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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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

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:

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

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:

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

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:

$$q_e = \frac{AC_e}{1 + BC_c^g} \qquad (3)$$

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:

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

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:

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

or

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

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:

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

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:

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

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):

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

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:

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

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
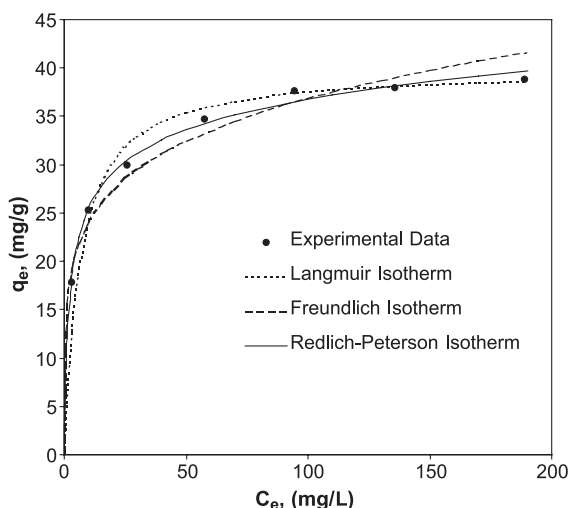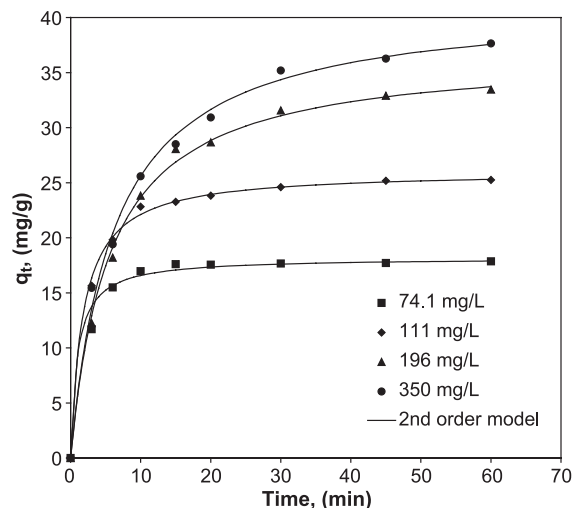

Fig. 2. Effect of time on sorbed lead concentrations for various initial Pb(II) concentrations.

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

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

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_o (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_o 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_o 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_o can be expressed as a function of C_0 for lead(II) as:

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

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

$$h_o = \frac{C_0}{0.181 C_0 - 9.71} \tag{13}$$

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).
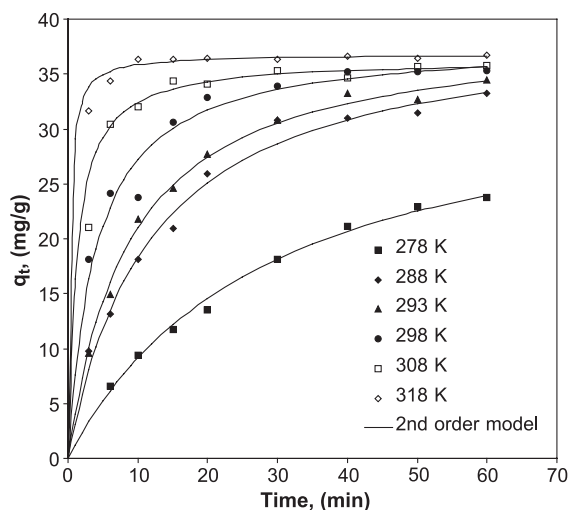

Fig. 3. Effect of time on sorbed lead concentrations for various temperatures.

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_o (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:

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

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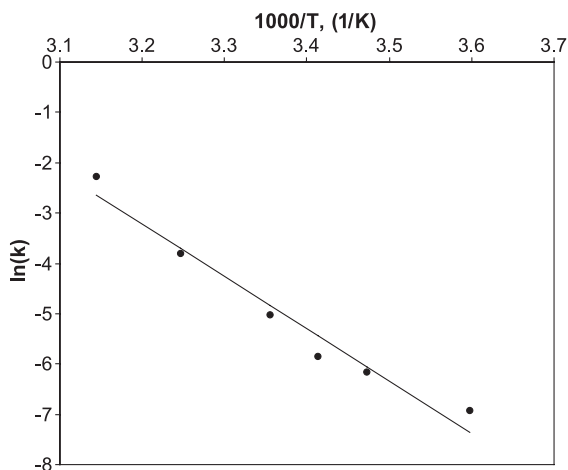
between k and T can be represented in an Arrhenius form as:

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

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-
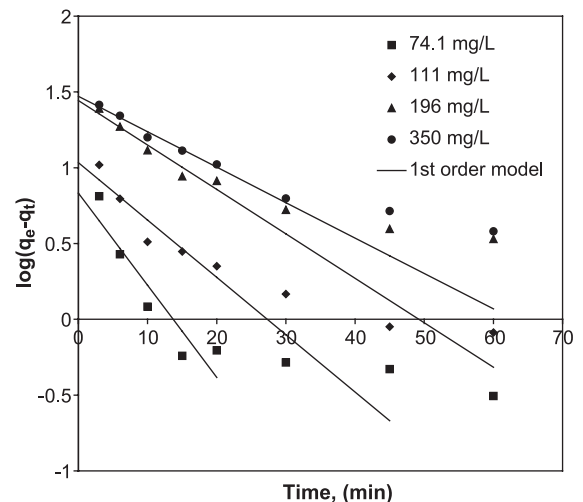
Fig. 4. The relationship between T and k.

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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