Sorption Kinetics for the Removal of Cadmium and Zinc onto Palm Kernel Shell Based Activated Carbon

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Abstract

The kinetics and mechanism of cadmium and zinc adsorption on palm kernel shell based activated carbons (PKSAC) have been studied. A series of batch laboratory studies were conducted in order to investigate the suitability of palm kernel shell based activated carbon (PKSAC) for the removal of cadmium (cadmium ions) and zinc (zinc ions) from their aqueous solutions. All batch experiments were carried out at pH 7.0 and a constant temperature of 30±1°C using an incubator shaker that operated at 150 rpm. The kinetics investigated includes the pseudo first order, the pseudo-second order and the intraparticle diffusion models. The pseudo-second order model correlate excellently the experimental data, suggesting that chemisorption processes could be the rate-limiting step.

Keywords: adsorption, cadmium, kinetics, palm kernel shell, zinc

1. Introduction

Heavy metal contamination exists in aqueous waste streams of many industries, such as metal plating, mining, as well as agricultural fields. Zinc and cadmium are among the harmful heavy metal waste produced by these industries, and pose a risk of contaminated groundwater and other water resources. Since heavy metals are not biodegradable and tend accumulate in living organisms, causing various disease and disorders.

The mechanism of sorption often involves chemical reaction between functional groups on the biosorbent and the metal ions, thus forming metal-organic complexes, or a cation exchange reaction due to the high cation-exchange capacity of the biosorbent. In addition, other mechanisms may be involved as well as mass-transport processes, such as transport in the bulk of the liquid phase, diffusion across the liquid film surrounding the solid particles and diffusion in macropores or micropores. 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 becomes slower as equilibrium is approached. Such kinetics are often described by a pseudo-second-order kinetics reaction (Taty et al., 2003; Rakshaaee et al., 2005; Horsfall et al., 2006).

Treatment processes for metals contaminated waste streams include chemical precipitation, membrane, filtration, ion exchange, carbon adsorption, and coprecipitation/adsorption. These processes are usually need an expensive facility and high maintenance cost. Adsorption using low cost sorbents such as palm kernel shell may be an economical alternative technology for the treatment of metals contaminated waste streams.

Natural materials that are available in large quantities, or certain waste products from or agricultural operations such as rice husk, straw and oil palmwastes, may have potential as inexpensive sorbents. These abundance and availability of agricultural byproducts make them good sources of raw materials for activated carbons. The possible use of palm shell as activated carbon precursor was highlighted by several investigators (Hussien et al., 1996; Daud et al., 2000) and they concluded that a good quality product can be obtained.

2. Methodology

2.1 Materials

In this study, analytical grade Cd(NO₃)₂·4H₂O and Zn (NO₃)₂·6H₂O used in the experiments were supplied by Fisher Scientific, Malaysia.
Stock solutions of metal ions were prepared using deionized water. All solutions were adjusted to pH 7.0 using dilute NaOH and HNO₃. The palm kernel shell activated carbon (PKSAC) was donated by K.D. Technology Sdn. Bhd., in granular form with particle sizes of 0.25 – 0.60 mm.

### 2.2 Procedure

Batch sorption studies were performed at different concentration (20, 30, and 40 mg/L) to obtain the equilibrium kinetics. The metals chosen for the investigation studies were cadmium (II), and zinc (II). A series of 1000 ml conical flask were employed. Each conical flask was filled with 500 ml of metal ion solution of varying concentrations and adjusted to pH 7.0. The conical flask with heavy metal ions solution was then shaken using an orbital incubator shaker, which operated at 150 rpm and 30±1°C. When the desired temperature was reached, a known amount of adsorbent was added into each conical flask and mechanical shaking agitated the solutions. Generally equilibrium was reached after six hours (from contact time studies). After this period the solution was filtered using Whatman Cat. No. 1002 110 filter paper and analyzed for the amount of cadmium or zinc ions sorbed on the surface of the activated carbon at any time t (mg/g). Integrating Eq. (2) for the boundary conditions t =0 to t and q₀ =0 to qₑ, yields:

\[
\log(qₑ - qₜ) = \log(qₑ) - \frac{k₁}{2.303} t
\]

(3)

If the pseudo first order kinetics are applicable to the system, then the plot of \(\log(qₑ-qₜ)\) versus \(t\) of equation (3) will give a linear relationship, with \(k января 2003 \times 2.303\) and \(\log(qₑ)\) as slope and intercept, respectively.

### 3.2 Pseudo Second-Order

The pseudo second-order kinetics rate equations can be written as follows (Ho and Ofomaja, 2005):

\[
\frac{dqₜ}{dt} = k₂(qₑ - qₜ)^2
\]

(4)

where \(k₂\) is the equilibrium rate constant of pseudo second-order sorption (g/mg min), \(qₑ\) is the amount of cadmium or zinc ions adsorbed at equilibrium (mg/g) and \(qₜ\) is the amount of cadmium or zinc ions adsorbed on the surface of the activated carbon at any time \(t\) (mg/g). Separating the variables in Eq. (4) gives:

\[
\frac{dqₜ}{(qₑ - qₜ)^2} = k₂ dt
\]

(5)

Integrating equation (5) for the boundary conditions \(t =0\) to \(t\) and \(qₜ =0\) to \(qₑ\), gives:

\[
\frac{1}{qₑ - qₜ} = \frac{1}{qₑ} + k₂ t
\]

(6)

A linear form of Eq. (6) can be obtained:

\[
\frac{t}{qₜ} = \frac{t}{k₂qₑ^2} + \frac{1}{qₑ}
\]

(7)

If the pseudo second-order kinetics are applicable to the system, then the plot of \(t/qₜ\) versus \(t\) of equation (7) will give a linear relationship, with \(1/qₑ\) and \(1/k₂qₑ²\) as a slope and intercept, respectively. The values of \(qₑ\) and \(k₂\) are determined from the slope and intercept. The pseudo second-order kinetics model has been successfully applied to several biosorption systems as reported by Ho and McKay (1999a).
3.3 Intraparticle Diffusion

For a solid–liquid sorption process, the mass transfer mechanism is usually characterized by external mass transfer, or intraparticle diffusion, or both. The three steps that describe the mechanisms of adsorption are: (i) mass transfer of solute from the bulk of the solution to the adsorbent’s particle surface (film diffusion), (ii) uptake of the adsorbate at the binding sites (solid diffusion), (iii) intraparticle diffusion of solute via either pore diffusion or solid diffusion (pore diffusion). A comprehensive three resistance model has recently been developed by Choong et al. (2006). This model requires rather involved computer programming and therefore will not be used in this work. The most widely used intraparticle diffusion equation is given by Weber and Morris (1963):

\[ q_t = k_d t^{0.5} \tag{8} \]

where \( k_d \) is the intra-particle diffusion rate constant (mg/g min\(^{0.5}\)). The \( k_d \) values were calculated from the slope of the straight line plot \( q_e \) versus \( t^{0.5} \). Equation (8) has been used by a number of researchers such as Ho and McKay (1999), Atun and Hisarli (2003); Koumanova et al. (2003), and Mall et al. (2006).

4. Results and Discussion

The experiments were carried out at three different initial concentrations i.e 20, 30 and 40 mg/L, at two different dosages of adsorbent, 2.0 and 3.0 g/L.

The relationship between contact time and heavy metal uptake by PKSAC was studied through batch kinetics experiments and the results were shown in Figures 1 and 2. Figure 1(a) showed that cadmium equilibrium was reached after 90 minutes, 100 minutes and 120 minutes for initial heavy metal concentrations of 20, 30 and 40 mg/L, respectively. Figure 1(b) showed that for zinc, the equilibrium time required for initial zinc concentrations of 20 mg/L, 30 mg/L and 40 mg/L are 90 minutes, 120 minutes and 180 minutes, respectively. For all cases under investigation, the metal uptake profile was a single, smooth, and continuous curve leading to saturation, suggesting the possible monolayer coverage of heavy metal on the surface of the adsorbent. As shown in Figures 1 and 2, the amount of cadmium and zinc ions adsorbed at equilibrium, \( q_e \), increased with increasing initial concentration. A longer time was needed to reach equilibrium for higher initial heavy metal concentrations. The adsorption process could be divided into three regimes. The first regime was fast as a result of the rapid attachment of heavy metal particles to the surface of the adsorbent. The second regime was slower possibly because adsorption took place in the pores (intraparticle diffusion) and in the third regime the adsorption process decreased, indicating the attainment of equilibrium. As initial heavy metal concentrations increased, a longer time was needed to reach equilibrium and the adsorption capacity was also found to be increased.

4.1 Pseudo First-Order

The Lagergren pseudo first-order kinetics model is the simplest rate equation proposed for the adsorption of liquid/adsorbent system based on adsorbent capacity. The linearised form of the pseudo first-order kinetics model is given in equation (3). The plots of \( \log (q_e - q_t) \) versus \( t \) are presented in Figures 3 and 4 to test the applicability of the experimental data to the pseudo first-order kinetics model. For plotting Figures 3 and 4, \( q_e, q_t \) needed to be obtained from equilibrium experiments.

The pseudo first order rate constant, \( k_1 \) and \( q_e (q_{e, calc}) \) were obtained from the slope and intercept of the plot and the results are tabulated in Tables 1 and 2. For the applicability of the pseudo first-order kinetics model, the correlation coefficient \( R^2 \) need to be sufficiently high and \( q_{e, exp} \) must be sufficiently close to \( q_{e, calc} \). In all cases, it was found that this model was only applicable over the initial stage of the adsorption processes and did not fit well to the whole range of contact time. This was because the sorption of cadmium and zinc ions was not the only ion-exchange mechanism but other sorption mechanisms were also occurring. In most cases from the literature, the pseudo-first order equation does not fit well over the range of contact times (Choy et al., 2004). This pattern was also observed by Tutem et al. (2000) for adsorption of chlorophenols from water by bituminous shale and also by Ho and McKay (1998b) for pollutant removal on various sorbents.
Table 1. Rate constants ($k_1$) and $R^2$ for adsorption of cadmium and zinc onto PKSAC for different initial concentrations by using the pseudo first-order kinetics model: adsorbent dosage = 2.0 g/L.

<table>
<thead>
<tr>
<th>Initial concentration mg/L</th>
<th>Cadmium</th>
<th>Zinc</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$k_1$ min$^{-1}$</td>
<td>$q_e$ exp mg/g</td>
</tr>
<tr>
<td>20</td>
<td>0.0076</td>
<td>6.03</td>
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<tr>
<td>30</td>
<td>0.0081</td>
<td>7.05</td>
</tr>
<tr>
<td>40</td>
<td>0.0090</td>
<td>9.07</td>
</tr>
</tbody>
</table>

Table 2. Rate constants ($k_1$) and $R^2$ for adsorption of cadmium and zinc onto PKSAC for different initial concentrations by using the pseudo first-order kinetics model: adsorbent dosage = 3.0 g/L.

<table>
<thead>
<tr>
<th>Initial concentration mg/L</th>
<th>Cadmium</th>
<th>Zinc</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$k_1$ min$^{-1}$</td>
<td>$q_e$ exp mg/g</td>
</tr>
<tr>
<td>20</td>
<td>0.0064</td>
<td>4.07</td>
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<tr>
<td>30</td>
<td>0.0092</td>
<td>5.43</td>
</tr>
<tr>
<td>40</td>
<td>0.0094</td>
<td>7.42</td>
</tr>
</tbody>
</table>

Figure 1. Contact time study of the removal of (a) cadmium and (b) zinc from aqueous solutions using PKSAC: Effect of initial heavy metal concentrations at 2.0 g/L dosage of PKSAC.

Figure 2. Contact time study of the removal of (a) cadmium and (b) zinc from aqueous solutions using PKSAC: Effect of initial heavy metal concentrations at 3.0 g/L dosage of PKSAC.
The values of correlation coefficient $R^2$ were considerably high. However, as shown in Tables 1 and 2, the values of $q_{e,\text{exp}}$ and $q_{e,\text{calc}}$ differ a lot. Therefore, it can be concluded that the pseudo first-order kinetics model do not describe well the adsorption kinetics of cadmium and zinc onto palm kernel shell based activated carbon (PKSAC).

### 4.2 Pseudo Second-Order

As shown in equation (7), the pseudo second-order rate constant $k_2$ and $q_e$ ($q_{e,\text{calc}}$) can be obtained from the slope of the plot of $t/q_t$ versus $t$ as shown in Figures 5 and 6, and the parameters of pseudo second-order were as listed in Tables 3 and 4. For the applicability of the pseudo second-order kinetics model, the correlation coefficient $R^2$ need to be sufficiently high and $q_{e,\text{exp}}$ must be sufficiently close to $q_{e,\text{calc}}$.

The adsorption kinetics of both cadmium and zinc were found to obey the pseudo second-order kinetics, with high values of the correlation coefficient, $R^2 (>0.99)$ and the values of $q_{e,\text{exp}}$ and $q_{e,\text{calc}}$ are sufficiently close. This indicated that the experimental data can be explained using this model. The rate of cadmium and zinc adsorption process appears to be controlled by chemisorption. The same phenomenon was reported by Jia and Aik (3003) on adsorption of sulphur dioxide onto activated carbon prepared from oil-palm shells and by Jia et al. (2005) on adsorption of NH$_3$ onto activated carbon prepared from palm shells.

**Table 3.** Rate constants ($k_2$) for the adsorption of cadmium and zinc onto palm kernel shell based activated carbon by using the pseudo second-order kinetics model: adsorbent dosage = 2.0g/L.

<table>
<thead>
<tr>
<th>Initial concentration mg/L</th>
<th>$k_2$ g mg$^{-1}$min$^{-1}$</th>
<th>$q_{e,\text{exp}}$ mg/g</th>
<th>$q_{e,\text{calc}}$ mg/g</th>
<th>$R^2$</th>
<th>$k_2$ g mg$^{-1}$min$^{-1}$</th>
<th>$q_{e,\text{exp}}$ mg/g</th>
<th>$q_{e,\text{calc}}$ mg/g</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0.024</td>
<td>6.03</td>
<td>6.09</td>
<td>0.999</td>
<td>0.014</td>
<td>2.97</td>
<td>3.04</td>
<td>0.992</td>
</tr>
<tr>
<td>30</td>
<td>0.020</td>
<td>7.05</td>
<td>7.07</td>
<td>0.999</td>
<td>0.009</td>
<td>5.40</td>
<td>5.61</td>
<td>0.998</td>
</tr>
<tr>
<td>40</td>
<td>0.014</td>
<td>9.07</td>
<td>9.12</td>
<td>0.999</td>
<td>0.008</td>
<td>7.73</td>
<td>7.89</td>
<td>0.999</td>
</tr>
</tbody>
</table>

**Table 4.** Rate constants ($k_2$) for the adsorption of cadmium and zinc onto palm kernel shell based activated carbon by using the pseudo second-order kinetics model: adsorbent dosage = 3.0g/L.

<table>
<thead>
<tr>
<th>Initial concentration mg/L</th>
<th>$k_2$ g mg$^{-1}$min$^{-1}$</th>
<th>$q_{e,\text{exp}}$ mg/g</th>
<th>$q_{e,\text{calc}}$ mg/g</th>
<th>$R^2$</th>
<th>$k_2$ g mg$^{-1}$min$^{-1}$</th>
<th>$q_{e,\text{exp}}$ mg/g</th>
<th>$q_{e,\text{calc}}$ mg/g</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0.024</td>
<td>4.07</td>
<td>4.06</td>
<td>0.998</td>
<td>0.020</td>
<td>2.00</td>
<td>1.99</td>
<td>0.991</td>
</tr>
<tr>
<td>30</td>
<td>0.018</td>
<td>5.43</td>
<td>5.48</td>
<td>0.998</td>
<td>0.010</td>
<td>3.87</td>
<td>4.01</td>
<td>0.998</td>
</tr>
<tr>
<td>40</td>
<td>0.015</td>
<td>7.42</td>
<td>7.49</td>
<td>0.999</td>
<td>0.007</td>
<td>6.62</td>
<td>6.88</td>
<td>0.998</td>
</tr>
</tbody>
</table>

**Figure 3.** Pseudo first-order kinetics model for the removal of (a) cadmium and (b) zinc from aqueous solutions using PKSAC: Effect of initial heavy metal concentrations at 2.0 g/L dosage of PKSAC.
In summary, a conclusion could be made that the most suitable model to describe the kinetics of experiment was pseudo second order kinetics model with correlation coefficient, $R^2 > 0.99$. The rate-limiting process is chemisorption.

To further show that the process is not intraparticle diffusion controlled, empirical correlations of the pseudo second-order rate constant, $k_2$, as a function of the initial concentration can be expressed as:

$$k_2 = 0.21C_0^{0.719} \quad (9)$$
(for cadmium with adsorbent dosage 2.0 g/L)

$$k_2 = 0.16C_0^{0.631} \quad (10)$$
(for cadmium with adsorbent dosage 3.0 g/L)

$$k_2 = 0.13C_0^{0.762} \quad (11)$$
(for zinc with adsorbent dosage 2.0 g/L)

$$k_2 = 2.02C_0^{0.547} \quad (12)$$
(for zinc with adsorbent dosage 3.0 g/L)

If the power of $C_0$ is around the value 0.5, then the intraparticle diffusion is a prominent factor in the adsorption process, all the values of power in equations (9 to 12) are negative and are different from 0.5, this confirms that the adsorption is not intraparticle diffusion controlled.

5. Conclusion

The analysis of contact time experiments suggests that the pseudo-second order kinetic model described well the dynamic behaviour for adsorption of both metal ions under different initial metal ions concentrations. This suggests that the chemisorption mechanism is the rate-limiting step in the adsorption uptake.

Nomenclature

- $C_e$: metal ions concentration in liquid phase at equilibrium (mg/L)
- $C_0$: initial metal ions concentration in liquid phase (mg/L)
- $k_1$: rate constant of pseudo first-order sorption (L/min)
- $k_2$: rate constant of pseudo second-order sorption (g/mg min)$^{-1}$
- $k_{id}$: intra-particle diffusion rate constant (mg/g min)$^{0.5}$
- $m$: mass of adsorbent (g)
- $q_e$: amount of metal ions adsorbed by activated carbon at equilibrium (mg/g).
- $q_t$: amount of metal ions sorbed on the surface of the activated carbon at any time (mg/g).
- $t$: time (min)
- $V$: total volume of metal ions solution (L)

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References


