

# Pseudo-isotherms for the sorption of cadmium ion onto tree fern

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## Abstract

The kinetics of cadmium sorption on to tree fern has been investigated based on the assumption of a pseudo-second order rate law. The batch sorption model has been applied to predict the rate constant of sorption and the equilibrium capacity with the effect of initial cadmium concentration. The experimental results have been analysed by pseudo-Langmuir, pseudo-Freundlich and pseudo-Redlich–Peterson isotherms based on pseudo-second order kinetic expression constant. Both pseudo-Langmuir and pseudo-Redlich–Peterson isotherms were found to represent the measured sorption data well. According to the evaluation using the pseudo-Langmuir equation, the monolayer sorption capacity was obtained to be 16.3 mg/g. In addition,  $\chi^2$  analysis was also used to determine the most suitable model. Pseudo-Langmuir and pseudo-Redlich–Peterson were also the best models for the experiment data from  $\chi^2$  analysis.

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## 1. Introduction

Kinetics describe the solute uptake rate which in turn controls the residence time of sorbate uptake at the solid–solution interface. Therefore, it is important to be able to predict the rate at which pollutant is removed from aqueous solutions in order to design appropriate sorption treatment plants. The rate law is determined by experimentation and it cannot be inferred by more examination of the overall chemical reaction equation. Numerous kinetic models have described the reaction order of sorption systems. Traditionally, the kinetics have been described by the first order equation typical of that derived by Lagergren [1]. In recent years, pseudo-second order rate law has been considerable as one of the most appropriate models [2]. An earlier yet important discussion of the use of this model in bi-metal/solutions was done by Ho et al. [3]. Several applications to metal [4–6], dye [7,8] and organic pollutant [9,10] sorption systems have also been reported. More recently, Ho and Chiang [11] have published extensively on the use of the model in mixed sorbents.

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. In many cases, the equilibrium sorption capacity is unknown and when chemisorption tends to become immeasurably slow and the amount sorbed is still significantly smaller than the equilibrium amount [12]. On the other hand, equilibrium takes 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 Blue RAWL takes 21 days to achieve equilibrium [13]. Sorption of propisochlor on soil takes more than 250 days to reach equilibrium [14]. However, the pseudo-second order equation has the following advantages: it allowed an effective sorption capacity; the sorption capacity and rate constant of pseudo-second order and initial sorption rate all can be determined from the equation without knowing any parameter beforehand.

This investigation studies the kinetics of the sorption of cadmium(II) using tree fern under various initial cadmium(II) concentrations. A batch sorption pseudo-isotherms were also developed by applying sorption capacity which obtained from Ho's pseudo-second order kinetic rate law and was used to predict the monolayer sorption capacities and sorption constants. A comparison of linear regression and  $\chi^2$  analysis of three isotherms: Langmuir; Freundlich; and Redlich–Peterson have been applied to the experiment of cadmium sorption on tree fern.

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## 2. Materials and methods

The raw tree fern was dried in an oven at 105 °C for 24 h. The sorbent was screened to obtain a geometrical size of 53–61 μm. Stock cadmium solutions were prepared with distilled water and Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O. All working solutions were prepared by diluting the stock solution with distilled water.

A range of cadmium(II) concentrations from 65.8 to 280 mg/dm<sup>3</sup> were used as simulated wastewater. 6.8 g sample of tree fern (53–61 μm) was added to each 1.7 dm<sup>3</sup> of cadmium solution to a 2 dm<sup>3</sup> sorber vessel. They were agitated with a speed of 300 rpm and a constant water bath at 25 °C for 120 min. 2.5 ml of the mixed mixture were withdrawn at suitable time intervals and filtered through a 0.45 μm membrane filter. These were analysed by an inductively coupled plasma atomic emission spectroscopy analyser (ICP-AES) for the concentration of cadmium.

## 3. Kinetics model

The 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 conditions where the reverse reactions do not contribute to the overall rate. The reaction order and rate constant must be determined by experiment. In 1995, Ho presented a sorption pseudo-second order rate law expression showed how the rate depends on the sorption capacity on solid phase but not

the concentration of the sorbate [2,15]:

$$\frac{dq_t}{dt} = k(q_e - q_t)^2, \quad (1)$$

Integrated pseudo-second order rate law can be obtained from Eq. (1) for the boundary conditions  $t=0 \rightarrow t$  and  $q_t=0 \rightarrow q_t$ , gives:

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + kt. \quad (2)$$

Eq. (2) can be rearranged to obtain a linear form:

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e} t, \quad (3)$$

where  $q_e$  is the amount of sorbate sorbed at equilibrium, (mg/g);  $t$  is the reaction time, (min);  $q_t$  is the amount of sorbate sorbed at time  $t$ , (mg/g);  $k$  is the equilibrium rate constant of pseudo-second order sorption, (g/mg min).

Ho's pseudo-second order rate law 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. (3), plotting  $t/q_t$ , versus  $t$  will give a straight line with slope  $1/q_e$ , and intercept  $1/kq_e^2$ .

## 4. Results and discussions

Fig. 1 shows a plot of Eq. (3) for the sorption of cadmium using tree fern. The results demonstrate a highly significant

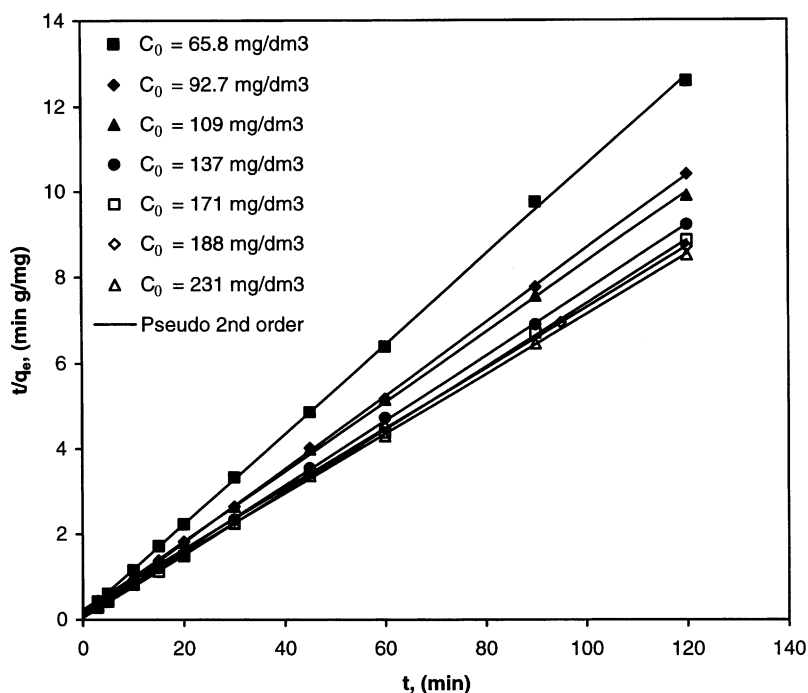


Fig. 1. Pseudo-second order sorption kinetics of cadmium on tree fern at various initial concentrations.

Table 1  
Kinetic parameters for sorption of cadmium on tree fern

$C_0$ (mg/dm <sup>3</sup> )	$C_{ep}$ (mg/dm <sup>3</sup> )	$q_e$ (mg/g)	$k$ (g/mg min)	$r^2$
65.8	27.6	9.53	0.0824	1.000
92.7	46.0	11.7	0.0851	1.000
109	59.8	12.2	0.0342	1.000
137	84.7	13.2	0.0594	1.000
171	117	13.6	0.122	1.000
188	131	14.2	0.0206	1.000
231	174	14.3	0.0305	1.000
280	219	15.2	0.0505	1.000

linear relationship between cadmium sorbed,  $t/q_t$ , and  $t$ . Kinetic parameters for sorption of cadmium on tree fern at various concentrations are shown in Table 1. The sorption capacity at equilibrium,  $q_e$ , increases from 9.53–15.2 mg/g while the concentration increased from 65.8 to 280 mg/dm<sup>3</sup> with a tree fern dose of 4 g/dm<sup>3</sup>. Table 1 lists 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. (3). The data illustrate good compliance with the pseudo-second order rate law based on sorption capacity because the coefficients of determination were all extremely high (=1.000).

The amount of sorbate sorbed at equilibrium can be obtained from pseudo-second order equation and the equilibrium liquid phase sorbate concentration can be calculated from the equation below:

$$C_{ep} = C_0 - \frac{q_e m_s}{V}, \quad (4)$$

$C_{ep}$  is the equilibrium liquid phase sorbate concentration, mg/dm<sup>3</sup>;  $C_0$  is the initial liquid phase sorbate concentration, mg/dm<sup>3</sup>;  $q_e$  is the equilibrium sorption capacity obtained from pseudo-second order rate law, mg/g;  $V$  is solution volume, dm<sup>3</sup>; and  $m_s$  is mass of mixed sorbent, g.

The isotherms and their respective linear forms were shown in Table 2 where the linear form of Langmuir-1 was more common. The coefficient of determination,  $r^2$ , has been used to determine the relationship between the experimental data and the isotherms in most studies. Table 3 showed that pseudo-Langmuir-1 and pseudo-Redlich–Peterson isotherm had the same  $r^2$  (0.999) but pseudo-Redlich–Peterson might be better fitting model because of its

Table 2  
Isotherms and their linear forms

	Isotherm	Linear form
Langmuir-1	$q_e = (q_m K_a C_e) / (1 + K_a C_e)$	$C_e/q_e = (1/q_m)C_e + 1/(K_a q_m)$
Langmuir-2		$1/q_e = (1/(K_a q_m))(1/C_e) + (1/q_m)$
Freundlich	$q_e = K_F C_e^{1/n}$	$\log(q_e) = \log(K_F) + 1/n \log(C_e)$
Redlich–Peterson	$q_e = AC_e / (1 + BC_e^g)$	$\ln(A(C_e/q_e) - 1) = g \ln(C_e) + \ln(B)$

Table 3  
Comparison of linear regression coefficient of determination,  $r^2$ ; and non-linear  $\chi^2$  test analysis

Isotherm	$r^2$	$\chi^2$
Pseudo-Langmuir-1	0.999	0.0242
Pseudo-Langmuir-2	0.993	0.0198
Pseudo-Redlich–Peterson	0.999	0.0198
Pseudo-Freundlich	0.944	0.0999

lower  $\chi^2$  value. The comparison of these two isotherms with experimental data is shown in Fig. 2. The coefficient of determination for pseudo-Langmuir-1 was 0.999 and was higher than pseudo-Langmuir-2 (0.993). It was clear that pseudo-Langmuir-2 might be a better fitting model because of its lower  $\chi^2$  value. Using the linear form of pseudo-Langmuir-1 for comparison, the pseudo-Redlich–Peterson isotherm was the most suitable isotherm for the data followed by pseudo-Langmuir-1 then pseudo-Freundlich isotherm. In contrast, if using the linear form of pseudo-Langmuir, pseudo-Redlich–Peterson and pseudo-Langmuir-2 isotherms were overlapped but was followed by pseudo-Langmuir-1 then pseudo-Freundlich isotherm (Fig. 2). The most suitable isotherm for the dataset was pseudo-Redlich–Peterson isotherm, but the difference between the two linear forms of pseudo-Langmuir isotherms were significant. Three linear equations had different axial settings and denoted that the axial difference would alter the result of linear regression and hence influence the determination process. On the other hand,  $\chi^2$  analysis avoided this error and also indicated not only that the pseudo-Redlich–Peterson isotherm was best fitting, but so as Langmuir-2 which corresponded to the result from Fig. 2. Different linear forms would conduct to different Langmuir isotherm variables. Hence,  $\chi^2$  analysis might be an alternative method of determination due to its unified axial setting.

The sorption behaviour of cadmium on tree fern was examined using the least squares linear regression analysis. The values of the pseudo-Langmuir isotherm constants were obtained from the slope and intercept of the straight line: the saturated monolayer sorption capacity,  $q_m$ , and sorption equilibrium constant,  $K_a$ , were 16.3 mg/g and 0.0499 dm<sup>3</sup>/mg from Langmuir-1 linear equation; as well as 16.1 mg/g and 0.531 dm<sup>3</sup>/mg from Langmuir-2 linear equation. The pseudo-Freundlich sorption isotherm constant  $K_F$  was 5.13 and  $1/n$  was 0.205; the pseudo-Redlich–Peterson isotherm constant  $A$  is 0.855,  $B$  was 0.0530 and  $g$  was 1.000. Under the basic condition of this sorption system, it was estimated to be more likely to be approaching the Langmuir form where it can be seen from the data where the values of  $g$  approached to 1.

The effect of isotherm shape can be used to predict whether a sorption system is 'favourable' or 'unfavourable'. According to Hall et al. [16], the essential features of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium pa-

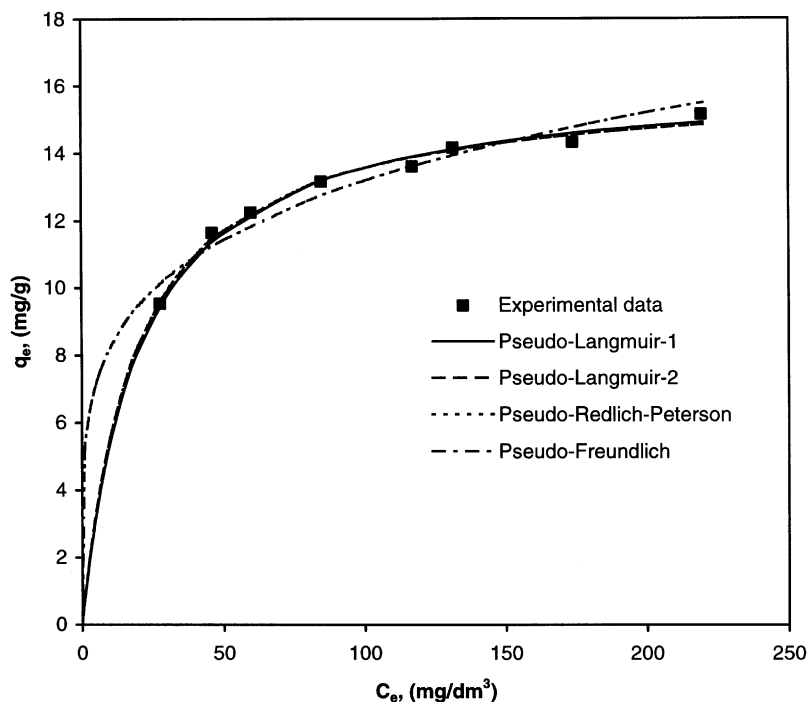


Fig. 2. Pseudo-isotherms of sorption cadmium on tree fern.

parameter  $K_R$ , which is defined by the following relationship:

$$K_R = \frac{1}{1 + K_a C_0}, \quad (5)$$

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 and nature of the sorption process as given below:

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 sorption of cadmium on tree fern increased from 0.0668 to 0.233 while the concentration increased from 65.8 to 280  $\text{mg}/\text{dm}^3$ . The sorption process was favourable for all systems. The  $K_R$  values indicated that sorption was more favourable for the lower initial metal ion concentrations than for the higher ones. Tree fern has previously been used effectively on the removal of divalent metal ions such as Zn(II), Cu(II) and Pb(II) from aqueous solutions [17]. According to this classification, removal ability tends to be in the order  $\text{Pb} > \text{Cu} > \text{Zn} > \text{Cd}$ .

## 5. Conclusion

This investigation was based on the assumption of a pseudo-second order mechanism in relation to the sorption

of cadmium on tree fern. From Linear regression, the results from the study showed high coefficients of determination for pseudo-Langmuir and pseudo-Redlich–Peterson. The results showed an excellent fit with the experimental data for both pseudo-Langmuir and pseudo-Redlich–Peterson. Based on the shape of Langmuir isotherm, tree fern is an effective sorbent. In addition,  $\chi^2$  analysis has also agreed to it where it may be considered being an alternative determination method than linear regression.

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