

# Removal of Lead from Aqueous Solution by Palm Kernel Fibre

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## ABSTRACT

The sorption of lead on palm kernel fibre, an agricultural waste product, has been studied. The sorption process was studied as a function of initial lead concentration and initial solution pH. The percentage lead removal was found to increase with increasing initial solution pH up to pH 5 and then to decrease as pH was increased to 6. The pseudo-second order kinetic rate model was employed in the analysis of the kinetics of lead uptake onto the palm kernel fibre. The results show that the pseudo-second order model fits the experimental data with high coefficients of determination ( $r^2$ ). The equilibrium sorption capacity was found to be  $33.33 \text{ mg g}^{-1}$  when 1.0 g of fibre was contacted with  $90 \text{ mg dm}^{-3}$  of lead solution at pH 5. Mathematical expressions were derived to relate the pseudo-second order rate constant,  $k$ , and the change in solution pH with initial lead concentration.

## KEYWORDS

Palm kernel fibre, kinetics, lead(II), sorption, change in solution pH.

## 1. Introduction

Water treatment by sorption of pollutants from aqueous solution has proven to be a cheap and efficient method of water purification, since it does not need huge sludge-handling processes. Recently, there has been considerable interest in the use of agricultural products and by-products as adsorbents for water and wastewater treatment. Some common agricultural products and by-products that have been used recently include groundnut husks,<sup>1</sup> sphagnum moss peat,<sup>2</sup> sago,<sup>3</sup> peanut hulls<sup>4</sup> and grains.<sup>5</sup>

Lead exposure affecting blood lead concentrations in the general population include drinking water distributed through lead pipes,<sup>6–8</sup> house paint containing lead<sup>9</sup> and lead-glazed household ceramics.<sup>10,11</sup> Therefore the application of agricultural products and wastes for lead sorption from aqueous solution present a cheap and cost-effective alternative for lead removal from drinking water.

Research reports by Onwuka *et al.*<sup>12</sup> from Nigeria showed that a variety of household wastes and crop residues exist and a common residue of interest is the palm kernel and its fibre. These crop residues are used to varying extents but, in some cases, they are burnt or left unutilized on the fields. According to their findings,<sup>12</sup> over 66% of the palm kernel and the fibre are burnt, a little over 5% is used as feed for animals and over 29% is left on the fields.

Palm kernel fibre is a cellulosic material that has lipids, carboxylic acids and palm oil residue coated on its surface after extraction of the palm oil. Sorption can occur on these groups on the fibre surface because of the polarity of the functional groups. Palm kernel fibre may be an adsorbent for lead ion removal from solution.

It is known that pH and initial concentration of sorbate in solution affect the sorption process. In this study, the effect of initial concentration of lead(II) and pH of solution on the adsorption of lead(II) from aqueous solution by palm kernel fibre was

examined. The pseudo-second order model was applied to describe the adsorption process and to determine the variation in kinetic parameters produced by the change in initial concentration and solution pH.

## 2. Materials and Methods

### 2.1. Materials

Palm kernel fibre used in this study was obtained from the Nigerian Institute for Oil Palm Research (NIFOR), Benin City, Nigeria. The palm kernel fibre was allowed to age or decay with the residual oil, after processing for about two months. The raw fibre was dried in an oven at  $80^\circ\text{C}$  for 6 h, ground and screened through a set of sieves to obtain particles of size  $50\text{--}60 \mu\text{m}$ . The sieved fibre was soaked in  $0.02 \text{ mol dm}^{-3}$  HCl overnight. The acid solution was filtered off and the fibre washed with distilled water until the wash became neutral. The fibre was dried at  $80^\circ\text{C}$  for 24 h and stored in an air-tight container. The stock solution of lead(II) ( $1000 \text{ mg dm}^{-3}$ ) was prepared in distilled water using lead nitrate salt (BDH Ltd, England). All working solutions were prepared by diluting the stock solution with distilled water.

### 2.2. Methods

#### 2.2.1. Effect of pH on Adsorption

A  $400 \text{ cm}^3$  volume of  $90 \text{ mg dm}^{-3}$  lead(II) solution was added to four  $1 \text{ dm}^3$  flasks and the pH of the solutions adjusted to 3, 4, 5 and 6 using  $0.1 \text{ M}$  HCl or NaOH, measured with a pH meter (WTW pH Meter 320, Germany). A  $1.0 \text{ g}$  sample of palm kernel fibre was added to each  $400 \text{ cm}^3$  volume of lead(II) solution and agitated at 200 rpm at a temperature of  $36^\circ\text{C}$ . After 30 min the solution was filtered and the filtrate analysed by atomic absorption spectrometry (AAS). The experiment was repeated using  $50$  and  $30 \text{ mg dm}^{-3}$  lead(II) solutions.

#### 2.2.2. Effect of Initial Concentration

A range of lead(II) concentrations ( $30\text{--}90 \text{ mg dm}^{-3}$ ) (adjusted to

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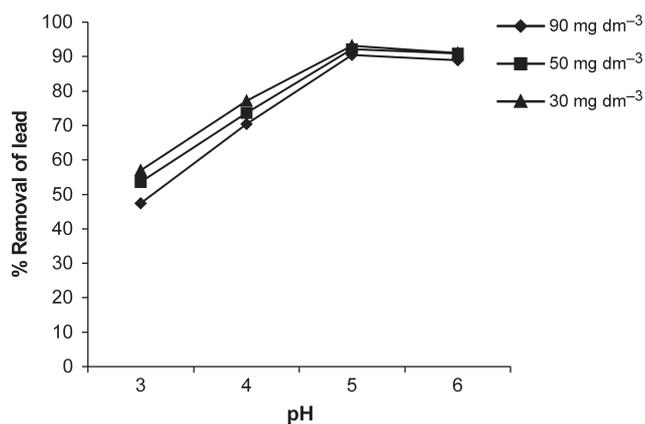


Figure 1 Effect of pH on lead(II) uptake on palm kernel fibre.

pH 5) was used and the flasks agitated for 14 min (preliminary experiments showed that 14 min was sufficient to attain equilibrium). A 1.0 g sample of palm kernel fibre was added to each 400 cm<sup>3</sup> volume of lead(II) solution and agitated at 200 rpm. The temperature was set at 36°C for all experiments. Samples (2.5 cm<sup>3</sup>) were withdrawn at suitable time intervals and the filtrate analysed by AAS.

### 2.2.3. Effect of Initial pH on Kinetics of Lead Adsorption from 90 mg dm<sup>-3</sup> Lead Solution

A 400 cm<sup>3</sup> volume of 90 mg dm<sup>-3</sup> lead(II) solution was added to four 1 dm<sup>3</sup> flasks and the pH of the solution adjusted to 5 using 0.1 M HCl or NaOH, measured with a pH meter. A 1.0 g sample of palm kernel fibre was added to 400 cm<sup>3</sup> of the lead(II) solution and agitated at 200 rpm at a temperature of 36°C. Samples (2.5 cm<sup>3</sup>) were withdrawn at suitable time intervals and the filtrate analysed by AAS.

## 3. Results and Discussion

### 3.1. Effect of pH on Adsorption

Figure 1 shows the effect of solution pH on the removal of lead(II) from aqueous solution by palm kernel fibre. Determining the optimum pH for lead(II) removal is important since the pH of the solution affects the surface charge of the adsorbent, the degree of ionization and metal speciation. From Fig. 1, it will be observed that increasing the solution pH increases the percentage lead uptake on palm kernel fibre. Increase in the pH of the solution from 3 to 4 increased the percentage removal of lead(II) by 33% for the 90 mg dm<sup>-3</sup> solution, 27% for the 50 mg dm<sup>-3</sup> solution and 26% for the 30 mg dm<sup>-3</sup> solution. Optimum lead(II) removal was achieved at pH 5 for all three concentrations of lead(II) used. Increasing percentage removal of metal ion with increasing initial pH of solution has been reported by various researchers<sup>3,13,14</sup> using biosorbents. The increase in percentage removal with pH is attributed to the fact that decreasing solution pH increases H<sup>+</sup> concentration in solution which will coordinate with -OH groups to form -OH<sub>2</sub><sup>+</sup> and will reduce the number of negative sites on the adsorbent and cause repulsion of lead(II) ions. On the other hand, increasing pH reduces the amount of H<sup>+</sup> in solution and promotes ionization of -OH groups, thus increasing cation exchange capacity.

### 3.2. Effect of Initial Concentration

The effect of contact time on adsorption of lead(II) for varying initial concentrations at 36°C and at pH 5 is shown in Fig. 2. The amount of lead(II) adsorbed per unit mass of the palm kernel fibre for a 90 mg dm<sup>-3</sup> solution increased from 24.80 mg g<sup>-1</sup> to

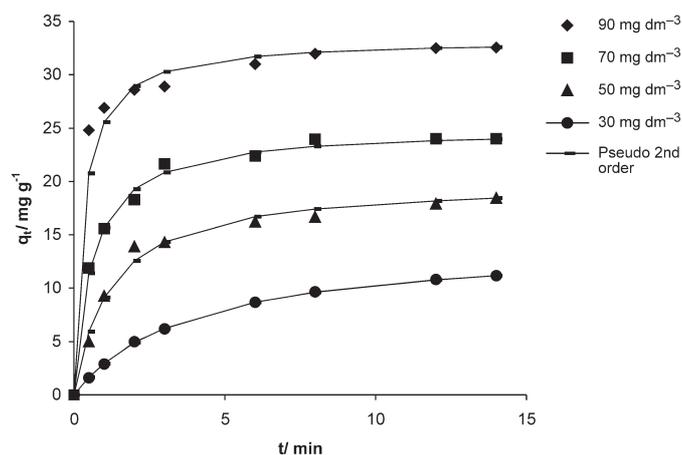


Figure 2 Effect of initial concentration on lead(II) uptake by palm kernel fibre.

Table 1 Pseudo-second order parameters for the effect of initial concentration on sorption of lead(II).

$C_0$ /mg dm <sup>-3</sup>	$q_e$ /mg g <sup>-1</sup>	$h$ /mg g <sup>-1</sup> min <sup>-1</sup>	$k$ /g mg <sup>-1</sup> min <sup>-1</sup>	$r^2$
90	33.33	111.11	0.100	0.9996
70	25	41.67	0.067	0.9995
50	20	16.67	0.042	0.9996
30	14.29	3.69	0.018	0.9999

$C_0$  is the initial concentration of lead(II) in solution.

32.56 mg g<sup>-1</sup> for a time period of 0.5 min to 14 min. For all initial concentrations used there was an initial rapid uptake of lead(II) from solution, which gave way to a slower sorption of lead(II) towards the end of the sorption process.

Figure 3 shows a linear variation of  $t/q_t$  with time,  $t$  (where  $q_t$  is the amount of lead(II) adsorbed at time  $t$ ), for a large fraction of the initial sorption period. Ho<sup>15-17</sup> proposed that if the experimental data for  $t/q_t$  versus  $t$  follow a straight line, then the sorption mechanism obeys pseudo-second order kinetics. Therefore, the linearity shown in Fig. 3 suggests that chemical sorption may play a role in the rate-limiting step of the sorption process and that the mechanism follows a pseudo-second order reaction scheme.<sup>15</sup> The results may also be analysed using the pseudo-second order model. Table 1 shows the rate constant,  $k$ , the equilibrium sorption,  $q_e$ , and the initial sorption rate,  $h$ , of the sorption at various initial concentrations of lead(II). These

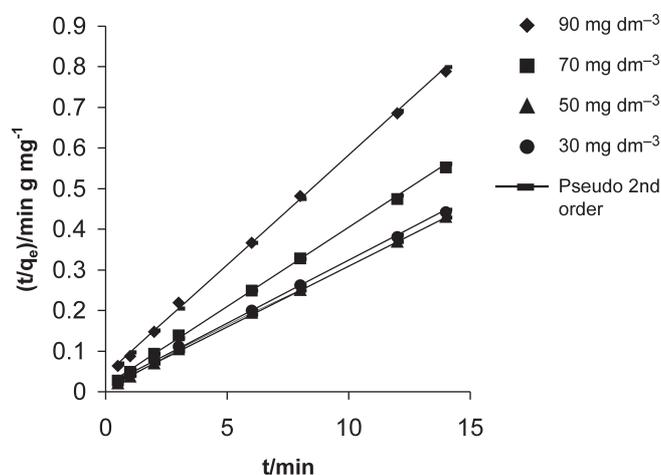


Figure 3 Pseudo-second order plot of adsorption of lead(II) on palm kernel fibre.

parameters were calculated from the intercept and slope of the straight line plot of  $t/q_t$  versus  $t$  according to equation (1) as proposed by Ho<sup>16</sup>

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

or

$$\frac{q_t}{t} = \frac{h}{1 + kq_e t} \quad (2)$$

where  $h$  can be regarded as the initial sorption rate as  $q/t$  when  $t \rightarrow 0$ , hence

$$h = kq_e^2 \quad (3)$$

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

The pseudo-second order rate constant,  $k$ , increased with increasing initial concentration of lead(II) (30–90 mg dm<sup>-3</sup>) in solution from 3.69 mg g<sup>-1</sup> min<sup>-1</sup> to 111.11 mg g<sup>-1</sup> min<sup>-1</sup> while the equilibrium sorption capacity increased from 14.29 mg g<sup>-1</sup> to 33.33 mg g<sup>-1</sup> as the initial concentration of lead(II) increased from 30 mg dm<sup>-3</sup> to 90 mg dm<sup>-3</sup>. Similar trends have also been observed by Ho and McKay<sup>17</sup> in the adsorption of dye on pith. The value of the rate constant also increased with increasing initial concentration of lead(II) in solution.

The solid curves in Fig. 3 are the theoretical plots indicating high values of  $r^2$  (>0.980). This finding suggests that the pseudo-second order model can describe the sorption of lead(II) on palm kernel fibre.

The pseudo-second order rate constant,  $k$ , obtained from the plot of  $t/q_t$  against  $t$ , increased with increasing initial concentration of lead(II),  $C_0$ , ranging from 30 to 90 mg dm<sup>-3</sup>. It was found that  $k$  is logarithmically related to  $C_0$ , therefore a plot of  $\ln k$  versus  $\ln C_0$  gave a straight line plot with a correlation coefficient ( $r^2$ ) of 0.999 (see Table 2), the relationship between  $k$  and  $C_0$  being of the type:

$$k = aC_0^b \quad (4)$$

The values of  $\ln a$  and  $b$  which are the intercept and slope of the plot of  $\ln k$  versus  $\ln C_0$  were found to be  $9.06 \times 10^{-5}$  and 1.56, respectively, so the equation can be written as

$$k = 9.06 \times 10^{-5} C_0^{1.56} \quad (5)$$

McKay *et al.*<sup>18</sup> reported that, in the case of adsorption of AB25 using chitin,  $b$  centred around 0.5, confirming that intraparticle diffusion was a prominent factor in the adsorption process. The result from this study showed that the value for  $b$  (1.56) is higher than 0.5 based on intraparticle diffusion, therefore intraparticle diffusion is not rate-controlling in the sorption process under investigation.

The solution pH change accompanying the adsorption of lead(II) from solution by palm kernel fibre when the initial lead(II) concentration was varied at constant dose and temperature is shown in Table 2. The values indicate that there is always a lowering of solution pH at equilibrium. This means that adsorption is accompanied by an increase in H<sup>+</sup> concentration of the solution. Two major reasons have been proposed to explain the increase in H<sup>+</sup> concentration during the sorption process. The first reason is that biosorbents contain acidic groups such as carboxylic, phenolic and enolic groups which are believed to be responsible for their cation exchange capacities, whose values lie between 2 and 5 milliequivalent g<sup>-1</sup>.<sup>19</sup> The second reason is based on the intrinsic ionization constant of carboxylic groups which appears to be about  $10^{-5}$  according to Dawson *et al.*<sup>20</sup> Carboxylic acid groups alone are thought to be ionized to an appreciable

**Table 2** Logarithmic plot relating rate constant and initial lead(II) concentration.

$\ln (C_0/\text{mg dm}^{-3})$	$\ln (k/\text{g mg}^{-1} \text{ min}^{-1})$	$\ln \Delta\text{pH}$
1.95	-1.00	-1.40
1.85	-1.17	-1.19
1.70	-1.38	-0.77
1.48	-1.74	-0.26

$C_0$  is the initial concentration of lead(II) in solution.

extent at a pH of 7.0 and below.

The values in Table 2 show that when the initial lead(II) concentration was varied between 30 mg dm<sup>-3</sup> and 90 mg dm<sup>-3</sup>, the change in H<sup>+</sup> concentration of the solution, expressed as  $\Delta\text{pH}$ , increased as the initial lead(II) concentration increased. Therefore as more lead(II) is removed from solution onto the palm kernel fibre, more hydrogen ions are released from the palm kernel fibre into the solution. Consequently, the pH of the reacting mixture is reduced.

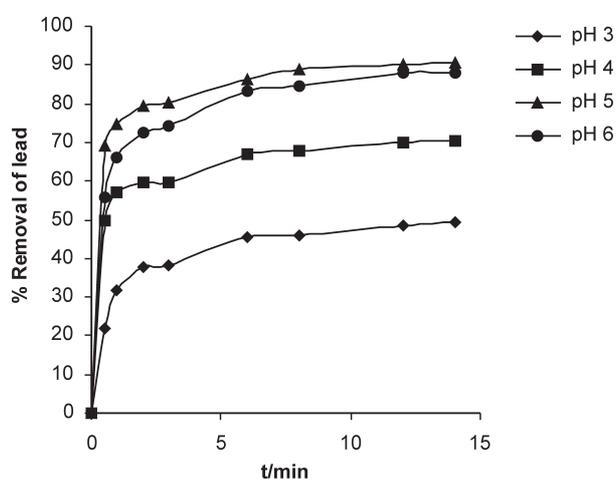
The resulting equilibrium pH can be said to be governed by the lead(II) present in solution initially when the temperature, initial pH and palm kernel fibre dose are fixed. This phenomenon can be represented as a functional relationship of these two parameters as follows:

$$\Delta\text{pH} = 3.39 C_0^{-2.46} \quad (6)$$

Therefore, ion exchange reactions and ionization of acid groups on the biosorbents are the likely reasons for the variation in pH of the reaction mixture.

### 3.3. Effect of Initial Solution pH on Sorption Kinetics from 90 mg dm<sup>-3</sup> Lead Solution

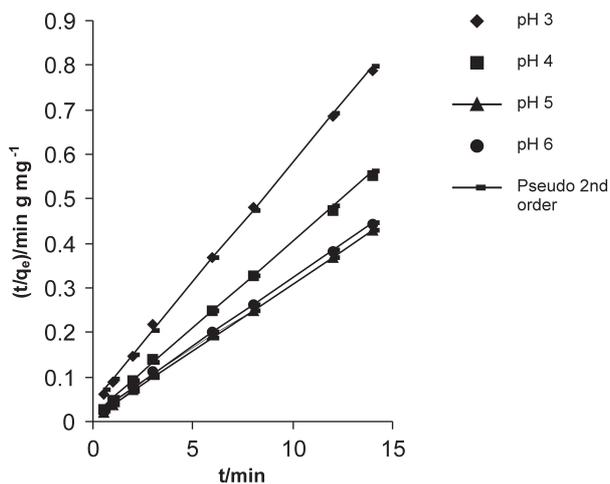
Figure 4 shows the plot of percentage lead(II) removal versus time. The percentage removal of lead(II) increased with increasing pH up to pH 5 and reduced at pH 6. It will also be observed that a large percentage of lead(II) was adsorbed in the first few minutes of contact and then the rate of removal gradually decreased to reach equilibrium. The initial rapid percentage removal of lead(II) is due to ion exchange with surface cations on the palm kernel fibre. The later slow sorption of lead(II) represents a gradual uptake of cation exchange at the inner surface.<sup>21</sup> The results have also been analysed by using the pseudo-second order model. As shown in Table 3, the correlation coefficient,  $r^2$ , rate constant,  $k$ , initial rate,  $h$ , and equilibrium sorption capacity,  $q_e$ , are obtained from the slope and intercept of Eq. (1) and  $h$  from



**Figure 4** Percentage removal of lead(II) versus time at different pH.

**Table 3** Pseudo-second order parameters for the effect of pH on sorption of lead(II).

pH	$q_e/\text{mg g}^{-1}$	$k/\text{g mg}^{-1} \text{min}^{-1}$	$h/\text{mg g}^{-1} \text{min}^{-1}$	$r^2$
3	18.52	0.068	23.26	0.9991
4	25.64	0.101	66.67	0.9994
5	33.33	0.100	111.11	0.9996
6	32.26	0.068	71.43	0.9995

**Figure 5** Pseudo-second order plot of adsorption of lead(II) on palm kernel fibre at different pH.

Eq. (3). The values of the rate constant, the initial sorption rate and the equilibrium sorption capacity all increased with increasing pH from 3 to 5, these values then decreased at pH 6. The solid curves in Fig. 5 are the theoretical plots indicating high values of  $r^2$  ( $>0.999$ ). The pseudo-second order model can describe the sorption of lead(II) on palm kernel fibre at different pH. Therefore, the possibility of chemical sorption involving valency forces through sharing or exchange of electrons between sorbent and sorbate correlates the data if the rate-limiting step is assumed. The results show that  $\text{H}^+$  ions in solution affect the kinetics of lead adsorption on palm kernel fibre and that the rate-limiting step of this adsorption may be chemical reaction rather than intraparticle diffusion.

#### 4. Conclusion

The effects of initial pH of solution and initial lead concentra-

tion were studied as they affect the uptake of lead from aqueous solution onto palm kernel fibre. The optimum pH at which the highest percentage removal of lead occurred was found to be pH 5 when 1.0 g of fibre was contacted with  $30 \text{ mg dm}^{-3}$  of lead solution. The kinetics of lead sorption from aqueous solution were found to be dependent on the initial lead concentration and the initial solution pH. The pseudo-second order kinetic model was used to describe the kinetic uptake of lead(II) onto palm kernel fibre.

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