

# Equilibrium sorption isotherm for metal ions on tree fern

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

*School of Public Health, Taipei Medical University, No. 250 Wu-Hsing Street, Taipei, Taiwan*

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## 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.

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## 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  $\text{Cu}^+$ . 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  $\mu\text{g}$  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

\* Corresponding author. Tel.: +886-2-2736-1661x6514; fax: +886-2-2738-4831.

E-mail address: [ysho@tmu.edu.tw](mailto:ysho@tmu.edu.tw) (Y.S. Ho).

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/dm<sup>3</sup>) 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/dm<sup>3</sup>.

### 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/dm<sup>3</sup>.

## 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  $\phi$ , 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  $\phi$  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

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

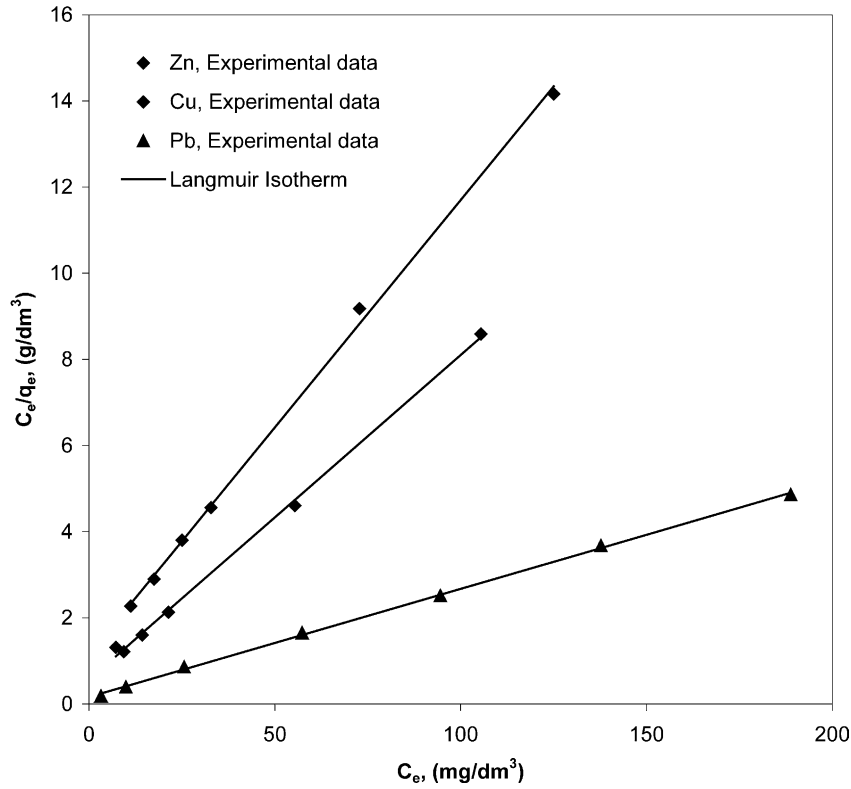


Fig. 1. Langmuir isotherms of metal ions sorbed on tree fern.

Since  $q_e$  is proportional to  $\phi$ :

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

The saturated monolayer sorption capacity,  $q_m$ , can be obtained. When  $\phi$  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/dm<sup>3</sup>);  $q_e$  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 (dm<sup>3</sup>/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:

$$q_e = \frac{A C_e}{1 + B C_e^g} \quad (10)$$

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

Table 1  
Isotherm constants for metal ions sorption onto tree fern

	Zn	Cu	Pb
<b>Langmuir</b>			
$q_m$ , (mg/g)	7.58	10.6	39.8
$K_a$ , (dm <sup>3</sup> /mg)	0.0926	0.134	0.156
$r^2$	0.998	0.998	0.999
<b>Freundlich</b>			
$K_F$ , (dm <sup>3</sup> /mg)(dm <sup>3</sup> /mg) <sup>1/n</sup>	2.49	3.24	15.5
1/n	0.222	0.261	0.222
$r^2$	0.940	0.818	0.953
<b>Redlich–Peterson</b>			
$g$ , (dm <sup>3</sup> /mg) <sup>1/n</sup>	0.932	0.929	0.907
$A$ , (dm <sup>3</sup> /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

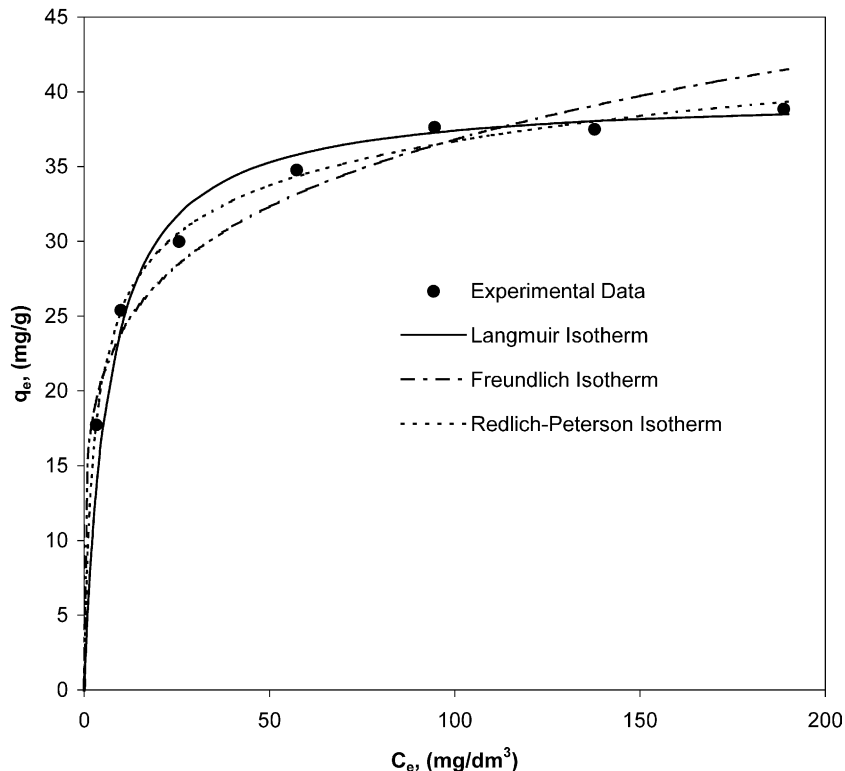


Fig. 2. Isotherms of lead ions sorbed on tree fern.

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.  $\text{MOH}^+$ ,  $\text{M(OH)}_2$ ,  $\text{M(OH)}_3^-$ , and  $\text{M(OH)}_4^{2-}$ ) are too small to affect the concentrations of  $\text{M}^{2+}$  in this study. Although many metal species can be viewed as potential sorbates in the uptake of  $\text{M}^{2+}$  from solution, the data presented in this study suggest that, under experimental conditions ( $\text{pH} < 6$ ), the species responsible for the sorptive removal of  $\text{M}^{2+}$  is the predominant one in the species distribution, namely the  $\text{M}^{2+}$ . Thus, sorption can be explained by elucidating the mechanism whereby the  $\text{M}^{2+}$  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,  $\text{m}^2/\text{g}$  tree fern;  $q_m$  is

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

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

monolayer sorption capacity, gram metal per gram tree fern;  $N$  is Avogadro number,  $6.02 \times 10^{23}$ ;  $A$  is the cross sectional area of metal ion,  $\text{m}^2$ ;  $M$  is molecular weight of metal. For  $\text{Zn}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  ions, the molecular weights are 65.4, 63.5 and 207 and the cross sectional areas of  $\text{Zn}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  have been determined to be  $1.72 \text{ \AA}^2$ ,  $1.58 \text{ \AA}^2$  and  $5.56 \text{ \AA}^2$  ( $\text{Zn}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  radius is  $0.74 \text{ \AA}$ ,  $0.71 \text{ \AA}$ , and  $1.33 \text{ \AA}$ , Cotton and Wilkinson, 1988) in a close packed monolayer. Therefore, the specific surface areas can be calculated for  $\text{Zn}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  (Table 2). The maximum specific surface area of tree fern towards  $\text{Zn}^{2+}$  binding is  $1.20 \text{ m}^2/\text{g}$ ;  $\text{Cu}^{2+}$  binding is  $1.59 \text{ m}^2/\text{g}$ ;  $\text{Pb}^{2+}$  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 ( $\text{mg}/\text{dm}^3$ ) and  $K_a$  is Langmuir constant ( $\text{dm}^3/\text{mg}$ ). 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  $\text{Pb} > \text{Cu} > \text{Zn}$ .

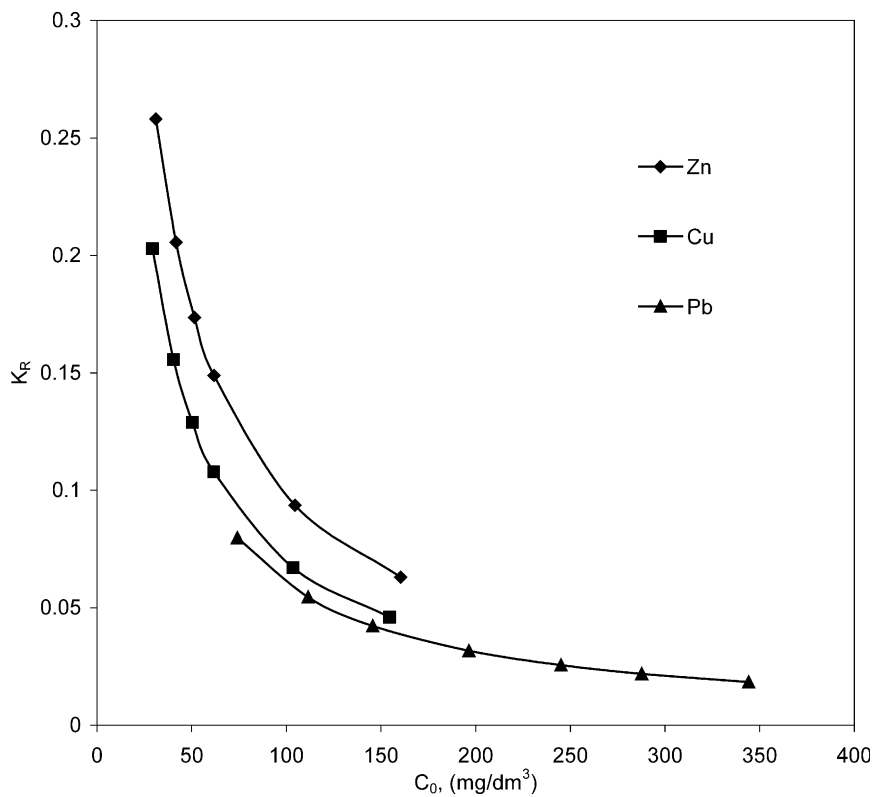


Fig. 3. Plot of  $K_R$  against initial metal concentration of Zn(II), Cu(II) and Pb(II).

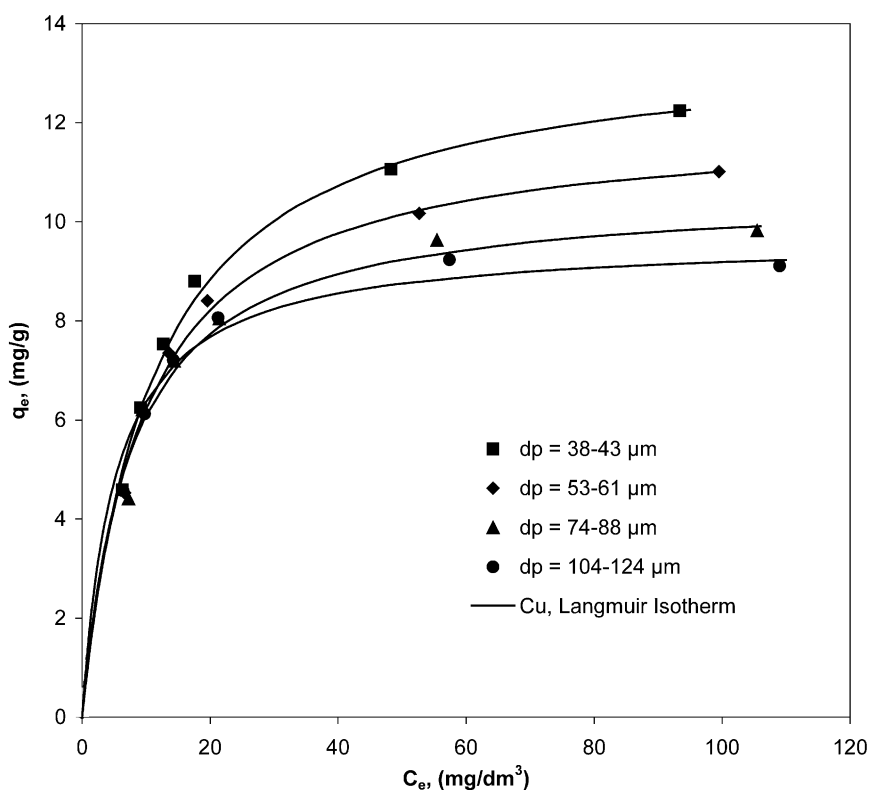


Fig. 4. Langmuir isotherms for the sorption of copper ions using tree fern at various particle sizes.

Table 3  
Langmuir sorption isotherm constants at different particle sizes

$d_p$ ( $\mu\text{m}$ )	$R^2$	$q_m$ (mg/g)	$K_a$ ( $\text{dm}^3/\text{mg}$ )	$S$ ( $\text{m}^2/\text{g}$ 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  $\mu\text{m}$ . 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:

$$q_m = \frac{d_p}{0.121d_p - 2.06} \quad (16)$$

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

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

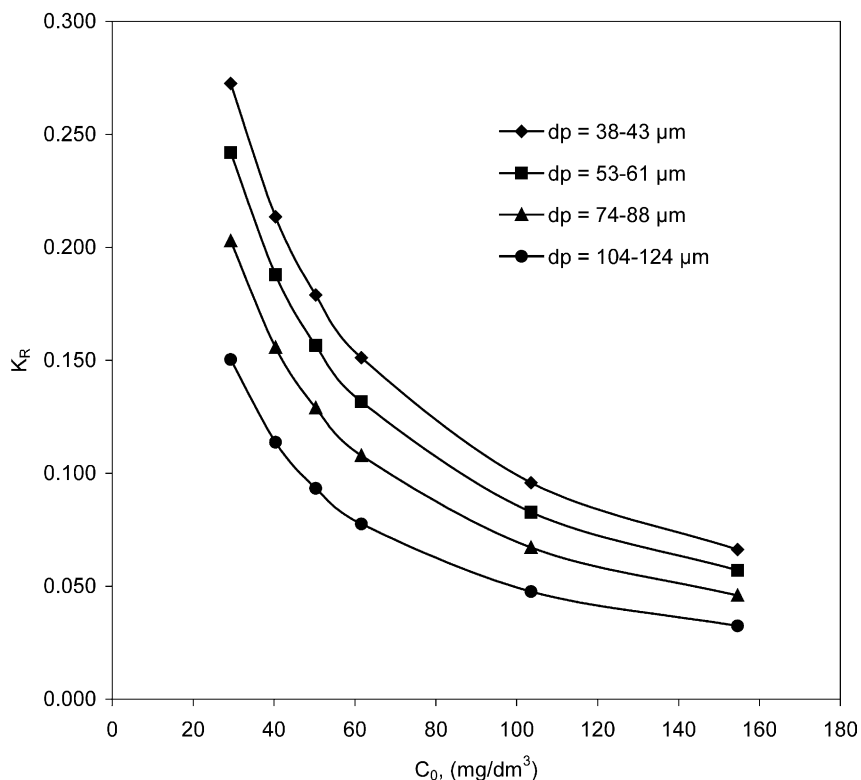


Fig. 5. Plot of  $K_R$  against initial copper ion concentration of various particle sizes.

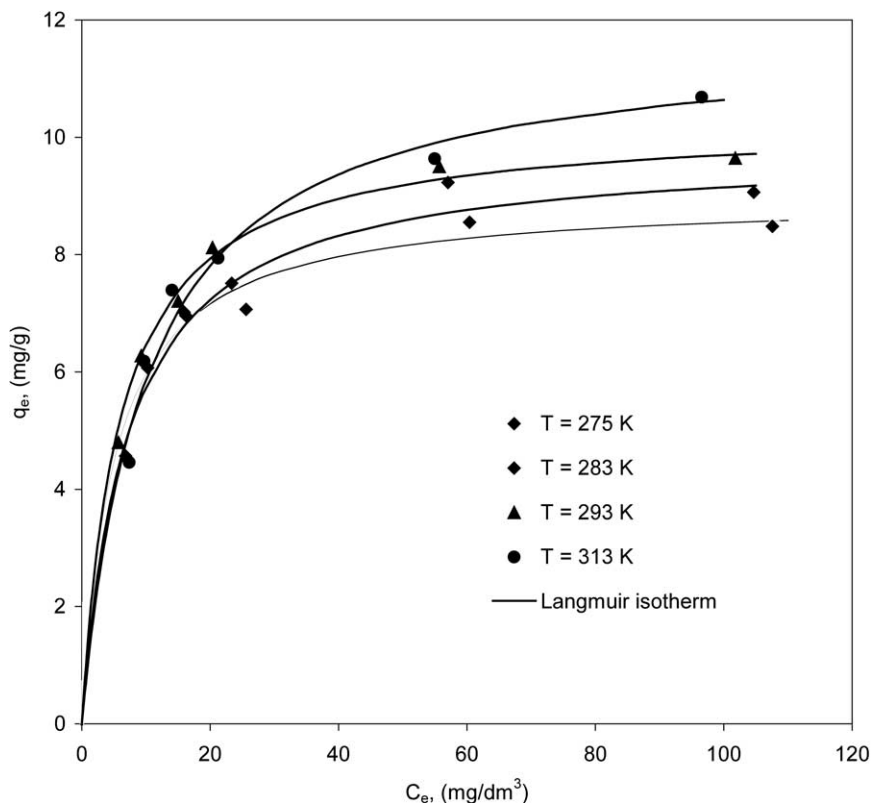


Fig. 6. Langmuir isotherms for the sorption of copper ions using tree fern at various temperatures.

Table 4  
Langmuir sorption isotherm constants at different temperatures

$T$ (K)	$r^2$	$q_m$ (mg/g)	$K_a$ (dm <sup>3</sup> /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  $Pb^{2+}$ .



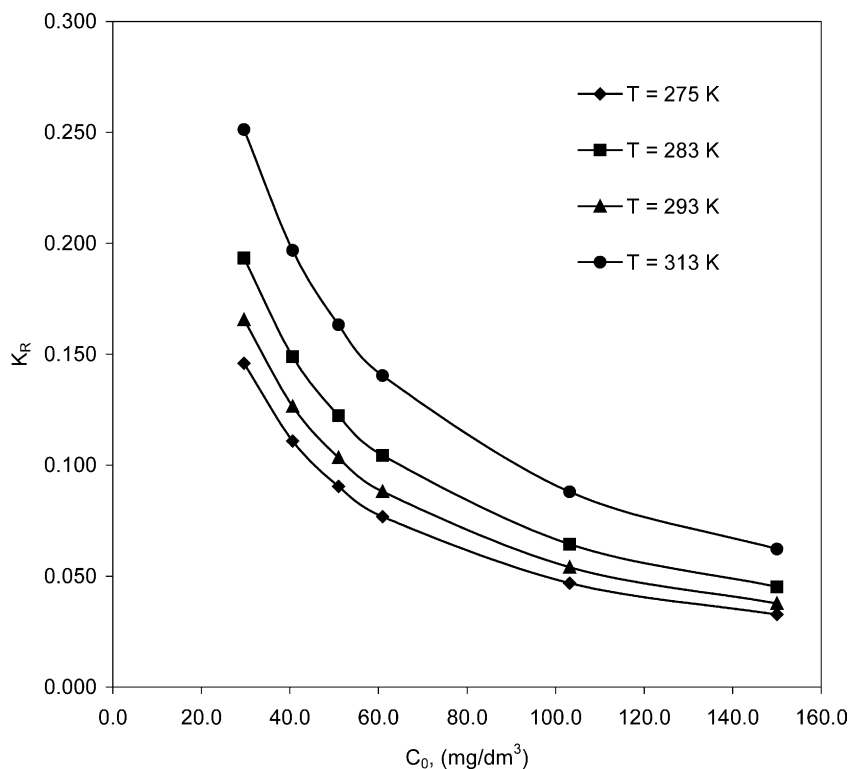


Fig. 7. Plot of  $K_R$  against initial copper ion concentration of various temperatures.

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