

Effect of pH on lead removal from water using tree fern as the sorbent

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Abstract

The sorption of lead from water onto an agricultural by-product, tree fern, was examined as a function of pH. The sorption processes were carried out using an agitated and baffled system. Pseudo-second-order kinetic analyses were performed to determine the rate constant of sorption, the equilibrium sorption capacity, and the initial sorption rate. Application of the pseudo-second-order kinetics model produced very high coefficients of determination. Results showed the efficiency of tree fern as a sorbent for lead. The optimum pH for lead removal was between 4 and 7, with pH 4.9 resulting in better lead removal. Ion exchange occurred in the initial reaction period. In addition, a relation between the change in the solution hydrogen ion concentration and equilibrium capacity was developed and is presented.

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1. Introduction

The sorption of metal ions from water plays an important role in water pollution control. Recently, there has been considerable interest in the use of agricultural by-products as sorbents for this purpose. The removal of lead from wastewaters has received considerable attention in recent years (Netzer and Hughes, 1984; Ho and McKay, 1999). Extensive investigations have also been carried out to identify suitable and relatively inexpensive agricultural sorbents which are capable of removing significant quantities of lead. Tree fern, a low-cost and readily available product in tropical and subtropical areas, is currently being studied for its ability to remove heavy metals from water. This variety of tree fern is generally marketed for horticultural purposes because of its character of sorbability which retains

water and manure for plants. Trunks of tree ferns are generally dark brown. It is a complex material containing lignin and cellulose as its major constituents (Newman, 1997). Chemical sorption occur through the polar functional groups of lignin, which include alcohols, aldehydes, ketones, acids, phenolic hydroxides, and others as chemical bonding agents (Adler and Lundquist, 1963). Because of the fairly polar character of tree fern, the specific sorption of dissolved solids such as transition metals and polar organic molecules can be high. Its character of removing metals from water has recently been investigated (Ho et al., 2002; Ho, 2003a,b).

Waste effluents are characterized by substantial variations in pH values. This work focuses on studying the possibility of utilizing tree fern for the sorption of lead from water. Kinetic studies were carried out using a shaking batch sorber to study the effect of the initial pH value of the solution. Kinetics analyses were performed to correlate the experimental data, based on a pseudo-second-order ion exchange model.

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2. 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. This process produced a uniform material for the complete set of sorption tests; the material was stored in an airtight plastic container for all investigations. A stock solution of lead (2000 mg/dm³) was prepared in distilled water using lead nitrate. All working solutions were prepared by diluting the stock solution with distilled water.

2.2. Effect of the initial pH value of the solution

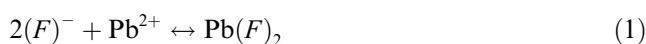
A range of initial pH values of the solution from pH 2.49–6.81 was used, and samples were agitated for 2 h. All contact investigations were carried out using a baffled, agitated 2-dm³ sorber vessel. Samples (3 ml) were withdrawn at suitable time intervals, filtered through a 0.45-μm membrane filter and then analyzed for lead concentration using an inductively coupled plasma atomic emission spectroscopy (ICP-AES) analyzer. A 6.8-g sample of tree fern (53–61 μm) was added to each 1.7-dm³ volume of lead solution with an initial concentration 200 mg/dm³, and an agitation speed of 300 rpm was used for all experiments. Studies were conducted at 20 °C using a temperature-controlled water bath.

3. Kinetics model

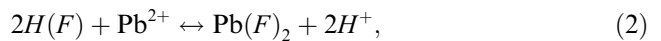
3.1. Reaction order model

The main purpose of this study was to evaluate the order of the reaction for the sorption of lead onto tree fern at various initial pH values of the solution. The second-order kinetic expression for the sorption system of divalent metal ions using sphagnum moss peat has been reported (Ho, 1995; Ho and McKay, 2000). In order to distinguish kinetics equation based on the sorption capacity of a solid from concentration of a solution, Ho's second-order rate equation has been called pseudo-second order. The kinetic expression has also been widely applied to a number of metal/sorbent sorption systems since then (Kapoor et al., 1999; Krishnan and Anirudhan, 2002; Ho, 2003a).

The kinetics of sorption processes are concerned with force fields between sites, and these lead and form an important area of surface chemistry. A pseudo-second-order mechanism can occur due to the ability of lead to sorb onto the tree fern in an aqueous solution. Thus, the lead/tree fern reaction may be represented in two ways:



and



where $(F)^-$ and $H(F)$ are polar sites on the tree fern surface.

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

$$\frac{d(F)_t}{dt} = k[(F)_0 - (F)_t]^2 \quad (3)$$

or

$$\frac{d(HF)_t}{dt} = k[(HF)_0 - (HF)_t]^2, \quad (4)$$

where $(F)_t$ and $(HF)_t$ are the number of active sites occupied on the tree fern at time t , and $(F)_0$ and $(HF)_0$ are the number of equilibrium sites available on the tree fern.

The kinetic rate equations can be rewritten as follows:

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

where k is the rate constant of sorption (dm³/mg min), q_e is the amount of lead sorbed at equilibrium (mg/g), and q_t is the amount of lead sorbed at time t (mg/g). Separating the variables in Eq. (5) gives

$$\frac{dq_t}{(q_e - q_t)^2} = k dt \quad (6)$$

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

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + kt, \quad (7)$$

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

Eq. (7) can be rearranged to obtain

$$q_t = \frac{t}{\frac{1}{kq_e^2} + \frac{t}{q_e}}, \quad (8)$$

which has the linear form of

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e}t. \quad (9)$$

If the initial sorption rate, as $h = q_t/t$ when t approaches 0, h (mg/g min), is

$$h = kq_e^2, \quad (10)$$

then Eqs. (8) and (9) respectively become

$$q_t = \frac{t}{\frac{1}{h} + \frac{t}{q_e}} \quad (11)$$

and

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e}t. \quad (12)$$

The constants can be determined experimentally by plotting t/q_t against t .

3.2. Ion exchange model

Boyd et al. (1947) developed a rate equation, which considered rates of ion exchange sorption in the exchange sorption of ions from aqueous solutions by organic zeolites. For the case of two monovalent ions, the mass law applies to the exchange when written as



If m_{A^+} and m_{B^+} denote the concentrations of the ions A^+ and B^+ in solution, and n_{AR} and n_{BR} the moles of A^+ and B^+ in the sorbent, then the net reaction rate can be written as follows:

$$\begin{aligned} \frac{dn_{AR}}{dt} &= k_1 m_{A^+} n_{BR} - k_2 m_{B^+} n_{AB} \\ &= -n_{AR}(k_1 m_{A^+} + k_2 m_{B^+}) + k_1 m_{A^+} E, \end{aligned} \quad (14)$$

where k_1 and k_2 are the forward and reverse specific rate constants and E is a constant defined by

$$E = n_{AB} + n_{BR}. \quad (15)$$

When the concentrations of A^+ and B^+ in solution are kept constant, then, on integration, Eq. (14) becomes

$$n_{AR} = \frac{k_1 m_{A^+} E}{k_1 m_{A^+} + k_2 m_{B^+}} (1 - e^{-St}) = q, \quad (16)$$

where q is the adsorption capacity at time t , $S = k_1 m_{A^+} + k_2 m_{B^+}$, and Eq. (16) can be rewritten as

$$q_e - q = q_e e^{-St}, \quad (17)$$

where q_e is the equilibrium capacity. Thus,

$$\log(1 - F) = -\left(\frac{S}{2.303}\right)t, \quad (18)$$

where F is the fractional attainment of equilibrium, $F = q_t/q_e$, and S (min^{-1}) is a constant.

4. Results and discussion

The initial pH value of the solution is an important factor which must be considered during sorption studies. Because ion exchange is one of the sorption processes, the rate of lead sorption onto tree fern was expected to be verified by the pH value of the solution in the experiments. In order to ascertain the order of the reaction, a pseudo-second-order model was applied. A series of experiments was undertaken to study the effect of the initial pH value of the lead solution using an initial lead concentration of 200 mg/dm^3 . The results are presented in Fig. 1, and show that the sorption was initially fast and then slowed until equilibrium was reached. Fig. 2 shows that the sorption of lead was affected by the initial

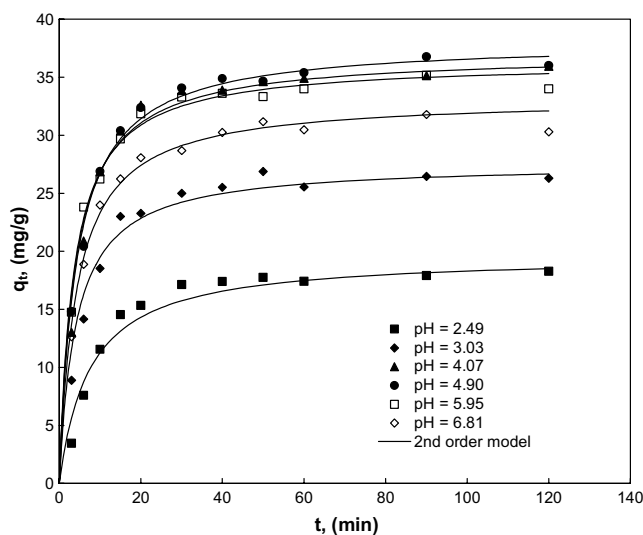


Fig. 1. Plot of the sorbed amount versus time for lead at various initial pH values.

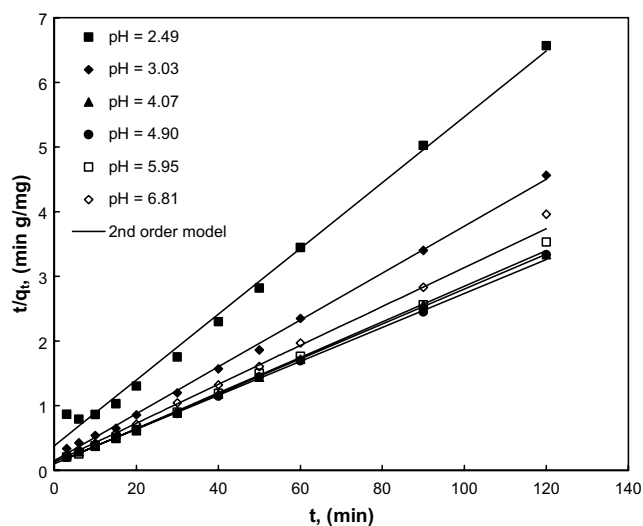


Fig. 2. Pseudo-second-order sorption kinetics of lead onto tree fern at various initial pH values.

pH value and was represented linearly when lead uptake is plotted via the pseudo-second-order Eq. (12) with the initial pH value of the lead solution ranging from 2.49 to 6.81. The pseudo-second-order rate parameters, k , h , and q_e , and the coefficient of determination, r^2 , are presented in Table 1. The data showed good compliance with the pseudo-second-order model, and the regression coefficients for the linear plots were higher than 0.994 for all systems in these studies.

In order to study the sorption mechanism, the rate of uptake of lead by tree fern in these studies was controlled by an ion exchange phenomenon, and the model of Boyd et al. (1947) showing the dependence of the rate of sorption on pH exhibited high coefficients of determination. Fig. 3 shows the variation in the initial pH value

Table 1
Pseudo-second-order and ion exchange model parameters for various pH values

Pseudo-second order model					Ion exchange model	
pH	q_e (mg/g)	k (g/mgmin)	h (mg/g min)	r^2	S (1/min)	r^2
2.49	19.7	6.80×10^{-3}	2.63	0.994	0.0990	1.000
3.03	27.6	8.71×10^{-3}	6.63	0.998	0.103	0.999
4.07	36.8	7.91×10^{-3}	10.7	0.999	0.122	0.999
4.90	38.1	6.17×10^{-3}	8.96	0.999	0.105	0.997
5.95	36.4	7.72×10^{-3}	10.2	0.999	0.105	0.896
6.81	33.3	7.04×10^{-3}	7.78	0.999	0.114	0.999

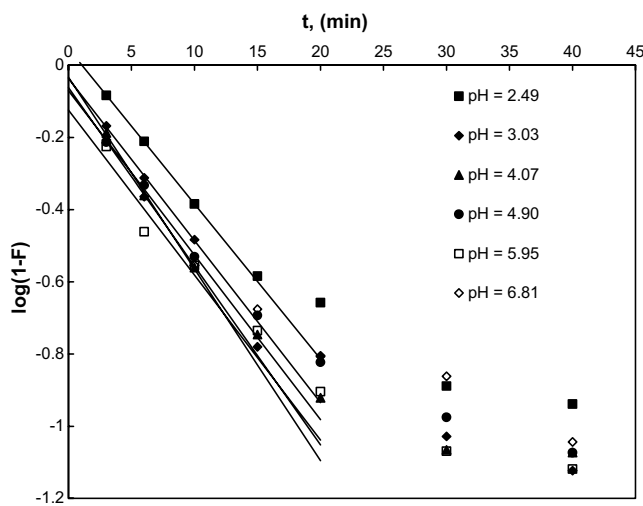


Fig. 3. Ion exchange sorption kinetics of lead onto tree fern at various initial pH values.

of the lead solution with good agreement existing between the experimental data and theoretical curves predicted using Eq. (18) in the initial 10-min period of the sorption process, and the overall line is not straight. Values of the constant, S , were calculated from the slopes of the respective linear plots and are listed in Table 1.

The effect of the initial pH on the sorption capacity of lead was studied. This trend has generally been observed in sorption studies such as the sorption of Cu(II) and Zn(II) by fly ash (Gupta and Ali, 2000) and the sorption of Cd(II) on *C. vulgaris* (Aksu, 2001). The equilibrium sorption capacity increased from 19.7 to 38.1 mg/g, when the initial pH value of the system varied from pH 2.49 to 4.90. However, the sorption capacity decreased slightly when the initial pH value changed from pH 4.90 to 6.81. Again, the initial sorption rate increased rapidly as the pH increased from 2.49 to 4.07 (Table 1). The increase in sorption depends on the surface properties and the chemical character of the lead ions. At low pH, tree fern ligands are closely associated with the hydronium ions (H_3O^+). The surface of the tree fern becomes positively charged. As the pH increases, more ligands such as carboxyl, phosphate, imidazole, and amino groups are exposed and carry negative

charges with subsequent attraction of positively charged lead ions and sorption onto the tree fern surface (Dönmez et al., 1999). Thus, at a lower pH, the sorption of cationic lead should be less because of the higher dissociation of lead, as well as the positively charged tree fern surface.

pH values were measured in the initial 10-min period of the sorption process (Fig. 4). Within the same sorbent dosage, concentration, and temperature, the pH values changed from the initial pH value of the lead solution, showing a sharp change during the first 3-min reaction period after reaching a plateau. There are two sources which may contribute to an increase in the hydrogen ion concentration during the sorption process. The pH variation could originate from the acidic groups of lignin that are believed to be responsible for the cation exchange capacity or ion exchange reactions, such as proton release when lead cations bind to the tree fern. It is clear that ion exchange may have occurred in the beginning stage of sorption. Table 2 illustrates the fact that when the initial pH value of the solution was between 2.49 and 6.81, the sorption capacities were

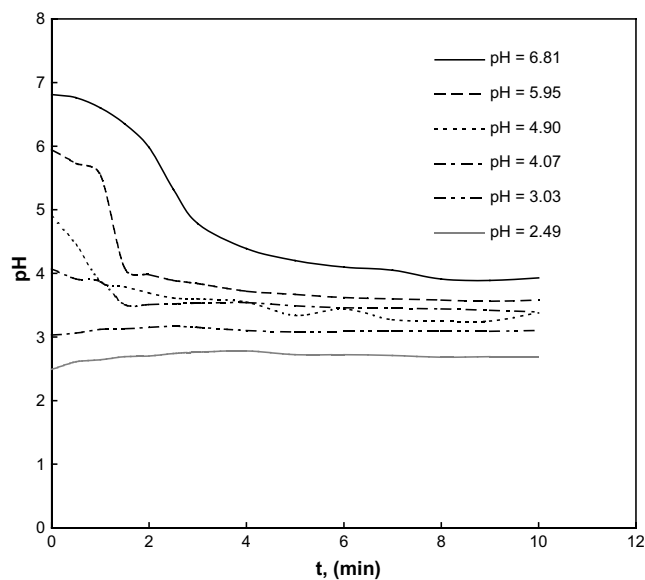


Fig. 4. Plot of pH of solution against time for lead sorption onto tree fern at various initial pH values.

Table 2
Changes in the solution hydrogen ion concentrations for different initial pH values of the lead solution

pH ₀	pH ₁₂₀	ΔH^+ (mmol/dm ³)	q_e (mg/g)
2.49	2.66	−1.05	19.7
3.03	3.06	−0.0623	27.6
4.07	3.10	0.709	36.8
4.90	3.13	0.727	38.1
5.95	3.41	0.388	36.4
6.81	3.63	0.234	33.3

influenced by changes in the solution hydrogen ion concentration, ΔH^+ . Higher capacities result in higher ΔH^+ values. This suggests that as more lead is sorbed onto the tree fern, more hydrogen ions are released from the tree fern into the solution. Consequently, the pH of the reaction mixture decreases. Higher pH values of the solution improve the ion exchange potential in the system when the sorption rate is largely controlled by ion exchange reactions rather than by complexing reactions. Clearly, the resulting equilibrium pH is governed by the factor of the initial pH value of the lead solution and the initial hydrogen ion concentration in the solution, when the temperature, initial lead concentration, and tree fern dose were fixed.

The corresponding linear plots of ΔH^+ against q_e were regressed to obtain expressions for these values in terms of ion exchange, with a high coefficient of determination. Therefore, it is further considered that q_e can be expressed as a function of ΔH^+ as follows:

$$q_e = 10.6\Delta H^+ + 30.3. \quad (19)$$

When the sorption system of initial and equilibrium hydrogen ion concentrations showed no change ($\Delta H^+ = 0$), the equilibrium capacity obtained from the intercept of Eq. (19) was 30.3 mg/g. The ion exchange rate can be determined from the slope of the straight line in Eq. (19) and was 10.6 mg/g mM of hydrogen ion concentration. When ΔH^+ was 2.88, no lead sorption occurred.

5. Conclusions

The agricultural by-product, tree fern, was found to be a suitable sorbent for the removal of lead from water. The lead-binding capacity of the tree fern was shown to be a function of the initial pH value of the solution, and the optimum pH for lead removal was 4.9. The kinetics of sorption of the lead on tree fern followed the ion exchange rate model of Boyd et al. (1947) which consid-

ers rates of ion exchange sorption during the first 10 min. Ion exchange may have occurred in the initial period of the reaction. The order of the reaction for the sorption of lead onto tree fern followed a pseudo-second-order rate expression.

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