Effects of calcium competition on lead sorption by palm kernel fibre

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Abstract

The kinetics of sorption of a mono-solute of lead ions and of a bi-solute of lead and calcium ions onto palm kernel fibre was investigated in a batch system. The experimental data were analysed based on an intraparticle diffusion equation and a pseudo-second-order mechanism, in both the mono- and bi-solute sorption systems, in order to predict the rate constant of sorption, the equilibrium capacity, and the initial sorption rate. The results indicate that the sorption mechanism is described by a pseudo-second-order equation. Intraparticle diffusion was significant in the lower-concentration systems. In addition, a modified intraparticle diffusion equation was applied to the sorption systems.

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1. Introduction

In recent years, there has been considerable interest in the use of low-cost sorbents, since activated carbon is quite expensive. The removal of lead ions from aqueous solutions has been studied using different biosorbents such as Microspora and Lemna minor [1], yeast [2], peat [3], tree fern [4], exopolysaccharide [5], waste biogas residual [6], peanut hulls [7], Rhizopus arrhizus [8], decaying leaves [9], and the fungus Penicillium purpuratum [10]. Chemical sorption can occur onto the polar functional groups of lignin, with alcohols, aldehydes, ketones, acids phenolic hydroxides, and ethers acting as chemical bonding agents [11]. Cellulose-based sorbents can be a suitable sorbate for the sorption of metal cations because of their polar and acidic characteristics. Many of the studies on lead biosorption have focused on simple metal sorption systems. Competitive sorption systems have also been reported, for example, lead and nickel by Microspora (a macro-alga) and Lemna minor (duckweed, an aquatic plant) [1], as well as lead/cadmium and lead/zinc by exopolysaccharide [5].

Lead sorption kinetics have been extensively studied, and it has been commonly observed that the sorption rate is very rapid at the beginning of the process, then the rate slows as equilibrium is approached. Several groups of researchers have described the reaction order of sorption in metal-biosorbent systems using various kinetic models. Traditionally, kinetics have been described by the Lagergren first-order equation [7,12]. However, it was reported that a pseudo-second-order model provides a more-appropriate description of the mono- and bi-solute binding of copper and nickel to peat [13] and Chlorella vulgaris [14] than does a first-order equation.

The sorption of lead ions onto palm kernel fibre was studied in this paper, and the effects of the initial lead ion concentration and the addition of calcium ions were investigated. A modified intraparticle diffusion and pseudo-second-order model was developed and was used to analyze the data for the sorption of lead ions onto palm kernel fibre.
2. Materials and methods

2.1. Materials

Palm kernel fibre was obtained from the Nigerian Institute for Oil Palm Research (NIFOR) of Benin City, Nigeria. After processing, palm kernel fibres were allowed to age 2 months. The raw fibres were dried in an oven at 80 °C for 6 h, ground and screened through a set of sieves to obtain particles sized 50–60 μm. The sieved fibres were soaked in 0.02 mol dm$^{-3}$ HCl overnight. The acid solution was filtered off, and the fibres were washed with distilled water until the pH of the wash became neutral. The fibres were dried at 80 °C for 24 h and then stored in an air-tight container. Stock solutions of lead(II) and calcium(II) (1000 mg dm$^{-3}$) were prepared in distilled water using lead nitrate and calcium chloride salts (BDH, Ltd.); all working solutions were prepared in distilled water using lead nitrate and calcium(II) solutions and agitated at 200 rpm, with the temperature set at 36 °C for all experiments. Samples (2.5 ml) were withdrawn at suitable time intervals and the filtrate was determined with a pH meter. The experiments were repeated using 90, 70, 50, and 30 mg dm$^{-3}$ of lead(II).

2.2. Methods

2.2.1. Effect of the initial concentration

A range of lead(II) concentrations (30–120 mg dm$^{-3}$) were used, and flasks were agitated for 14 min. A 1.0 g sample of palm kernel fibre was added to each 400 ml volume of the lead(II) solution and agitated at 200 rpm, with the temperature set at 36 °C for all experiments. Samples (2.5 ml) were withdrawn at suitable time intervals and the filtrate was analyzed by atomic absorption spectrophotometry (AAS).

2.2.2. Effect of the addition of calcium ions

Appropriate amounts of lead(II) and calcium(II) were added to produce solutions containing 120 mg dm$^{-3}$ lead(II) and 40 mg dm$^{-3}$ calcium(II), 120 mg dm$^{-3}$ lead(II) and 80 mg dm$^{-3}$ calcium(II), 120 mg dm$^{-3}$ lead(II) and 120 mg dm$^{-3}$ calcium(II). A 1.0 g sample of palm kernel fibre was added to each 400 ml volume of the various lead(II) and calcium(II) solutions and agitated at 200 rpm, with the temperature set at 36 °C for all experiments. Samples (2.5 ml) were withdrawn at suitable time intervals, and the filtrate was analyzed by atomic absorption spectrophotometry (AAS). The pH values of the initial and equilibrium solution, were determined with a pH meter. The experiments were repeated using 90, 70, 50, and 30 mg dm$^{-3}$ of lead(II).

3. Results and discussion

In order to investigate the mechanism of sorption, the sorption reaction order and intraparticle diffusion of lead were determined using a pseudo-second-order mechanism expression [3,15,16] and the equation of Weber and Morris [17].

3.1. Pseudo-second-order model

The reaction rate of a reaction is defined as the change in concentration of a reactant or product per unit time. The concentrations of 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 experiments. A pseudo-second-order rate law expression demonstrates how the rate depends on the sorption capacity but not the concentration of the sorbate (3, 15, 16). The sorption kinetics may be described as being pseudo-second-order. The differential equation is

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

where \(k\) is the rate constant of sorption (g mg$^{-1}$ min$^{-1}$), \(q_t\) the amount of lead ions sorbed at equilibrium (mg g$^{-1}$), and \(q_e\) the amount (mg g$^{-1}$) of lead ions sorbed onto the surface of the palm kernel fibre at any time, \(t\).

Separating the variables in the equation above gives

$$\frac{dq}{(q_e - q_t)^2} = kdt,$$

Integrating this for the boundary conditions \(t = 0\) to \(t = t\) and \(q_t = 0\) to \(q_t\), gives

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + kt,$$

which is the integrated rate law for a pseudo-second-order reaction and with Eq. (3) can be rearranged to obtain

$$q_t = \frac{t}{1/kq_e^2 + 1/q_e},$$

which has the linear form of

$$t = \frac{1}{kq_e^2} \cdot \frac{1}{q_t} + \frac{1}{q_e}.$$  

As \(h\) can be regarded as the initial sorption rate as \(q_0/t\) when \(t = 0\), then:

$$h = kq_e^2.$$  

Thus, a plot of \(t/q_t\) against \(t\) of Eq. (6) should give a linear relationship with a slope of \(1/kq_e^2\) and an intercept of \(1/q_e^2\).

3.2. Intraparticle diffusion model

Theoretical treatments of intraparticle diffusion yield rather complex mathematical relationships which differ in form as functions of the geometry of the sorbent particle. A functional relationship common to most treatments of intraparticle diffusion is that uptake varies almost proportionately with the half-power of time, \(t^{\frac{1}{2}}\), rather than \(t\), a nearly linear variation in the quantity sorbed with \(t^{\frac{1}{2}}\) is predicted for a large initial fraction of reactions controlled by rates of intraparticle diffusion. Good linearization of the data is observed
for the initial phase of the reaction in accordance with expected behavior if intraparticle diffusion is the rate-limiting step [17]. According to Weber and Morris [17] if the rate-limiting step is intraparticle diffusion, a plot of solute sorbed against the square root of the contact time should yield a straight line as the rate is proportional to the driving force of higher concentrations. The observed dependence of the rate on the initial concentration of lead(II) indicates that removal of lead(II) from an aqueous solution should present no significant obstacle, since sorption relative to the initial concentration of lead(II) is more rapid the more dilute the solution is. Fig. 1 shows a plot of the experimental data points for the sorption of lead(II) by palm kernel fibres as a function of time. These plots show that, for all initial lead concentrations, the amount of lead(II) sorbed increased rapidly with time at the beginning and became very slow towards the end of the process. The plots also demonstrate that

3.3. Effect of initial lead concentration

The rate of lead sorption onto palm kernel fibres was determined as a function of the initial lead concentration using initial concentrations of 30, 50, 70, 90, and 120 mg dm$^{-3}$. The results in Table 1, show the applicability of the pseudo-second-order equation for the system of lead with palm kernel fibre for initial lead(II) concentrations ranging from 30 to 120 mg dm$^{-3}$. Table 1 lists the rate constant, $k_i$, the equilibrium sorption, $q_i$, and the initial sorption rate, $h_i$, of sorption at various initial concentrations of lead(II); they were calculated from the intercept and slope of straight line plots of $t_{eq}$ versus $t$ according to Eq. (5). The initial sorption rate increased from 16.3 to 206 mg g$^{-1}$ min$^{-1}$, the equilibrium sorption increased from 19.8 to 40.6 mg g$^{-1}$, and the value of rate constant increased from $4.15 \times 10^{-3}$ to 0.125 g mg$^{-1}$ min$^{-1}$ with an increase in the initial concentration of lead(II) from 30 to 120 mg dm$^{-3}$, respectively. This could have been due to the driving force of higher concentrations. The observed dependence of the rate on the initial concentration of lead(II) indicates that removal of lead(II) from an aqueous solution should present no significant obstacle, since sorption relative to the initial concentration of lead(II) is more rapid the more dilute the solution is. Fig. 1 shows a plot of the experimental data points for the sorption of lead(II) by palm kernel fibres as a function of time. These plots show that, for all initial lead concentrations, the amount of lead(II) sorbed increased rapidly with time at the beginning and became very slow towards the end of the process. The plots also demonstrate that

![Image of a graph showing the effect of initial concentration of lead on its sorption onto palm kernel fibre.](image_url)
the sorption increased for lower initial lead concentrations at any specific time. Furthermore, a large fraction of the total amount of lead(II) was removed within a short period of time. There was also an effect on the contact time required to reach saturation due to the variation in the initial lead concentration. The pseudo-second-order rate constant, $k$, was found to decrease non-linearity with the increasing initial concentration of lead within the range from of 30 to 120 mg dm$^{-3}$.

Intraparticle diffusion is characterised by dependence between the sorption capacities at any reaction time, $q_t$, and the square root of time, with the slope of the relationship being the intraparticle diffusion rate parameter expressed in Eq. (7). As can be seen from a typical set of data for the systems investigated (Fig. 2), the relationships are not linear for the entire range of reaction time. This non-linearity has been reported previously [19,20] and has been explained in terms of both diffusion processes having an effect on the sorption. It is clear from Fig. 2 that the relationships yield a straight line passing through the origin for the beginning part, and this was more likely to occur at lower initial lead concentrations. This phenomenon has been reported with the sorption of Acid Blue 25 onto wood [21]. It may be concluded that the rate-limiting step is intraparticle diffusion in the initial period of the reaction.

Accordingly, a correlation was empirically made of the pseudo-second-order rate constant, $k$, as a function of the initial concentration of lead as follows:

$$k = mC_0^n$$

McKay et al. [22] reported that in the case of sorption of AB25 using chitin, $n$ centers around 0.5 values, confirming that intraparticle diffusion is a prominent factor in the sorption process. In cases of sorption of larger molecular dyes, the sorption rate was slower and intraparticle diffusion was the rate-limiting step [23,24]. Conversely, in cases of sorption of metal ions, the sorption rate was generally faster and was not affected by intraparticle diffusion [4,25]. In addition, a negative value of $n$ was reported for the lead sorption on peat for which the second-order chemisorption is important [26]. The results from this study suggest that the relationship between the pseudo-second-order rate constant, $k$, and the initial lead concentration follows Eq. (9) with a coefficient of determination of 0.978 as shown in the following equation:

$$k = 6.24 \times 10^{-4} C_0^{1.11}$$

The value of $n$ (1.11) differs from 0.5 based on intraparticle diffusion. This indicates that the kinetics of lead sorption using palm kernel fibre is described by a pseudo-second-order expression rather that by intraparticle diffusion, and intraparticle diffusion is not the rate-limiting step.

3.4. Effect of added calcium

The effect of added calcium was evaluated for various initial lead concentrations (30, 50, 70, 90, and 120 mg dm$^{-3}$). In each initial lead concentration, various calcium concentrations (40, 80, and 120 mg dm$^{-3}$) were mixed with the lead solutions. Fig. 3 shows typical pseudo-second-order curves with experimental data at the initial lead concentration of 120 mg dm$^{-3}$. The pseudo-second-order constants from a series of kinetics experiments are listed in Table 1. The data show good compliance with the pseudo-second-order model with high coefficients of determination. The results in Table 1 also show that increasing concentrations of calcium had a significant effect on the uptake of lead in the bi-solute system. The equilibrium sorption capacity, the equilibrium rate constant, and the initial sorption rate all increased with an increase in the initial lead concentrations in all cases at a partic-
ular calcium concentrations such as 40, 80, and 120 mg dm$^{-3}$. At a particular initial lead concentration, the equilibrium sorption capacity and the initial sorption rate decreased with an increase in calcium concentration. This may have been due to competition occurring in the bi-solute sorption systems of lead and calcium on the fibre. Furthermore, the hydrogen ion concentrations changed between the initial and equilibrium, $\Delta [H^+]$, as determined by measuring pH values of the solution. Values of $\Delta [H^+]$ increased with an increase in the initial lead concentrations in all cases as calcium concentrations increased from 0 to 120 mg dm$^{-3}$ (Table 1). However, at a particular initial lead concentration, the values of $\Delta [H^+]$ decreased with an increase in the calcium concentration. It can be seen that calcium appears to have a greater influence on the ion exchange between ions in solution and hydrogen on the sorbent surfaces. The lead ion loading capacity increased with increasing pH under acidic conditions, presumably as a function of lead speciation and due to $H^+$ competition at the same binding sites, as was concluded for the sorption of lead by the fungus, *Penicillium purpurogenum* [10].

Fig. 4 shows how the presence of calcium ions affects the sorption of lead(II), and although this figure contains only data for an initial concentration of 90 mg dm$^{-3}$, the pattern of behaviour is typical of the other concentrations. The presence of the second solute has a distinct impact on the sorption of lead(II). The equilibrium capacities of lead onto palm kernel fibre were lower than in their respective mono-solute systems. Table 1 shows the effect of added calcium on the sorption capacity at various initial lead concentrations. Fig. 5 demonstrates this effect and shows that, as the calcium concentration increased from 0 to 120 mg dm$^{-3}$, the lead sorption capacity decreased following an empirical relationship with a high coefficient of determination, as expressed by

$$ q_e = \exp(MC_a + B) $$  \hspace{1cm} (10)

where $C_a$ is the calcium concentration added (mg dm$^{-3}$), and $M$ and $B$ are characteristics of the lead sorption capacity/calcium concentration added curve, $\exp(B)$ is the equilibrium lead sorption capacity when $C_a = 0$. Values for $M$ and $B$ at the various initial lead concentrations, $C_0$, are shown in Table 2.

In most cases, the line of Eq. (7) cannot through the origin (as the intercept is not 0). A modified intraparticle diffusion equation can thus be considered by incorporating $t_0$ into the equation as follows:

$$ q_t = k_i(t + t_0)^{0.5} $$ \hspace{1cm} (11)

where the time constant, $t_0$ (min), can be evaluated from the linear plot represented by Eq. (7) using a trial-and-error optimization method.

The experimental data for the beginning 3 min were analyzed and plots of $q_t$ versus $t^{0.5}$ using Eq. (11) are shown in Fig. 6 for the sorption of lead at the lower initial concentration 30 mg dm$^{-3}$ with different calcium concentrations. Values of $k_i$ are shown in Table 1 for all systems. Intraparticle diffu-

<table>
<thead>
<tr>
<th>$C_0$ (mg dm$^{-3}$)</th>
<th>$M$</th>
<th>$B$</th>
<th>$r^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>120</td>
<td>-0.00239</td>
<td>3.70</td>
<td>1.000</td>
</tr>
<tr>
<td>90</td>
<td>-0.00445</td>
<td>3.49</td>
<td>0.993</td>
</tr>
<tr>
<td>70</td>
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<td>3.21</td>
<td>0.997</td>
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<tr>
<td>50</td>
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<td>0.994</td>
</tr>
<tr>
<td>30</td>
<td>-0.0183</td>
<td>2.72</td>
<td>0.976</td>
</tr>
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</table>
Concentrations of 0, 40, 80, and 120 mg dm\(^{-3}\) at various concentrations of added calcium, sorbent dose: 1.0 g; solution volume: 400 ml; temperature: 36 °C; agitation speed: 200 rpm.

Intraparticle diffusion constant and the mass transfer coefficient were well correlated by a pseudo-second-order expression. Intraparticle diffusion was the rate-limiting step only for low lead ion concentrations. The equilibrium sorption capacity, the equilibrium rate constant, and the initial sorption rate decreased with an increase in the initial calcium concentration. Calcium appears to enhance hydrogen release from the surface of the sorbent.

4. Conclusions

The kinetics of a sorption of mono-solute of lead ions and a bi-solute of lead and calcium ions onto palm kernel fibre were well correlated by a pseudo-second-order expression. Intraparticle diffusion was the rate-limiting step only for lower lead ion concentrations. The equilibrium sorption capacity, the equilibrium rate constant, and the initial sorption rate increased with an increase in the initial lead concentration in all cases at the particular calcium concentrations of 0, 40, 80, and 120 mg dm\(^{-3}\).

References