results revealed the potential of tree fern, an agriculture product, as a low-cost sorbent. The Langmuir isotherm was found to represent the measured sorption data well. The dye sorption capacity of tree fern increased as the sorbent particle size decreased. Maximum saturated monolayer sorption capacity of tree fern for Basic Red 13 was 408 mg/g. Various thermodynamic parameters such as ΔG° , ΔH° and ΔS° were calculated indicating that this system was a spontaneous and endothermic process.

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Keywords: Equilibrium sorption; Isotherm; Basic dye; Tree fern; Biosorption; Agricultural by-products

1. Introduction

The removal of dye from textile effluents is one of the most significant environmental problems. Dyes are used widely in modern industrial society. Since they have a synthetic origin and complex aromatic molecular structures which make them inert and difficult to biodegrade when discharged into waste streams, people always overlook their undesirable nature. Some are harmful to aquatic life in rivers where they are discharged. The occupational exposure of workers in the textile industries is linked to a higher bladder cancer risk [1]. The use of hair colouring products and breast cancer have also been linked [2]. Consequently, methods to remove dye species from wastewaters have been the subject of several research papers.

The most widely used industrial sorbent is activated carbon. However, it is an expensive material unless regeneration becomes relatively easy but is unlikely to be cost-effective. Various agricultural products and by-products have been investigated to remove dyes from aqueous solutions. These include cotton waste, rice husk, bark [3], sugar industry mud

[4], palm-fruit bunch [5,6], Jack fruit peel [7], wood [8], orange peel [9], sugar cane dust [10], peat [11] and pith [12]. The obvious advantage of this method is the lower costs involved. Hence, there is a need to search for more economical and effective sorbents.

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 retain water and manure for plants. Tree fern is generally dark brown in colour and is a complex material containing lignin and cellulose as major constituents [13]. Chemical sorption can occur via the polar functional groups of lignin, which include alcohols, aldehydes, ketones, acids, phenolic hydroxides and ethers as chemical bonding [14] and ion exchange [15]. Tree fern, an agricultural by-product, has been currently investigated to remove heavy metals from aqueous solutions [16,17].

The equilibrium sorption isotherm is fundamentally important in the design of sorption systems. Equilibrium studies give the capacity of the sorbent and describe the sorption isotherm by constants whose values express the surface properties and affinity of the sorbent. Equilibrium relationships between sorbent and sorbate are described by sorption isotherms, usually the ratio between the quantity sorbed and that remaining in the solution at a fixed

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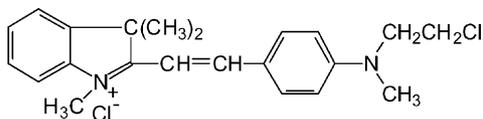
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temperature at equilibrium. The major interest of this study was to investigate sorption of basic dye, Basic Red 13, from aqueous solution using tree fern. The system variables studied include sorbent particle size and temperature.

2. Materials and methods

This study was focused in investigating sorption of basic dye using tree fern. The raw tree fern was dried in an oven at 100 °C for 24 h. The sorbent was screened to obtain four different ranges of geometrical sizes: 38–45 μm, 61–74 μm, 74–88 μm and 104–124 μm. The solutions of dye were prepared in distilled water using C.I. Basic Red 13. All working solutions were prepared by diluting the stock solution with distilled water.

The sorbate (C.I. Basic Red 13) used in the experiments and their structure is listed below. The maximum adsorption wavelength in the visible light range is 524 nm.



Batch sorption experiments were conducted at a constant temperature on a rotary shaker at 100 rpm using 250 ml capped conical flasks. In all sets of experiments, 0.25 g of tree fern was thoroughly mixed into 250 ml of dye solution with initial pH value of 5. After shaking the flasks for 24 h, the tree fern was separated by filtration through a membrane filter (0.25 μm). The filtrate was analysed for the concentration of dye.

2.1. Temperature effect

Batch sorption experiments were carried out at the desired temperature (10, 20, 30 and 40 °C) using particle size of 74–88 μm and each used a range of initial dye concentrations from 0.25 to 1.8 mmol/dm³.

2.2. Particle size effect

Batch sorption experiments were performed at a constant temperature (30 °C). Each used four different tests at particle sizes ranged 38–45 μm, 61–74 μm, 74–88 μm and 104–124 μm and a range of initial dye concentrations from 0.25 to 1.8 mmol/dm³.

3. Results and discussion

Basic forms of Langmuir sorption isotherm [18] have reasonable agreement with a large number of experimental isotherms including those have different interfaces between the two phases [3,4,16,17]. Therefore, the Langmuir sorption isotherm is most widely used for the sorption of a solute

from a liquid solution assuming the sorption takes place at specific homogeneous sites within the sorbent. Furthermore, it also assumes that once a dye occupies a site, no further sorption can take place at that site. The rate of sorption to the surface should be proportional to a driving force times an area. The driving force is the concentration of the solution and the area is the amount of bare surface. If the fraction of covered surface is ϕ , the rate per unit of surface is:

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

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

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

where k_a and k_d are the rate constants, r_a the sorption rate, r_d the desorption rate, C the concentration in the solution and ϕ the fraction of the surface covered.

The two rates are equal at equilibrium and we find that:

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

and

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

Since q_e is proportional to ϕ :

$$\phi = \frac{q_e}{q_m} \quad (5)$$

The saturated monolayer sorption capacity, q_m , can be obtained. When ϕ approaches 1, then $q_e = q_m$.

The saturated monolayer isotherm can be represented as a linear form:

$$q_e = \frac{q_m K_a C_e}{1 + K_a C_e} \quad (6)$$

The above equation can be rearranged to the following:

$$\frac{C_e}{q_e} = \frac{1}{K_a q_m} + \frac{1}{q_m} C_e \quad (7)$$

where C_e is the equilibrium concentration (mmol/dm³), q_e the amount of dye sorbed (mmol/g), q_m is q_e for a complete monolayer (mmol/g), K_a the sorption equilibrium constant (dm³/mmol). A plot of C_e/q_e versus C_e should indicate a straight line of slope $1/q_m$ and an intercept of $1/K_a q_m$.

The structure of tree fern is cellulose-based and the surface of cellulose in contact with water is negatively charged [16]. Basic Red 13 will ionise to give the coloured cationic dye base and this will undergo attraction on approaching the anionic tree fern structure. On this basis, it is expected that a basic dye will have a strong sorption affinity for tree fern.

3.1. Particle size effect

Isotherm experiments were carried out and the data analysed using the linear form of the Langmuir equation to determine the effect of particle sizes on the dye removal capacity

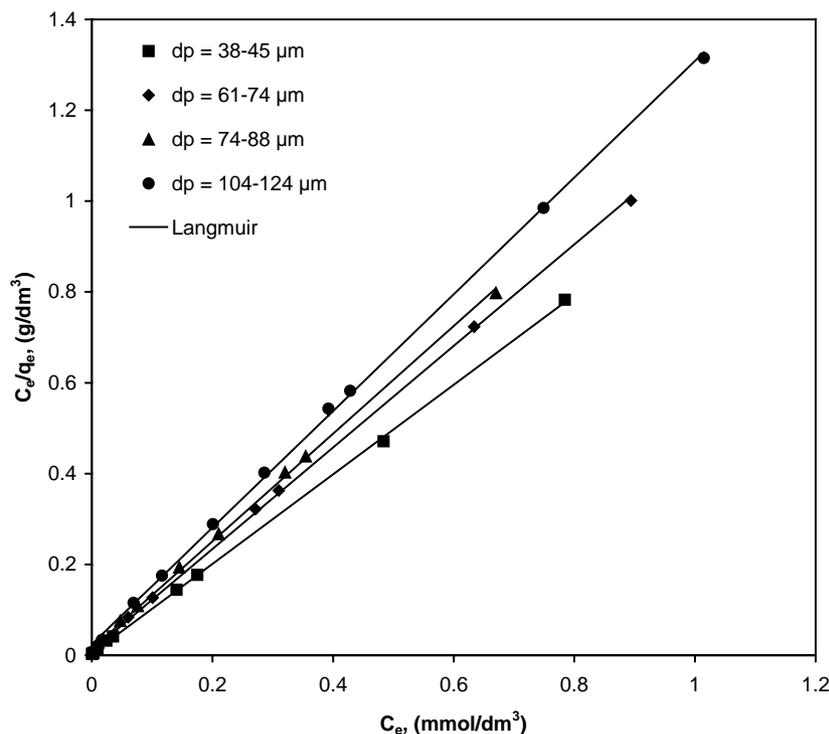


Fig. 1. Langmuir isotherms for the sorption of Basic Red 13 by using tree fern at various particle sizes.

of the various dye/tree fern systems. Isotherms were determined for four tree fern particle size ranges from 38–45 μm to 104–124 μm with constant contact time of 24 h. Fig. 1 showed these isotherms were found to be linear in the concentration range studied and the coefficients of determination, r^2 , were fairly high (Table 1). These values of r^2 indicated the dye/tree fern sorption data strongly followed the Langmuir model of sorption. The isotherm constants, q_m and K_a were presented in Table 1. The monolayer saturation capacities, q_m , increased from 0.778 to 1.01 mmol/g as the tree fern particle sizes decreased ranging from 104–124 μm to 38–45 μm . Therefore, with a given mass of tree fern, smaller particle size would increase surface area availability hence the number of sites increased. Furthermore, the effect was probably due to the inability of the large dye molecule to penetrate all the internal pore structure of the tree fern particles. Values of the monolayer equilibrium capacity of other sorbents from the literature are given in Table 2 for comparison. The square of mean diameter of the tree fern,

Table 1
Langmuir isotherm constants for the Basic Red 13 at various tree fern particle sizes

d_p (μm)	r^2	q_m (mmol/g)	K_a (dm^3/mmol)
38–45	1.000	1.01	256
61–74	1.000	0.894	109
74–88	0.999	0.844	82.8
104–124	0.999	0.778	53.4

d_p^2 , the Langmuir sorption constant, K_a , and the monolayer coverage, q_m , from Table 1 can be used to derive a mathematical relationship. The relationship having a coefficient of determination as high as 0.995 are:

$$q_m = \frac{d_p^2}{1.34d_p^2 - 818} \quad (8)$$

Table 2
Comparison of monolayer equilibrium capacity for basic dye with other agriculture sorbents

q_m (mg/g)	Sorbents	Sorbates	Reference
1120	Bark	Safranine	[3]
915	Bark	Methylene Blue	[3]
875	Cotton waste	Safranine	[3]
838	Rice husk	Safranine	[3]
519	Sugar-industry-mud	Basic Red 22	[4]
320	Palm-fruit bunch	Basic Yellow	[5]
312	Rice husk	Methylene Blue	[3]
278	Cotton waste	Methylene Blue	[3]
253	Peat	Basic Blue 69	[11]
242	Palm-fruit bunch	Basic Red 18	[6]
166	Jack fruit peel	Malachite Green	[7]
71.9	Wood	Basic Blue 69	[8]
22.4	Orange peel	Congo Red	[9]
14.4	Peat	Acid Blue 25	[11]
4.88	Sugar cane dust	Malachite Green	[10]
4.26	Sugar cane dust	Rhodamine B	[10]
3.23	Orange peel	Rhodamine B	[9]
1.33	Orange peel	Procion Orange	[9]
408	Tree fern	Basic Red 13	This study

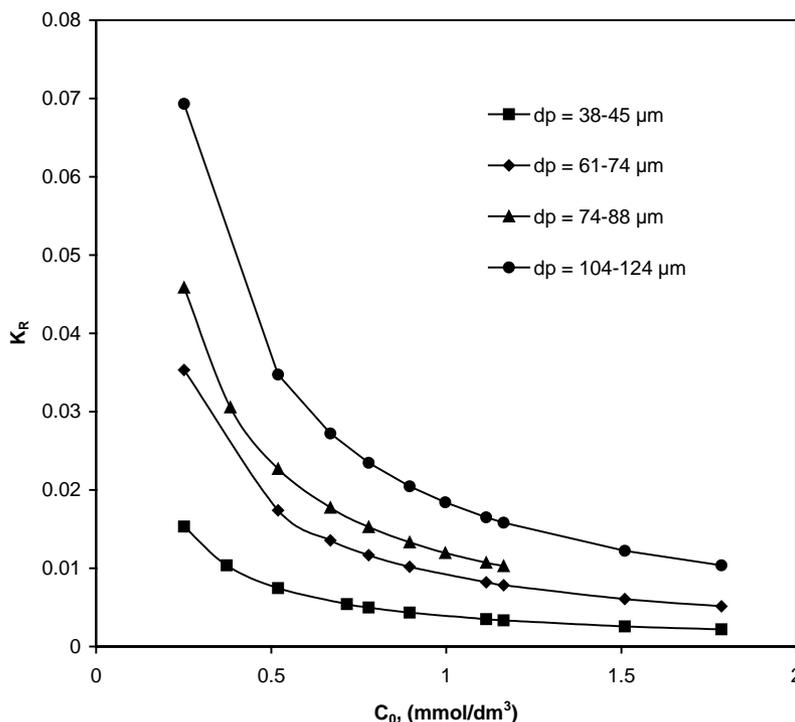


Fig. 2. Values of the separation factor, K_R , for the sorption of Basic Red 13 by using tree fern at various particle sizes.

$$K_a = \frac{6.97 \times 10^4}{(d_p^2)^{0.762}} \quad (9)$$

The effect of isotherm shape can be used to predict whether a sorption system is 'favourable' or 'unfavourable' both in fixed-bed systems [19] as well as in batch processes [20]. According to Hall et al. [21], 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:

$$K_R = \frac{1}{1 + K_a C_0} \quad (10)$$

where K_R is a dimensionless separation factor, C_0 the initial concentration (mmol/dm³) and K_a the Langmuir constant (dm³/mmol). The parameter K_R 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 for Basic Red 13 at different particle sizes are shown in Fig. 2. The K_R values indicated that sorption was more favourable for the higher initial dye concentrations than the lower ones. However, the sorption process became more favourable with decreasing particle size of tree

fern. Nevertheless, referring to Fig. 2, it was obvious that tree fern would be an effective sorbent for removing dye from solution.

3.2. Temperature effect

The temperature effect on the sorption of Basic Red 13 on tree fern is shown in Fig. 3. The results revealed that the sorption capacity increased from 0.702 to 0.900 mmol/g with the temperature increasing from 283 to 313 K. Since the sorption increased when temperature rose, therefore this system was endothermic. It was a chemisorption mechanism where an increase in number of molecules acquiring sufficient energy to undergo chemical reaction with lignins and hemicelluloses in the tree fern. A conventional mechanism, physisorption systems, where the increase of temperature usually increases the rate of approach to equilibrium, but decreases the equilibrium capacity. In addition, the creation of some new active sites for additional sorption on the surface of the sorbent also was endothermic [22].

3.3. Thermodynamic parameters

Based on fundamental thermodynamics concept, it is assumed that in an isolated system, energy cannot be gained or lost and the entropy change is the only driving force. In environmental engineering practice, both energy and entropy factors must be considered in order to determine which process will occur spontaneously. The Gibbs free energy change, ΔG° , is the fundamental criterion of spontaneity. Reactions

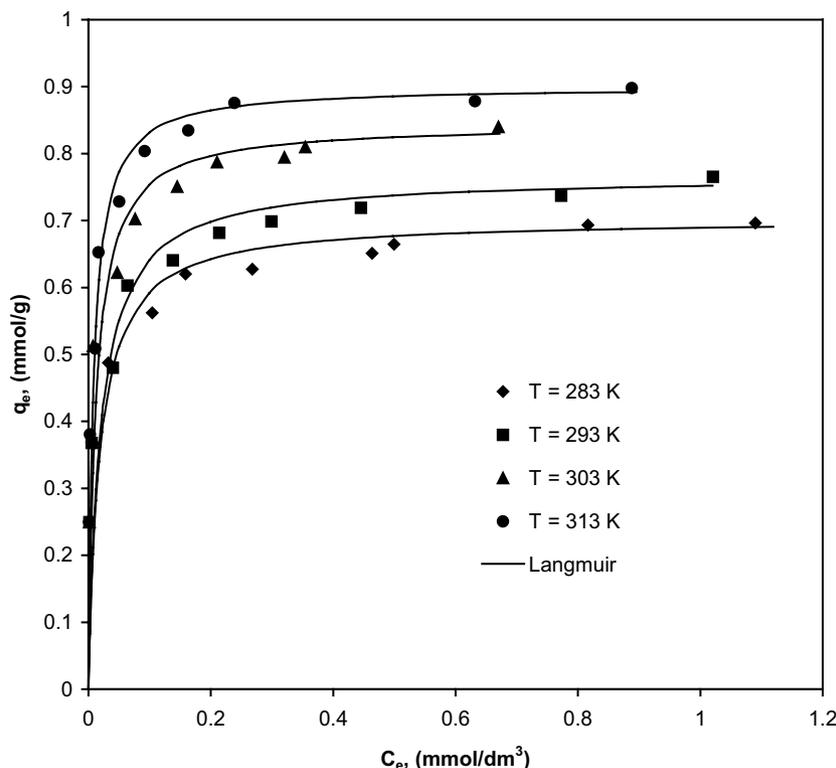


Fig. 3. Langmuir isotherms for the sorption of Basic Red 13 by using tree fern at various temperatures.

occur spontaneously at a given temperature if ΔG° is a negative quantity. The free energy of the sorption reaction, considering the sorption equilibrium constant, K_a , is given by the following equation:

$$\Delta G^\circ = -RT \ln K_a \quad (11)$$

where ΔG° is the standard free energy change (J); R the universal gas constant, 8.314 J/K mol and T the absolute temperature (K).

The Gibbs free energy change, ΔG° , can be represented as follows:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (12)$$

A plot of ΔG° versus T was linear. Enthalpy change, ΔH° , and entropy change, ΔS° , were determined from the slope and intercept of the plots. The values for the sorption equilibrium constant, K_a , decreased with increasing temperature. The thermodynamic parameters Gibbs free energy change, ΔG° , for the sorption processes are shown in Table 3. The

negative values of ΔG° confirmed the feasibility of the process and the spontaneous nature of sorption with a high preference of Basic Red 13 dye on tree fern. The value of ΔH° was positive (21.7 kJ/mol), indicating that the sorption reaction was endothermic. The positive value of ΔS° (0.109 J/mol K) reflected the affinity of the tree fern for the dye and suggested some structural changes in dye and tree fern [23]. In addition, positive value of ΔS° also showed the increase of randomness at the solid/liquid interface during the sorption of dye on tree fern.

4. Conclusion

It is evident that tree fern, a commercially available natural material, is a good sorbent for Basic Red 13 and it can be suggested for the removal of basic dye from wastewater. Both the increase of the temperature and decrease of the tree fern particle size resulted in a higher dye loading per unit weight of the sorbent. Values of the separation factor, K_R , indicated the dye/tree fern system was a favourable sorption. The results gained from this study were extremely well described by the theoretical Langmuir isotherm. The equilibrium monolayer sorption capacity of tree fern for Basic Red 13 was 1.01 mmol/g when the temperature was 30 °C and the tree fern particle size range was 38–45 μm . The thermodynamics of the system pointed out the system was spontaneous and endothermic.

Table 3
Langmuir isotherm constants for the Basic Red 13 at various temperatures

T (K)	r^2	q_m (mmol/g)	K_a (dm ³ /mmol)	ΔG° (kJ/mol)
283	0.999	0.702	53.9	-9.38
293	0.999	0.766	51.2	-9.59
303	0.999	0.844	82.8	-11.1
313	1.000	0.900	122	-12.5

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