

# Pseudo-second-order model for lead ion sorption from aqueous solutions onto palm kernel fiber

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## Abstract

The sorption of lead ion onto palm kernel fiber was studied by performing batch kinetic sorption experiments. The batch sorption model, based on a pseudo-second-order mechanism, was applied to predict the rate constant of sorption, the equilibrium capacity and the initial sorption rate with the effects of the initial solution pH and fiber dose. Equilibrium concentrations were evaluated with the equilibrium capacity obtained from the pseudo-second-order rate equation. In addition, pseudo-isotherms were also obtained by changing fiber doses using the equilibrium concentration and equilibrium capacity obtained based on the pseudo-second-order constants.

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## 1. Introduction

Equilibrium analysis is fundamental for the evaluation of the affinity or capacity of a sorbent. However, thermodynamic data can only predict the final state of a system from an initial non-equilibrium mode. It is, therefore, important to determine how sorption rates depend on the concentrations of sorbate in a solution and how rates are affected by the sorption capacity or by the character of the sorbent in terms of kinetics. Many attempts have been made to formulate a general expression describing the kinetics of sorption on solid surfaces for liquid–solid phase sorption systems. In recent years, sorption mechanisms have been reported and involved kinetic-based models. The most often cited literature involves first-order [1] and second-order [2] reversible reactions, first-order [3] and second-order [4] irreversible reactions, pseudo-first-order [5] and pseudo-second-order [6] reactions based on solution concentration, the Elovich model [7] and Lagergren's first-order [8] and Ho's second-order [9] reactions based on the capacity of the sorbent.

Equilibrium studies are described by a sorption isotherm and characterized by certain constants whose values express the sur-

face properties and affinity of the sorbent. In many cases, the equilibrium sorption capacity is unknown, chemisorption tends to become immeasurably slow, and the amount sorbed is still significantly smaller than the equilibrium amount [10]. On the other hand, it takes a long time to achieve equilibrium in some sorption systems. For instance, sorption of propisochlor on soil takes more than 250 days to reach equilibrium [11]. However, the pseudo-second-order equation has the following advantages: it allows the evaluation of effective sorption capacity, initial sorption rate and the rate constant of the pseudo-second-order kinetic model without knowing any parameter beforehand.

In the present research, kinetic studies were carried out using an agitation batch sorber to study the effects of the initial solution pH and fiber dose. A kinetics analysis was carried out to correlate the experimental data based on a pseudo-second-order kinetics model. In addition, an isotherm was predicted by changing fiber doses using the equilibrium concentration and equilibrium capacity obtained based on the pseudo-second-order constants.

## 2. Materials and methods

### 2.1. Materials

Palm kernel fiber was obtained from the Nigerian Institute for Oil Palm Research (N.I.F.O.R.) of Benin City, Nigeria. Palm

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kernel fiber was allowed to age or decay with the residual oil, after processing for about 2 months. The treated fiber was dried in an oven at 80 °C for 6 h, ground and screened through a set of sieves to obtain particles of size 50–60 μm. The sieved fiber was soaked in 0.02 mol/dm<sup>3</sup> HCl overnight. The acid solution was filtered off, and the fiber was washed with distilled water until the pH of the wash became neutral. The fiber was dried at 80 °C for 24 h and stored in an air-tight container. The stock solution of lead(II) (1000 mg/dm<sup>3</sup>) was prepared in distilled water using lead nitrate salt (BDH); all working solutions were prepared by diluting the stock solution with distilled water.

## 2.2. Methods

A range of initial solution pH values (pH 3–6) was used, and flasks were agitated for 20 min. All contact investigations were performed in a 1-dm<sup>3</sup> flask. A 0.6 g sample of palm kernel fiber was added to 400 ml of a lead ion solution and agitated at 200 rpm for all experiments. For the effect of sorbent dose, a range of palm kernel fiber doses from 1.5 to 5 g/dm<sup>3</sup> was used, and agitation was carried out for 20 min. A reaction temperature of 36 ± 3 °C was used for each 400 ml volume of lead ion solution with an initial concentration of 120 mg/dm<sup>3</sup>, and an agitation speed of 200 rpm was employed.

The experiments were carried out at an initial lead concentration 120 mg/dm<sup>3</sup> for all studies. Samples (2.5 ml) were withdrawn at suitable time intervals and filtered, and the filtrate was analyzed for the remaining lead concentration with atomic absorption spectrophotometry (AAS).

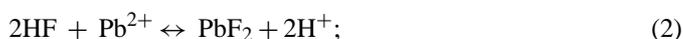
## 3. Results and discussion

The reaction order and rate constant must be determined by experiments. A pseudo-second-order rate law expression was applied, which demonstrated how the rate depended on the sorption capacity but not the concentration of the sorbate [9].

Palm kernel fiber, a cellulose-based sorbent, contains polar functional groups that can be involved in chemical bonding and are responsible for the cation exchange capacity of the palm kernel fibers. Thus, the palm kernel fibers and lead reaction may be represented in two ways [9,12,13]:



and



where F<sup>-</sup> and HF are polar sites on the palm kernel fiber surface.

The rate of sorption to the surface should be proportional to a driving force times an area. The rate of the pseudo-second-order reaction may be dependent on the amount of solute sorbed on the surface of the palm kernel fiber at any time and the amount sorbed at equilibrium. The rate expression for the sorption described is:

$$\frac{dF_t}{dt} = k[F_e - F_t]^2 \quad (3)$$

or

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

where  $F_t$  and  $(HF)_t$  are the number of active sites occupied on the palm kernel fiber at any time  $t$ , and  $F_e$  and  $(HF)_e$  are the number of equilibrium sites available on the palm kernel fiber. The driving force is related to  $q_e - q_t$ . Thus, 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 (g/(mg min)),  $q_e$  the amount of lead ions sorbed at equilibrium (mg/g), and  $q_t$  is the amount of lead ions sorbed on the surface of the palm kernel fiber at any time  $t$  (mg/g).

Separating the variables in the equation above gives:

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

and integrating this for the boundary conditions  $t=0-t$  and  $q_t=0-q_t$  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. This and Eq. (7) can be rearranged to obtain:

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

which has a linear form:

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

or

$$\frac{q_t}{t} = \frac{h}{1 + kq_e t}; \quad (10)$$

where  $h$  can be regarded as the initial sorption rate as  $q_t/t$ , when  $t$  approaches 0. Hence,

$$h = kq_e^2. \quad (11)$$

Thus, a plot of  $t/q_t$  against  $t$  of Eq. (11) should give a linear relationship with a slope of  $1/q_e$  and an intercept of  $1/kq_e^2$ .

In order to investigate the mechanism of the sorption of lead ions onto palm kernel fiber, a pseudo-second-order mechanism was studied. For the sorption of metal ions, which are small compared with dye molecules, and with a short contact time to equilibrium, the pseudo-second-order kinetic expression was considered likely to be more appropriate [14].

### 3.1. Effect of pH

Variations in the amount of lead(II) sorbed were noted in the series of contact time studies, when the pH of the lead(II) solution was set to pH 3–6, and results are presented in Fig. 1. In the contact time experiment, the agitation speed was 200 rpm,

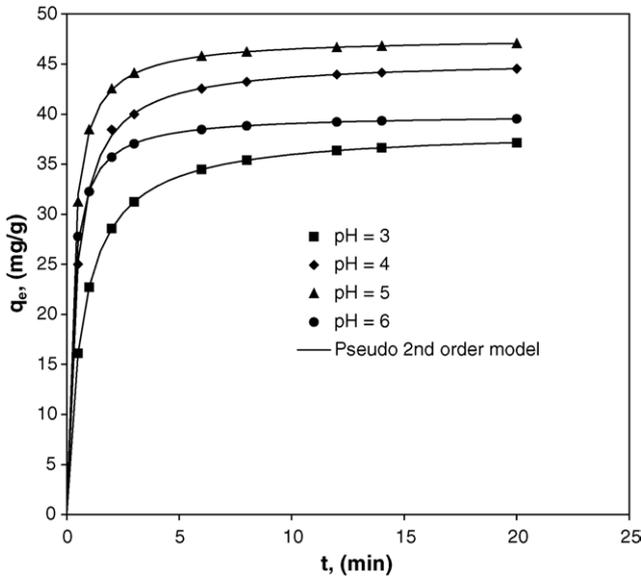


Fig. 1. Plot of the sorbed amount vs. time for lead ion at various palm kernel fiber doses. Initial concentration = 120 mg/dm<sup>3</sup>, dose = 0.6 g, agitation = 200 rpm, temperature = 36 ± 4 °C.

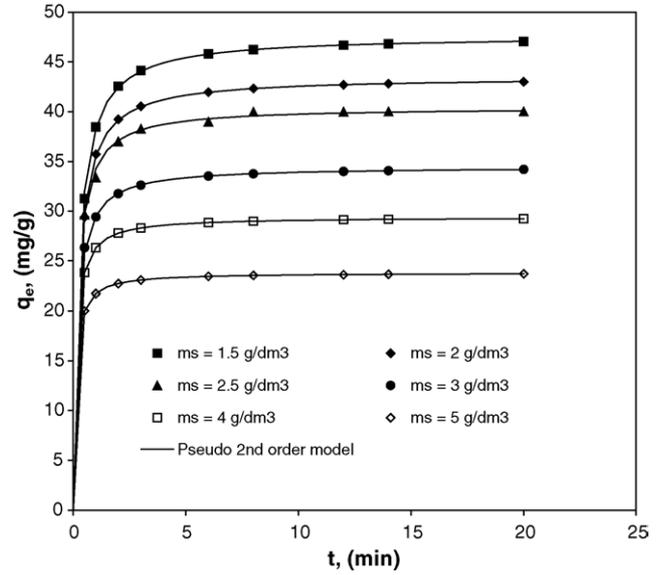


Fig. 2. Plot of the sorbed amount vs. time for lead ion at various palm kernel fiber doses. Initial concentration = 120 mg/dm<sup>3</sup>, dose = 0.6 g, agitation = 200 rpm, temperature = 36 ± 4 °C.

the fiber dose was 1.5 g/dm<sup>3</sup>, the initial lead concentration was 120 mg/dm<sup>3</sup>, and the lead(II) solution pH was set to pH 3–6. The results obtained were analyzed using the pseudo-second-order model and coefficient of determination,  $r^2$ , the rate constant,  $k$ , the initial sorption rate,  $h$ , and the sorption capacity,  $q_e$ , were obtained from the slope and intercept of Eq. (9). Individual values are presented in Table 1. The amount of metal ions removal from solution was shown to be strongly affected by the pH of the solution, because it affects the surface charge, degree of ionization and speciation of the metal. The adsorption of lead(II) onto sphagnum moss peat, for example, was found to vary with pH in the range 4–6, and the pH of maximum lead(II) uptake was found to be pH 5 [15]. Srivastava et al. also obtained similar results for lead(II) uptake in the pH range 4–6 [16]. In this current study, it is observed that the variation in pH values of the lead(II) solution from pH 3 to 5 produced an increase in sorption capacity of from 38.5 to 47.6 mg/g and a corresponding increase in the initial sorption rate. It is also observed that as the pH increased from 5 to 6, the sorption capacity decreased. At a low pH, H<sup>+</sup> ions increase in solution and H<sup>+</sup> ions coordinate with –OH groups to form –OH<sub>2</sub><sup>+</sup>. This gives the sorbent surface a positive character which leads to repulsion of the positively charged lead(II) from the sorbent surface. The coordination of H<sup>+</sup> ion with –OH groups also reduces the cation exchange capacity of the sorbent. At higher pH values, however, the –OH groups on the

sorbent surface ionize to produce negatively charged oxygen (–O<sup>–</sup>) which enhances the cation exchange capacity.

### 3.2. Effect of fiber dose

Variations in the rate of lead(II) sorption from a 120 mg/dm<sup>3</sup> solution of lead(II) ions in contact with various doses of palm kernel fiber were studied to ascertain the effect of fiber dose on lead(II) uptake from solution. A plot of the experimental sorption capacity curve for the sorption of lead(II) ions at various palm kernel doses is shown in Fig. 2. The sorption rate for a particular dose was initially rapid, and then, slowed as equilibrium was approached. According to Low and Lee, the initial sorption of lead can be attributed to ion exchange of the surface functional groups on the adsorbent and is followed by a gradual uptake of lead(II) on inner surfaces of the palm kernel fiber [17]. The rate constants of sorption at different palm kernel fiber doses were calculated from the intercept and slope of the straight-line plots of  $t/q_t$  versus  $t$  obtained by the application of Eq. (9). The coefficient of determination,  $r^2$ , the pseudo-second-order rate constant,  $k$ , the initial sorption rate,  $h$ , and the equilibrium sorption capacity,  $q_e$ , are shown in Table 2. The initial sorption rates

Table 1  
Pseudo-second-order rate parameters for sorption of lead on palm kernel fiber at various initial solution pH values

pH	$q_e$ (mg/g)	$k$ (g/(mg min))	$h$ (mg/(g min))	$r^2$
3	38.5	0.0376	55.6	1.000
4	45.4	0.0552	114	1.000
5	47.6	0.0859	195	1.000
6	40.0	0.106	170	1.000

Table 2  
Pseudo-second-order rate parameters for sorption of lead on palm kernel fiber at various palm kernel fiber doses

$m_s$ (mg/dm <sup>3</sup> )	$C_e$ (mg/dm <sup>3</sup> )	$R_e$ (%)	$q_e$ (mg/g)	$k$ (g/(mg min))	$h$ (mg/(g min))	$r^2$
5.00	0.942	99.2	23.8	0.440	250	1.000
4.00	2.35	98.0	29.4	0.290	251	1.000
3.00	16.6	86.2	34.5	0.173	205	1.000
2.50	18.9	84.3	40.5	0.137	224	1.000
2.00	33.0	72.5	43.5	0.103	195	1.000
1.50	48.5	59.6	47.6	0.0859	195	1.000

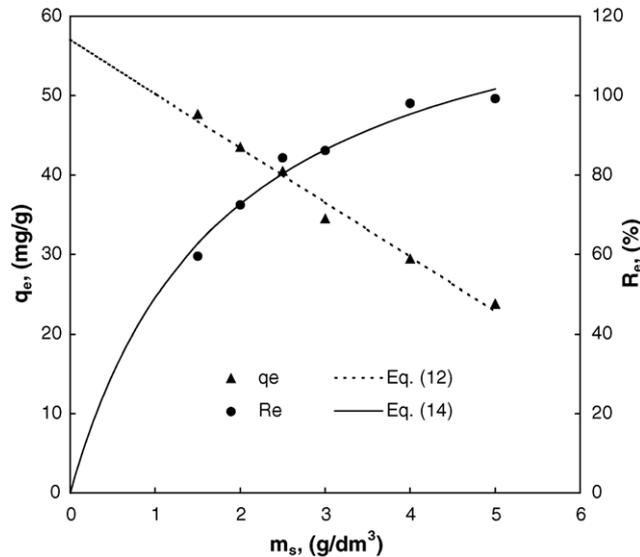


Fig. 3. Variation in the sorption capacity and percent lead removal against the palm kernel fiber dose. Initial pH 5.0, initial concentration = 120 mg/dm<sup>3</sup>, agitation = 200 rpm, temperature = 36 ± 4 °C.

of the palm kernel fiber increased from 195 to 250 mg/(g min), and the values of the rate constants were found to increase from 0.0859 to 0.440 g/(mg min) with an increase in the palm kernel fiber dose from 1.5 to 5 g/dm<sup>3</sup>. As the palm kernel fiber dose,  $m_s$ , was increased from 1.5 to 5.0 g/dm<sup>3</sup>, the equilibrium sorption capacity,  $q_e$ , decreased from 47.6 to 23.8 mg/dm<sup>3</sup> (Fig. 3). However, the percentage lead(II) removal, increased from 59.6 to 99.2% with an increase in palm kernel fiber dose of from 1.5 to 5.0 g/dm<sup>3</sup>. A similar trend for the sorption of nickel and copper on peat was also reported [18,19]. It is clear that the equilibrium sorption capacity of the lead(II) ion is a function of the palm kernel fiber dose.

Variations in the equilibrium sorption capacity,  $q_e$ , in relation to the palm kernel fiber dose,  $m_s$ , are shown in Fig. 3. Over the fiber dose range that was examined, the relationship between the equilibrium sorption capacity,  $q_e$ , and the fiber dose,  $m_s$ , was found by linear regulation and obtained a high coefficient of determination ( $r^2 = 0.985$ ). It can be expressed as:

$$q_e = Sm_s + Y; \quad (12)$$

where the constant,  $Y$ , at 57.1 mg/g is the maximum sorption capacity, when the fiber dose approaches 0, and  $S$  at -6.84 (dm<sup>3</sup> mg)/g<sup>2</sup> is related to the sorption potential of the fiber. The negative value of  $S$  shows that with the increase in fiber dose, the equilibrium sorption capacity,  $q_e$ , was decreased.

The amount of lead(II) ions sorbed at equilibrium can be obtained from the pseudo-second-order equation from Table 2, and the equilibrium liquid phase lead(II) concentration can be calculated from the equation below [20,21]:

$$C_e = C_0 - \frac{q_e W}{V}; \quad (13)$$

where  $C_e$  is the equilibrium liquid phase lead ion concentration (mg/dm<sup>3</sup>),  $C_0$  the initial liquid phase lead ion concentration

(mg/dm<sup>3</sup>),  $q_e$  the equilibrium sorption capacity (mg/g),  $V$  the solution volume (dm<sup>3</sup>), and  $W$  is the mass of mixed sorbent (g).

The equilibrium lead(II) removal,  $R_e$ , was obtained by calculation using following equation [18,19]:

$$R_e = \frac{C_0 - C_e}{C_0} \times 100. \quad (14)$$

The equilibrium lead(II) removal,  $R_e$ , against the fiber dose is shown in Fig. 3. Thus, within the fiber dose range of 1.5–5.0 g/dm<sup>3</sup>, the relationship between the equilibrium percentage removal,  $R_e$ , and the fiber dose,  $m_s$ , was found by linear regulation and obtained a high coefficient of determination ( $r^2 = 0.985$ ). It can be expressed as [18,19]:

$$R_e = \frac{m_s}{1.31 \times 10^{-2} + 7.22 \times 10^{-3} m_s}. \quad (15)$$

These two empirical relationships, therefore, provide a technique for predicting the Langmuir-type sorption for any fiber dose.

The sorption capacity of a sorbent can be obtained from data on its equilibrium sorption of a sorbate from solution. These data can be described by a sorption isotherm characterized by certain constants whose values express the surface properties and affinity of a sorbent. The sorption equilibrium is said to be established, when the concentration of a sorbate in bulk solution is in a dynamic balance with that of the interface. The relationship between the sorbate sorbed and the sorbate concentration remaining in solution at equilibrium is described by the sorption isotherm. Generally, sorption data are obtained by shaking a fixed dose of sorbent with a constant volume of solution at a given temperature while changing the concentration of the solution. In addition, the data may also be obtained by changing the dose of the sorbent, when all other conditions are fixed.

An error function is required to evaluate the fit of the equation to the experimental data obtained from the optimization process employed. In this study, the linear coefficient of determination and non-linear Chi-square determination were used. The linear coefficient of determination,  $r^2$ , found from evaluation of data by the linear model, was calculated with the aid of the equation:

$$r^2 = \frac{S_{xy}^2}{S_{xx} S_{yy}}; \quad (16)$$

where  $S_{xx}$  is the sum of squares of  $x$ .

$$S_{xx} = \sum_{i=1}^n x_i^2 - \frac{\sum_{i=1}^n x_i}{n}, \quad (17)$$

where  $S_{yy}$  is the sum of squares of  $y$ .

$$S_{yy} = \sum_{i=1}^n y_i^2 - \frac{\sum_{i=1}^n y_i}{n}, \quad (18)$$

where  $S_{xy}$  is the sum of squares of  $x$  and  $y$ , and

$$S_{xy} = \sum_{i=1}^n x_i y_i - \frac{(\sum_{i=1}^n x_i)(\sum_{i=1}^n y_i)}{n}. \quad (19)$$

Table 3  
Isotherms and their linear forms

Isotherm	Linear form	References
Langmuir-1	$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{K_a q_m}$	[22]
Langmuir-2	$\frac{1}{q_e} = \left(\frac{1}{K_a q_m}\right) \frac{1}{C_e} + \frac{1}{q_m}$	
Freundlich	$\log(q_e) = \log(K_F) + \frac{1}{n} \log(C_e)$	[23]
Redlich–Peterson	$\ln\left(A \frac{C_e}{q_e} - 1\right) = g \ln(C_e) + \ln(B)$	[24]

The Chi-square test statistic is basically the sum of the squares of the differences between the experimental data and data obtained by calculating from models, with each squared difference divided by the corresponding data obtained by calculating from the models. The equivalent mathematical statement is:

$$\chi^2 = \sum \frac{(q_e - q_{e,m})^2}{q_{e,m}}; \tag{20}$$

where  $q_{e,m}$  is equilibrium capacity obtained by calculating from the model (mg/g) and  $q_e$  is experimental data of the equilibrium capacity (mg/g). If data from the model are similar to the experimental data,  $\chi^2$  will be a small number, while if they differ,  $\chi^2$  will be a bigger number. Therefore, it is necessary to also analyze the data set using the non-linear Chi-square test to confirm the best-fit isotherm for the sorption system.

A series of isotherm is shown in Fig. 4. The graphs are plotted in the form of lead(II) sorbed per unit mass of palm kernel fiber,  $q_e$ , obtained from the pseudo-second-order model, against the concentration of lead(II) remaining in solution,  $C_e$ , obtained from  $q_e$ , using Eq. (15). Fig. 4 also shows the opposing line, which was also generated with a slope of the solution vol-

ume/fiber mass. Therefore, an operating line can be expressed as follows:

$$q_e = -\frac{V}{W} C_e + C_0; \tag{21}$$

where  $V$  is the volume ( $\text{dm}^3$ ),  $W$  the fiber dose (g), and  $C_0$  is the initial lead(II) concentration ( $\text{mg}/\text{dm}^3$ ).

The various isotherms and their respective linear forms are shown in Table 3, with the linear Langmuir-1 being the most commonly used. The sorption behavior of lead on palm kernel fiber was described by a series of pseudo-isotherms using  $C_e$  and  $q_e$  values calculated from the pseudo-second-order model [20,21]. The coefficient of determination,  $r^2$ , was applied to determine the relationship between the experimental data and the isotherm in most studies. The results displayed in Table 4 show the calculated values for both coefficient of determination,  $r^2$ , and non-linear Chi-square values for two Langmuir isotherms, the Redlich–Peterson and Freundlich isotherms. The Redlich–Peterson isotherm appears to be the better-fitting model because it has the highest  $r^2$  (0.998) and lower  $\chi^2$  (0.607) values. The two Langmuir isotherms had higher values of  $\chi^2$  than both the Redlich–Peterson and Freundlich isotherms. A comparison between the two linear Langmuir isotherms formed with experimental data is shown in Fig. 4. The coefficient of determination for the pseudo-Langmuir-1 was 0.985 and was much higher than that of the pseudo-Langmuir-2 (0.885). However, it is clear that the pseudo-Langmuir-2 is a better-fitting model, because it had a much lower  $\chi^2$  value. The  $\chi^2$  values for the Redlich–Peterson and Freundlich isotherms, on the other hand, were identical, and they seem to be the best-fitting model for the experimental results shown in Fig. 4. But the linear regression indicates a different outcome. Consequently, the Redlich–Peterson and Freundlich isotherms were the most-suitable models for this sorption system. The pseudo-Freundlich sorption isotherm constant,  $K_F$  is  $24.4 (\text{mg}/\text{g}) (\text{dm}^3/\text{mg})^{0.162}$  and  $1/n$  is 0.162, while the pseudo-Redlich–Peterson isotherm constant  $A$  is  $4.28 \times 10^3 \text{ dm}^3/\text{g}$ ,  $B$  is

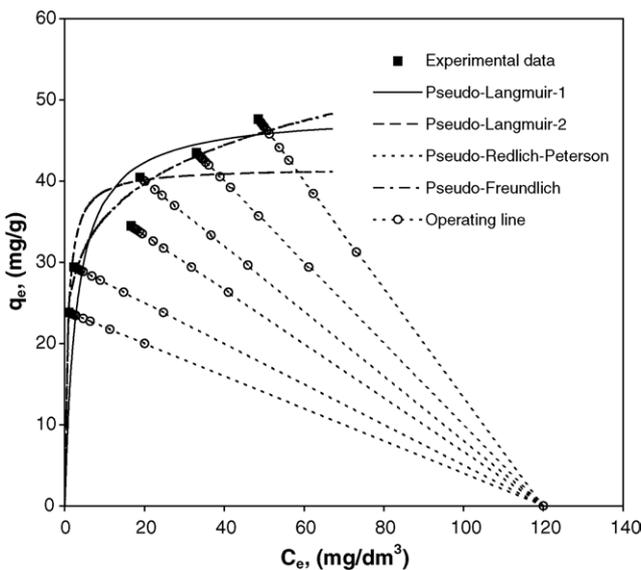


Fig. 4. Pseudo-isotherms of the sorption of lead on palm kernel fiber with operating lines. Initial pH 5.0, initial concentration =  $120 \text{ mg}/\text{dm}^3$ , agitation = 200 rpm, temperature =  $36 \pm 4 \text{ }^\circ\text{C}$ .

Table 4  
Comparison of linear regression coefficients of determination,  $r^2$ , and non-linear  $\chi^2$  test analysis

Isotherm	$r^2$	$\chi^2$
Pseudo-Langmuir-1	0.985	16.4
Pseudo-Langmuir-2	0.885	2.16
Pseudo-Redlich–Peterson	0.998	0.607
Pseudo-Freundlich	0.949	0.605

$1.75 \times 10^2 (\text{dm}^3/\text{mg})^{0.839}$ , and  $g$  is 0.839. Under the basic conditions of these sorption systems, the sorption was estimated to more likely approach the Freundlich form as can be seen from the data, where values of  $g$  did not approach 1. Unlike the linear analysis, different forms of the equation will significantly affect  $r^2$  and impact the final determination, while the non-linear Chi-square analysis is a method of avoiding such errors.

#### 4. Conclusions

This investigation was based on the assumption of a pseudo-second-order mechanism in relation to the sorption of lead on palm kernel fiber. The results showed high coefficients of determination. The pseudo-second-order rate constant, the initial sorption rate, and the equilibrium sorption capacity were a function of palm kernel fiber dose. An isotherm was obtained by changing fiber doses using the equilibrium concentration and the equilibrium capacity obtained based on the pseudo-second-order constants. It is not appropriate to use the coefficient of determination of the linear regression analysis to compare the best fit of the Freundlich and both linear Langmuir isotherms. Non-linear Chi-square analysis may be a better method. Freundlich is a special case of the Redlich–Peterson isotherm, when constants  $A$  and  $B$  are high. It was clear that both the two-parameter pseudo-Freundlich and the three-parameter pseudo-Redlich–Peterson isotherms were the best-fitting models for the experiment results.

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