Kinetic Studies of Copper(II) and Nickel(II) Adsorption by Oil Palm Ash

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Abstract: This paper presents a surface reaction rate model that can be used to describe the batch adsorption of metal ions onto unconventional adsorbent materials. Kinetic data of Cu(II) and Ni(II) adsorption on oil palm ash were compared with predictions of the theoretical model following determination of its parameters from small-scale experiments. In all cases studied it was possible to obtain excellent agreement between the experimental data and predicted results throughout the whole time course of adsorption. The apparent success of the model in accounting for experimental observations suggests that it can be used for the design and optimization of stirred batch adsorption systems.

Keywords: adsorption, ash, kinetics, metal ions, modeling

Introduction

Rapid industrialization in Asia has generated large volumes of aqueous wastes containing toxic metals. If these metals are discharged into the environment they may get into the food cycle, causing deleterious effects on humans as well as other animals. Chemical precipitation is the most common method used by industry to treat metal-bearing wastewater. However, it is ineffective or expensive when applied to large volumes of wastewater containing trace quantities of metal ions. Adsorption technology is one of the few alternatives available for such situations. Activated carbon has long been recognized as an effective adsorbent for this purpose. In recent years numerous low cost adsorbent materials have been proposed as potential replacement for the effective but expensive activated carbon. These adsorbents have been tested for their capacity to remove a wide range of heavy metals from aqueous solutions, as documented in a recent review [1]. The efficiency of metal removal by these adsorbents varies from one material to another. Since little is known about the surface property of most of these adsorbents and the mechanism of adsorption is not well elucidated, the metal binding mechanism is largely unpredictable, which makes time-consuming experimental procedures the only means of evaluating their metal adsorption properties.

In this work oil palm ash, a solid by-product of the palm oil industry in Southeast Asia, was tested for its capacity to remove heavy metal ions from aqueous solutions. Palm fibers and shells are often used as boiler fuel by palm oil mill plants to produce steam for electricity generation and palm oil extraction. The ash produced after burning, designated as oil palm ash, requires ultimate disposal. The use of ash particles derived from the combustion of agricultural wastes or coal as metal adsorbents would therefore be most ideal since these materials are inexpensive and available in abundance [2-13].

Information on adsorption kinetics and equilibrium is needed for adsorbent evaluation and/or process design and optimization. Such information is usually obtained from experimental studies. Mathematical models can then be developed and validated based on this information. The resulting model represents a powerful tool that can be used to quantify and predict the extent of adsorption under various conditions, resulting in a significant reduction in the experimental work required for such studies. In this work a second-order surface reaction rate model was employed to describe the dynamics of Cu(II) and Ni(II) adsorption by oil palm ash.

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in batch systems. Although full-scale adsorption processes are often carried out in fixed-beds, batch stirred-tank systems are simple to operate and cost-effective and may find application in small and medium-scale wastewater processing facilities using simple and readily available mixing vessels.

Experimental

Samples of oil palm ash supplied by the Palm Oil Research Institute of Malaysia were washed with water, treated with nitric acid, and rinsed again thoroughly with water until stabilization of pH. The ash particles were then dried at 60°C to a constant weight. The specific surface area of the ash particles determined by the nitrogen-BET method was 23.4 m²/g. Metal stock solutions were prepared by dissolving Ni(NO₃)₂·6H₂O and Cu(NO₃)₂·3H₂O in deionized water. Batch equilibrium experiments were carried out by adding 0.5 g of the ash particles to a series of flasks containing known concentrations of Cu(II) or Ni(II). The pH of all the metal solutions was adjusted to 5.0. The flasks were agitated in a rotary shaker at 200 rpm and 25°C. Sufficient time was allowed for the metal uptake process to reach equilibrium. Following equilibration, the metal solutions were filtered and analyzed for their metal concentrations by an inductively coupled plasma spectrophotometer (Baird ICP 200, USA). The amount of metal taken up by the ash particles in each flask was determined from a mass balance. Flasks containing oil palm ash in deionized water and metal solutions with no oil palm ash were used as controls. To generate the time profiles of metal adsorption, similar experiments were carried out and samples were taken at fixed time intervals for analysis. During all kinetic experiments, the ash particles were uniformly dispersed in the solution. Each experiment was carried out in duplicate and the average results are presented in this work.

Results and Discussion

In the development of the surface reaction rate model it is assumed that metal uptake is limited to the surface of oil palm ash. The interaction between a metal ion and the ash particles can be considered in terms of a second-order reversible reaction of the following form:

\[ M + A \rightleftharpoons k_1 \leq k_2 M \cdot A \]  

where \( M \) is the metal ion in solution, \( A \) is the adsorption site on adsorbent surface, and \( M \cdot A \) is the metal-adsorbent complex. The parameters \( k_1 \) and \( k_2 \) are the forward and reverse rate constants, respectively, for the adsorption process. The rate of metal uptake by the adsorbent in an interaction described by Equation (1) is given by

\[ \frac{dq}{dt} = k_1 c (q_m - q) - k_2 q \]  

(2)

where \( q \) is the solid phase concentration of the adsorbed metal (\( \mu \)mol/g), \( q_m \) is the maximum adsorption capacity of the adsorbent (\( \mu \)mol/g), \( c \) is the concentration of metal ion in solution (\( \mu \)mol/L), and \( t \) is the time (min). The rate constants \( k_1 \) (L/\( \mu \)mol.min) and \( k_2 \) (min⁻¹) are not the intrinsic rate constants for metal interaction with the ash adsorbent, but rather lumped forward and reverse rate constants which include the contributions of mass transfer resistances. In the case of very fast mass transfer relative to the adsorption step, however, the rate constants will correspond to the intrinsic parameters.

At equilibrium, \( dq/dt \) equates to zero and Equation (2) reduces to the familiar Langmuir isotherm model:

\[ q = \frac{q_m c}{K_d + c} \]  

(3)

where \( K_d \) (\( \mu \)mol/L) is the apparent dissociation constant given by

\[ K_d = \frac{k_2}{k_1} \]  

(4)

The extent of metal ion uptake as a function of time can be found from the integration of the rate expression [Equation (2)] together with the appropriate initial conditions and the mass conservation equation for a stirred batch system. The analytical solution to Equation (2) is given by [14]

\[ c = c_0 - \frac{m}{v} \left[ \frac{(b + a) \left[ 1 - \exp \left( -2a \frac{m}{v} k_1 t \right) \right]}{b - a} - \exp \left( -2a \frac{m}{v} k_1 t \right) \right] \]  

(5)

where \( c_0 \) is the initial metal concentration (\( \mu \)mol/L), \( m \) is the mass of adsorbent (g) and \( v \) is the volume of solution (L). The parameters \( a \) and \( b \) are defined as \( a^2 = b^2 - c_0 q_m/v/m \) and \( b = 0.5(c_0 v/m + q_m + K_d v/m) \). The change in the concentration of metal ions in the solution phase as a function of time can be calculated from Equation (5) once values of the operating parameters \( c_0, m, v, \) and \( K_d \) and model parameters \( q_m, K_a, \) and \( k_1 \) are known. The values of \( q_m \) and \( K_d \) can be estimated from equilibrium isotherm data while \( k_1 \) can be extracted from transient uptake data.

Equilibrium data for the adsorption of Cu(II) and Ni(II) on oil palm ash particles measured at pH 5.0 and 25°C.
Figure 1. Adsorption equilibria of Cu(II) and Ni(II) on oil palm ash at pH 5.0 and 25°C.

Table 1. Langmuir and Rate Constants for Cu(II) and Ni(II) Adsorption on Oil Palm Ash

<table>
<thead>
<tr>
<th></th>
<th>( q_m (\mu\text{mol/g}) )</th>
<th>( K_d (\mu\text{mol/L}) )</th>
<th>( k_i (L/\mu\text{mol.min}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(II)</td>
<td>200.4</td>
<td>3.2</td>
<td>( 6.0 \times 10^4 )</td>
</tr>
<tr>
<td>Ni(II)</td>
<td>168.8</td>
<td>6.8</td>
<td>( 2.4 \times 10^4 )</td>
</tr>
</tbody>
</table>

are shown as symbols in Figure 1. Solution pH can affect the extent of metal adsorption because it influences the metal chemistry in solution as well as the surface chemistry of adsorbent. Because both metals exist as divalent ions under the experimental conditions employed in this study, adsorption data reported here are a reflection of the association between \( Cu^{2+} \) or \( Ni^{2+} \) and the ash particle surface. The equilibrium results are represented by steep curves in the initial solution concentration range which are characteristic of highly favorable adsorption. Oil palm ash is therefore an efficient adsorbent for metal removal from dilute solutions.

The Langmuir model [Equation (3)] was fitted to each set of the experimental data by a nonlinear least-squares regression analysis. The fitted values of the maximum adsorption capacity \( (q_m) \) and apparent dissociation constant \( (K_d) \) are presented in Table 1. It can be seen from Table 1 that the maximum adsorption capacity of the ash for Cu(II) is slightly higher than that for Ni(II) while the dissociation constant for Cu(II) is about half of that for Ni(II) on a molar basis. It can therefore be concluded that the ash adsorbent has a higher affinity for Cu(II) than for Ni(II). The best-fit isotherms predicted by these estimates are plotted in solid lines in Figure 1. A statistical comparison between the experimental and calculated data was made by computing the normalized sum of squared errors (SSE) using Equation (6):

\[
SSE = \sqrt{\frac{\sum (e_i - s_i)^2}{(n - 1)}}
\]

Figure 2. Batch adsorption profile for the uptake of Cu(II) by oil palm ash. Initial Cu(II) concentration = 629.5 \( \mu\text{mol/L} \). Adsorbent dosage = 2.5 g/L.

Figure 3. Batch adsorption profile for the uptake of Ni(II) by oil palm ash. Initial Ni(II) concentration = 681.3 \( \mu\text{mol/L} \). Adsorbent dosage = 2.5 g/L.

where \( e_i \) is the \( i \)th experimental data point of adsorbent phase metal concentration, \( s_i \) is the corresponding model-predicted value, and \( n \) is the number of data points. The SSE values for Cu(II) and Ni(II) are 0.12 and 0.11, respectively. In general the experimental data are well represented by the Langmuir model.

Transient profiles were collected for batch adsorption of Cu(II) and Ni(II) on oil palm ash. The experimental results, shown in Figures 2 and 3, indicate that about 88% of the total Cu(II) removal and 70% of the total Ni(II) removal were achieved in the first 10 minutes of contact time. After a period of 20 min, 98% of the total adsorbed Cu(II) and 88% of the total adsorbed Ni(II) were attached to the ash adsorbent. The high initial rates of metal uptake suggest that the adsorption occurred mainly at the ash exterior surface. The experimental profiles were compared with the predictions of the surface reaction rate model described above.

The only unknown parameter in Equation (5) is the lumped forward rate constant \( (k_1) \) as the values of the isotherm parameters \( q_m \) and \( K_d \) are taken to be those
determined in the equilibrium experiments described above and the other parameters ($c_0$, $m$, and $v$) are known from the conditions of the experiments. The values of $k_1$, estimated by fitting Equation (5) to each set of the experimental data using a nonlinear least-squares regression analysis, are tabulated in Table 1. The forward rate of adsorption ($k_1$) of Cu(II) to the ash adsorbent is about 2.5 times faster than the rate of binding of Ni(II). This difference probably reflects the fact that oil palm ash has a higher affinity for Cu(II) than for Ni(II).

Calculated model solutions are represented by solid lines in Figures 2 and 3. In general, it was possible to obtain a good fit over the complete time course of adsorption.

The feasibility of using the same value of $k_1$ to predict the kinetic profiles of Cu(II) and Ni(II) adsorption under different experimental conditions was investigated. Experiments were conducted for each metal ion with the initial metal concentration of Cu(II) reduced from 629.5 $\mu$mol/L to 472.1 $\mu$mol/L and of Ni(II) from 681.3 $\mu$mol/L to 511 $\mu$mol/L (adsorbent dosage = 2.5 g/L) and adsorbent dosage reduced from 2.5 g/L to 1.5 g/L (initial metal concentration: Cu(II) = 629.5 $\mu$mol/L and Ni(II) = 681.3 $\mu$mol/L). Figures 4 and 5 show the experimental results and theoretical predictions of the kinetic profiles using the model parameter values listed in Table 1. In all cases it was possible to obtain a good correspondence between the shapes of the experimental curves and the predicted results. A unique value of $k_1$ can indeed be used to generate predictions that fitted all the experimental results for each metal-adsorbent system studied. The excellent agreement suggests that the simple surface reaction rate model may be used for practical and scaling-up studies.

It is important to realize that the values of the rate constant $k_1$ reported here for the interaction between oil palm ash and the two metal ions are only applicable to the conditions under which they were measured. As mentioned earlier, $k_1$ and $k_2$ are both lumped parameters which contain the effects of both the intrinsic kinetics and mass transfer (film and intraparticle diffusion). It has been proposed that the relative magnitudes of these processes for spherical adsorbents may be estimated from the following expression [15]:

$$\frac{1}{k_1} \approx \frac{1}{k_{1,i}} + \frac{q_m R^2}{30 \left(1 + \frac{c_0}{K_d}\right)} \left[\frac{1}{D_e} + \frac{5}{k_f R}\right]$$

(7)

where $k_{1,i}$ is the intrinsic rate constant (L/$\mu$mol.min), $R$ is the adsorbent particle radius (m), $D_e$ is the effective diffusivity of the metal in the adsorbent matrix (m$^2$/min), and $k_f$ is the film mass transfer coefficient (m/min). Under this theoretical framework, the lumped forward rate constant is approximately equal to the intrinsic rate constant ($k_1 = k_{1,i}$) for cases in which the intrinsic adsorption kinetics is the rate-limiting step. In principle, the measured value of $k_1$ is independent of the operating conditions of the batch vessel. However, for cases in which mass transfer dominates the overall rate of adsorption $k_1$ is expected to be a function of the operating conditions. For example, it is well known that the film mass transfer coefficient $k_f$ is affected by the mixing intensity of the stirred batch system. According to Equation (7), different $k_1$ values will therefore be obtained under different mixing conditions when external mass transfer is the rate-limiting step.

Models providing "first-principles" description of the processes underlying metal ion adsorption kinetics have recently been developed. These models include mechanistic characterization of the ion exchange and surface complexation phenomena as well as mass
transfer resistances [16]. These models can be used to predict the effect of various solution variables such as pH and ionic strength on the kinetics of metal ion adsorption. However, the use of these models in modeling metal ion adsorption requires determination of a large number of parameters. By contrast, simple models with good predictive capability such as the surface reaction rate model described in this work could be calibrated and validated within a reasonable amount of time and with a limited amount of experiments. Due to their mathematical simplicity, such models are especially useful for cases in which the mechanism of adsorption is not well elucidated.

Conclusions

This work has successfully demonstrated the use of a simple surface reaction rate model to describe the time course of Cu(II) and Ni(II) adsorption [17,18] onto oil palm ash. An appropriate rate model should give correct predictions of both equilibrium and kinetic data. The surface reaction rate model described here fulfills this requirement as it utilizes equilibrium constants derived from the Langmuir isotherm. Any batch adsorption systems employing adsorbent that exhibits Langmuir-type adsorption can therefore be simulated effectively with this model. The model is useful for the prediction of metal ion adsorption to unconventional adsorbent materials such as the oil palm ash used in this work, given its simplicity and the small amount of experiments required to determine its parameters. The model can be used to assess the effects of alteration of operational parameters without the need to carry out extensive experimental work.

References