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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 dm^3 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 dm^3 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:

$$2(\mathrm{TF})^- + \mathrm{Cu}^{2+} \leftrightarrow \mathrm{Cu(TF)}_2 \tag{1}$$

and

$$2\mathrm{H(TF)} + \mathrm{Cu}^{2+} \leftrightarrow \mathrm{Cu(TF)}_2 + 2\mathrm{H}^+ \tag{2}$$

where $(\mathrm{TF})^-$ and (TF) are polar sites on the tree fern surface.

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

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

or

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

where $(\mathrm{TF})_t$ and $[\mathrm{H(TF)}]_t$ are the number of active sites occupied on the tree fern at time t, and $(\mathrm{TF})_0$ and $[\mathrm{H(TF)}]_0$ are the number of equilibrium sites available on the tree fern.

The kinetic rate equations can be rewritten as follows:

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

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:

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

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

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

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 (g mg^{-1} 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:

$$q_e = \frac{q_m K_a C_e}{1 + K_a C_e} \tag{8}$$

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

$$\frac{C_e}{q_e} = \frac{1}{K_a q_m} + \frac{1}{q_m} C_e \tag{9}$$

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 (dm^3 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:

$$q_e = \frac{A C_e}{1 + B C_e^g} \tag{10}$$

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:

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

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

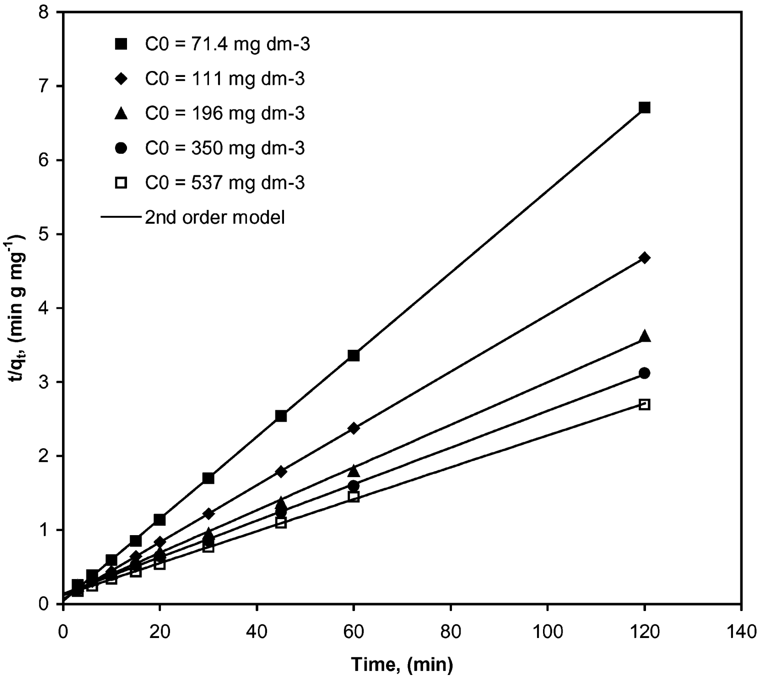

Figure 1. Pseudo-second order sorption kinetics of lead onto tree fern at various initial concentrations.

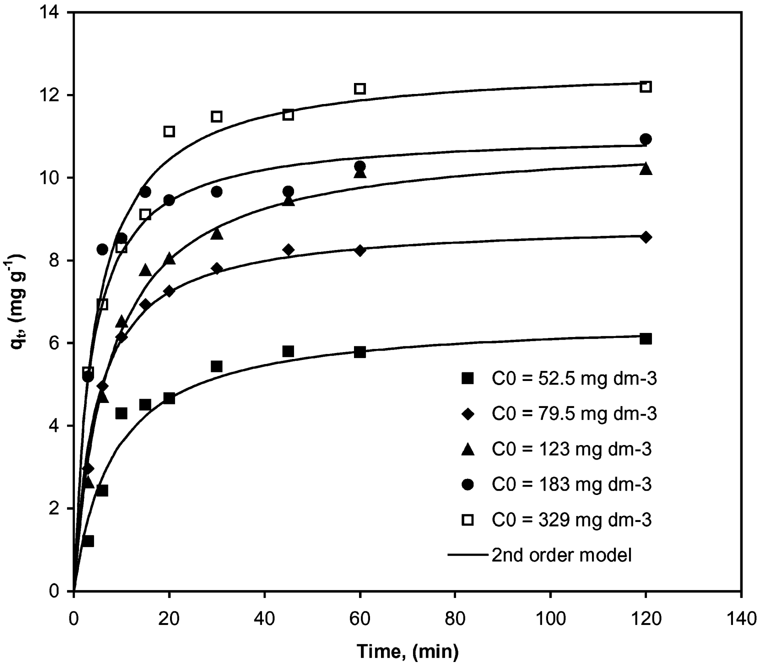

Figure 2. Plot of sorbed amount versus time for copper at various initial concentrations.

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:

$$C_e = C_0 - \frac{q_e m_s}{V} \tag{12}$$

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, dm^3, 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

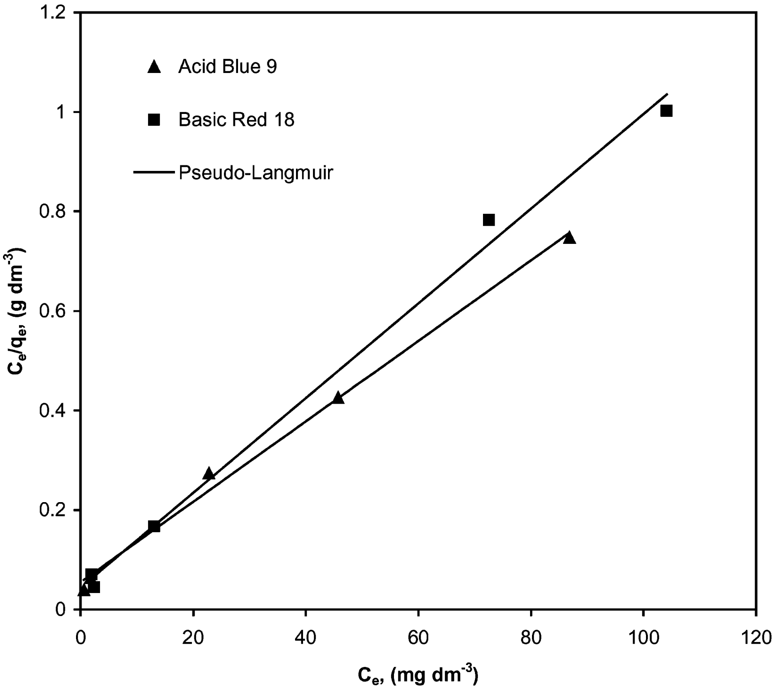

Figure 3. Pseudo-Langmuir isotherm for sorption of dyes onto activated clay.

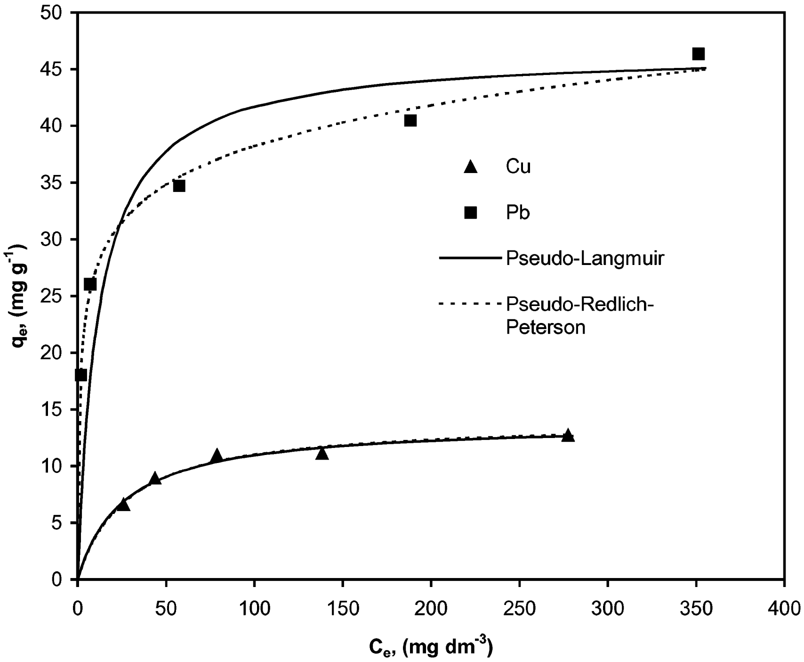

Figure 4. Pseudo-Langmuir and Pseudo-Redlich-Peterson isotherm for sorption of metal ions onto tree fern.

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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