REMOVAL OF METAL IONS FROM SODIUM ARSENATE SOLUTION USING TREE FERN

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T he sorption of metal ions from sodium arsenate solution by using an agricultural by-product, tree fern, has been investigated. The sorption of sodium cation on tree fern has been studied in terms of pseudo-second-order sorption processes. The pseudo second-order kinetic model has been developed to predict the rate constant of sorption, the equilibrium capacity and initial sorption rate with the effect of initial metal ion concentration. The Henry's law, Langmuir and Redlich–Peterson isotherms were used to correlate experimental isotherms. The sorption of sodium cation follows Henry's law and a modified Redlich–Peterson isotherm. However, the arsenic could not be removed from sodium arsenate solution by the sorption for the reason that arsenic is in the form of anion as arsenic acids in the solution and because of the negative charge of tree fern surface.

Keywords: isotherm; adsorption; kinetic model; tree fern; agricultural by-product; sodium.

INTRODUCTION

The sorption of gases on a solid phase has long been investigated and theorized (Langmuir, 1916). The theories and experiences of sorption of gases on a solid phase have been extended to the liquid phase sorption. Sorption has been accepted as one of the most appropriate processes, for the purification of drinking water and wastewater. The sorbent used most widely for industrial applications is activated carbon. However, it is an expensive material despite its ability to be regenerated. Therefore, in recent years extensive studies have been undertaken to find low-cost sorbents to remove pollutants from drinking water and aqueous effluents (Lee *et al.*, 1999; Fu and Viraraghavan, 2001; Ho and McKay, 1999a,b; Manju *et al.*, 1998).

Two important physicochemical aspects for the evaluation of the sorption process as a unit operation are the equilibria of the sorption and the kinetics. Equilibrium studies in sorption give the capacity of the sorbent. It is described by a sorption isotherm characterized by certain constants whose values express the surface properties and affinity of the sorbent. Sorption equilibrium is established when the concentration of sorbate in the bulk solution is in dynamic balance with that of the interface. Equilibrium relationships between sorbent and sorbate are described by sorption isotherms, usually the ratio between the quantity sorbed and that remains in the solution at a fixed temperature at equilibrium. The studies of isotherm in the sorption of pollutants from solution include Freundlich, Langmuir, BET and Redlich–Peterson isotherms (Lee *et al.*, 1999; Fu and Viraraghavan, 2001; Ho and McKay, 1999a,b). The most widely applied kinetic model is the Lagergren's pseudo-first-order kinetic model (Lagergren, 1898). In recent years, the pseudo-second-order kinetic expression

(Ho, 1995) has also been applied for the sorption of metal on peat (Ho and McKay, 1999a), pith (Ho and McKay, 1999b), *Aspergillus niger* (Kapoor *et al.*, 1999) and *Chlorella Vulgaris* (Aksu, 2001) as well as dyes on peat (Ho and McKay, 1998) and *Aspergillus niger* (Fu and Viraraghavan, 2001) from aqueous solution.

The objective of this work is to study the possibility of the utilization of tree fern for the sorption of metal ions from sodium arsenate solution. Variables of the system include sodium arsenate concentration and temperature. The isotherms for the Henry's law, Langmuir and Redlich–Peterson isotherms have been compared. In addition, the kinetics of the sorption of sodium cation by tree fern under the effects of initial sodium arsenate concentration was performed to correlate the experimental data, based on the pseudo-second-order kinetic expression for the sorption system.

MATERIALS AND METHODS

Tree fern is commercially available in Taiwan. The raw tree fern was dried in an oven for 24 h at $100°C$, and then was screened through a sieve to get size 53–61 μm. This was done to produce a uniform material for the complete set of sorption tests. A stock solution of $2000\,mg\,dm^{-3}$ was prepared by dissolving $Na_2HAsO_4 7H_2O$ in distilled water.

Equilibrium Studies

A volume of 50 ml of arsenate solution with a concentration in the range of $30–180\,mg\,dm^{-3}$ was placed in a 125 ml conical flask. An accurately weighed tree fern sample 0.25 g with a particle size of 53–61 μm was then added to the solution. A series of such 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 a day, the tree fern was separated by filtration through a nylon membrane filter (0.45 μm). The filtrate was analysed for the remaining arsenic and sodium ion concentration by inductively coupled plasma atomic emission spectrophotometer (ICP-AES).

Effect of Temperature

A volume of 50 ml of arsenic solution with a concentration 71.8 mg dm^{-3} was placed in a 125 ml conical flask. An accurately weighed tree fern sample 0.25 g with a particle size of 53–61 μm was then added to the solution and then agitated at a constant speed of 100 rpm in a shaking water bath at different temperatures from 10 to 40°C. After shaking the flasks for 3 h, the tree fern was separated by filtration. The filtrate was analysed for the sodium cation concentration.

Kinetic Studies

A range of sodium cation concentrations from 60 to 150 mg dm^{-3} was used and agitation was carried out for 1 h. All contact investigations were carried out 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 with an inductively coupled plasma atomic emission spectrophotometer (ICP-AES). A 6.8 g sample of tree fern (53–61 μm) was added to each 1.7 dm^3 volume of metal cation solution and an agitation speed of 300 rpm was used for all experiments of 20°C in a temperature controlled water bath.

THEORY

Langmuir Isotherm

The Langmuir isotherm (Langmuir, 1916) can be represented as:

$$q_e = \frac{q_m K_s C_e}{1 + K_s C_e} \tag{1}$$

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

$$\frac{C_e}{q_e} = \frac{1}{K_s q_m} + \frac{1}{q_m} C_e \tag{2}$$

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}), and K_s is sorption equilibrium constant (dm^3 mg^{-1})

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

If equilibrium concentration, C_e, is low. $1 \gg K_s C_e$ and $q_e = K_H C_e$. Langmuir isotherm becomes Henry's law.

Redlich–Peterson Isotherm

The Redlich–Peterson isotherm (Redlich and Peterson, 1959) can be described as follows:

$$q_e = \frac{AC_e}{1 + BC_e^g} \tag{3}$$

It has three isotherm constants, namely, A, B and g $(0 < g < 1)$, which characterize the isotherm. Its limiting behaviour could be summarized: when $g = 1$, then

$$q_e = \frac{AC_e}{1 + BC_e} \tag{4}$$

i.e. the Langmuir form results. When $g = 0$, then

$$q_e = \frac{AC_e}{1 + B} \tag{5}$$

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

Equation (4) can be converted to a linear form by taking logarithms:

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

Three isotherm constants, A, B and g can be evaluated from the linear plot represented by equation (6) using a trial and error optimisation method.

A general trial and error procedure which is applicable to computer operation was developed to determine the coefficient 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.

Pseudo-second-order Model

In order to investigate the mechanism of sorption, the constants of sorption were determined to use equation of pseudo-second-order equation (Ho, 1995). Ho developed a pseudo-second-order kinetic expression for the sorption systems of divalent metal ions using sphagnum moss peat. The pseudo-second-order kinetic expression has been applied to the solid–liquid sorption systems. The linear form of pseudo-second-order model of Ho is generally expressed as follows:

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e}t \tag{7}$$

where q_e and q_t are the sorption capacity at equilibrium and at time t, respectively (mg g^{-1}) and k is the rate constant of pseudo-second-order sorption, (g mg^{-1} min^{-1}).

$$h = kq_e^2 \tag{8}$$

where h is the initial sorption rate (mg g^{-1} min^{-1}) as q_t/t approaches 0, and Equation (7) can be rearranged to obtain:

$$q_t = \frac{t}{1/h + (1/q_e)t} \tag{9}$$

RESULT AND DISCUSSION

Equilibrium Studies

Tree fern is naturally, commercially and easily 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 (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 the tree fern can be a suitable sorbate for sorption of metal cation because of its polar and acid characters (Ho *et al.*, 2002).

The sorption of metal ions from sodium arsenate solution by using tree fern at 20°C is shown in Figure 1. The curve for sodium cation indicates that the rate of sorption is very fast initially and reaches a plateau at equilibrium. However, sorption of arsenic was negligible. No sorption occurred in the anions/tree fern system because of the negative charge of tree fern surface (Ho *et al.*, 2002). The same result has been reported for the sorption of arsenic(V) from solution by rice husk (Lee *et al.*, 1999). A blank experiment was performed with a volume of 50 ml of distilled water (pH = 6.61) placed in a 125 ml conical flask. A change of pH value from 6.61 to 5.51 showed that hydrogen ions were released from the tree fern into solution. Consequently, tree fern surface is negatively charged. The sorption of arsenic anion was negligible unless the sorbate has to be quatermized (Lee *et al.*, 1999). In addition, tree fern is a complex material containing cellulose as its major constituents and the surface of cellulose in contact with water is negatively charged. Arsenate ion species are $H_2AsO_4^-$ and $HAsO_4^{2-}$, the distribution of which depends on the solution pH, in the experimental conditions. The approach of an arsenic anion will suffer coulombic repulsion due to the presence of the strong anionc groups in tree fern. Sodium cation will undergo attraction on approaching the anionic tree fern structure. On this basis, it is to be expected that a cation will have a strong sorption affinity for tree fern. The same phenomena has also been reported for the sorption of divalent metal ions such as Zn(II), Cu(II) and Pb(II) from aqueous solutions by tree fern (Ho *et al.*, 2002).

The sorption of metal ions has been widely studied using the Langmuir isotherm (Lee *et al.*, 1999; Ho and McKay, 1999b; Ho *et al.*, 2002) and the Redlich–Peterson isotherm (Lee *et al.*, 1999; Ho *et al.*, 2002). Figure 2 shows that both
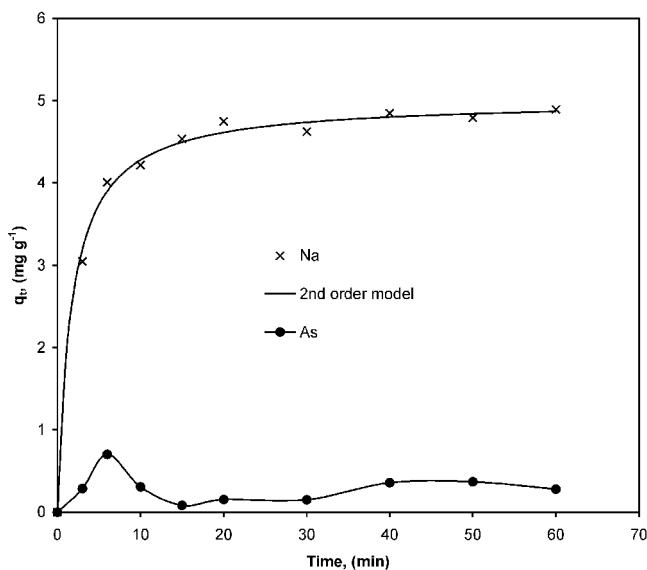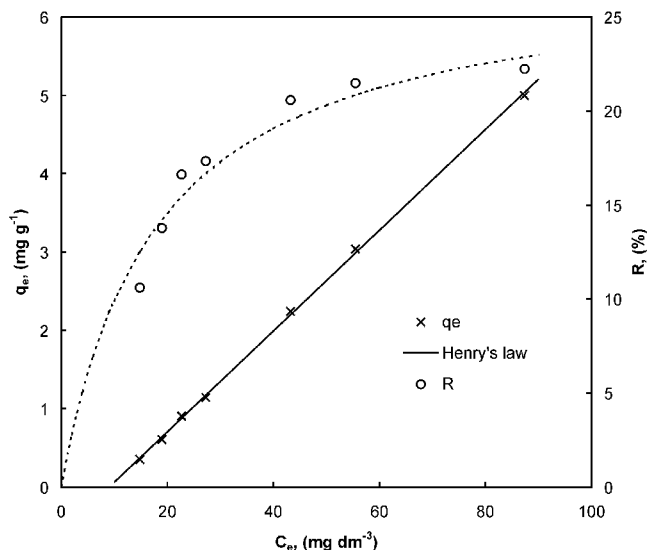

Figure 2. Variation of sorption capacity, q_e, and percent sodium removal, R, in relation to equilibrium concentration, C_e.

the equilibrium capacity, q_e, and percentage sodium cation removal, R, increased with increasing equilibrium concentration, C_e. This result was not similar to most sorption systems (Lee *et al.*, 1999). Therefore, the Redlich–Peterson isotherm had to be modified for the sorption system. The modified Redlich–Peterson model (MRP model) is as follows:

$$q_e = \frac{AC_e}{1 + B/C_e^y} \tag{10}$$

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

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

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 coefficients of determination were 0.560, 0.997 and 0.999 for the Langmuir, the modified Redlich–Peterson isotherm and Henry's law respectively. The modified Redlich–Peterson isotherm constant A was $0.0587 \, dm^3 \, g^{-1}$, B was 610 $(dm^3 \, mg^{-1})^g$ and y was 2.25. Henry's constant, K_H, was determined from the slope of the plot of q_e vs C_e and found to be $0.0643 \, dm^3 \, g^{-1}$. Figure 3 shows the experimental data with Henry's law and the modified Redlich–Peterson isotherm. Both of these two isotherms fitted extremely well.

The temperature has the effect on the sorption capacity of the tree fern of removing sodium cation from solution at an initial concentration of $71.8 \, mg \, dm^{-3}$ and a pH value of 6.6. The amount sorption increased slightly from 2.74 to $3.10 \, mg \, g^{-1}$ with an increase in solution temperature from 10 to 40°C.

Kinetic Studies

The experimental results of sorption of sodium cation on tree fern at various concentrations are shown in Figure 4. The curves indicate that the rate of sorption was very fast initially and reached a plateau at equilibrium. The pseudo-
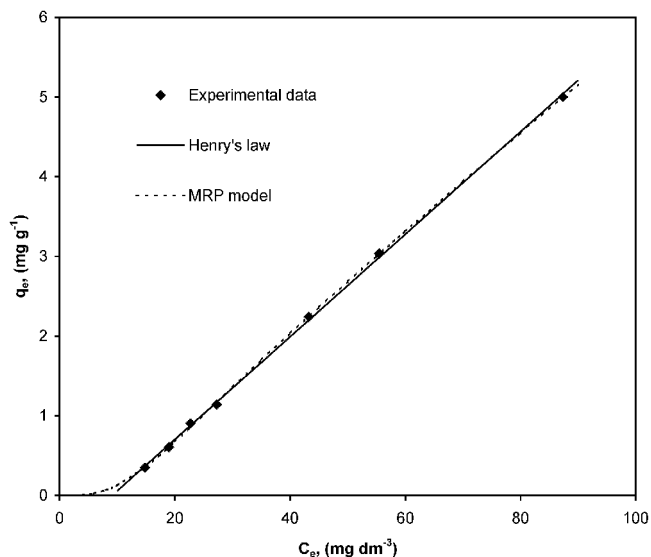

Figure 1. Plot of sorbed capacity vs time for effect of metal ions on the sorption kinetics of metal ions on tree fern at temperature 20°C and tree fern dose $4 \, g \, dm^{-3}$.

Figure 3. Henry's law and modified Redlich–Peterson isotherm for the sorption of sodium cation using tree fern.

second-order coefficients of determination, r^2, the rate parameters, k, equilibrium sorption capacity, q_e, and initial sorption rate, h, for various initial sodium cation concentrations are presented in Table 1. The data showed a good compliance with the pseudo-second-order model and the regression coefficients for the linear plots were higher than 0.997 for all the systems in these studies. The sorption curves were typical for the effect of initial metal ion concentration on the sorption kinetics of metal ion onto tree fern. Similar results have been reported for the sorption of dye onto peat (Ho and McKay, 1998) and pith (Ho and McKay, 1999a). Table 1 shows that the equilibrium sorption capacity increased from 3.56 to $6.15\,\mathrm{mg\,g^{-1}}$, the values of the rate constant were found to increase from 0.184 to $0.265\,\mathrm{g\,mg^{-1}\,min^{-1}}$ and the initial sorption rate increased
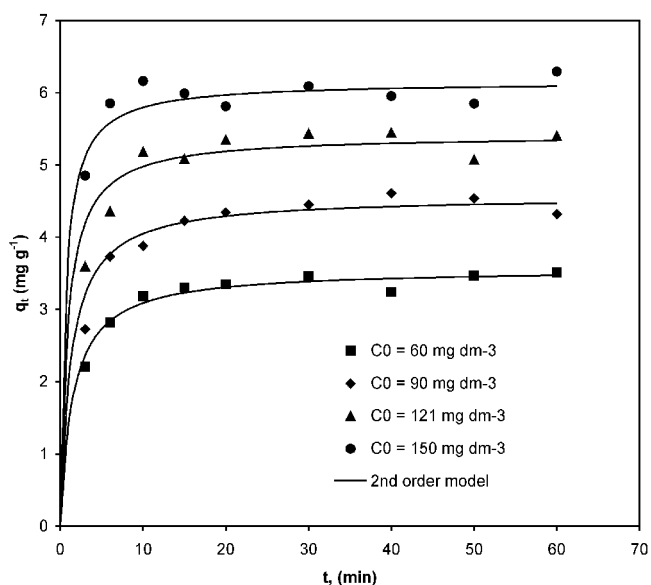
Table 1. Pseudo-second-order rate constant for effect of initial concentration.

C_0 (mg dm^{-3})	q_e (mg g^{-1})	k (g mg^{-1} min^{-1})	h (mg g^{-1} min^{-1})	r^2
59.9	3.56	0.184	2.34	0.998
90.1	4.57	0.171	3.57	0.997
121	5.42	0.210	6.15	0.997
150	6.15	0.265	10.0	0.997

from 2.34 to $10.0\,\mathrm{mg\,g^{-1}}$ min as the initial sodium cation concentration varied from 60 to $150\,\mathrm{mg\,dm^{-3}}$. The corresponding linear plots of the values of q_e and h against C_0 were regressed to obtain expressions for these values in terms of the initial sodium cation concentration with high coefficients of determination (>0.998). Therefore, q_e and h can be expressed as a function of C_0 as follows:

$$q_e = 0.312 C_0^{0.595} \tag{12}$$

$$h = \exp(0.0163 C_0 - 0.154) \tag{13}$$

Substituting the values of q_e and h from Equations (12) and (13) into Equation (9), the rate law for a pseudo-second-order and the relationship of q_t, C_0 and t can be represented as follows:

$$q_t = \frac{t}{\exp(0.154 - 0.0163 C_0) + 3.20 C_0^{-0.595} t} \tag{14}$$

This equation can then be used to derive the sorption capacity, q_e, at any given initial sodium cation concentrations, C_0, and reaction time, t. Figure 5 shows that sorption capacity increased with an increase of initial sodium cation concentration and reaction time. The increase occurred more obviously at the lower concentration and at the start.

CONCLUSIONS

Tree fern is a suitable sorbent for sorption of sodium cation because of its polar and acid characters. The sorption of sodium cation from sodium arsenate solution followed

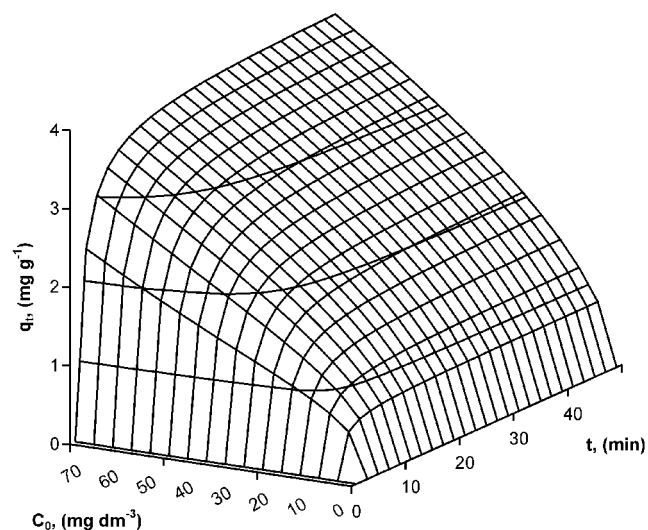Figure 4. Plot of sorbed amounts vs time at various initial concentrations of sodium cation.

Figure 5. Effect of initial sodium concentration on the sorption of sodium cation on tree fern at various reaction times.

the Henry's law and a modified Redlich–Peterson isotherm. Arsenical anion cannot be removed from solution because of the negative charge of tree fern surface. The sorption of sodium cation onto tree fern using an agitated sorber can be described by a pseudo-second-order kinetic expression that includes the rate constant of sorption, the equilibrium sorption capacity and the initial sorption rate.

NOMENCLATURE

A	constant of Redlich–Peterson isotherm, $dm^3 g^{-1}$
B	constant of Redlich–Peterson isotherm, $(dm^3 mg^{-1})^g$
C_0	initial sodium cation concentration, $mg\,dm^{-3}$
C_e	equilibrium concentration, $mg\,dm^{-3}$
g	constant of Redlich–Peterson isotherm $(0 < g < 1)$
h	initial sorption rate, $mg\,g^{-1}\,min^{-1}$
k	rate constant of pseudo-second-order sorption, $g\,mg^{-1}\,min^{-1}$
K_H	Henry's constant, $dm^3 g^{-1}$
K_s	sorption equilibrium constant, $dm^3 mg^{-1}$
q_e	amount of metal ion sorbed, $mg\,g^{-1}$
q_m	saturated monolayer sorption capacity, $mg\,g^{-1}$
q_t	sorption capacity at time t, $mg\,g^{-1}$
r^2	coefficient of determination
R	percent sodium cation removal, %
t	reaction time, min
y	constant of modified Redlich–Peterson isotherm

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