Kinetics and Thermodynamic Study of Lead Adsorption from Aqueous Solution onto Rubber (*Hevea brasiliensis*) Leaf Powder

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Abstract: The ability of rubber or *Hevea Brasiliensis* (HB) leaf powder to adsorb Pb**+** from aqueous solution has been investigated through batch experiments. The Pb**+** adsorption was found to be dependent on contact time, initial Pb**+** concentration and temperature. The kinetic processes of Pb**+** adsorption onto HB leaf powder were described by applying pseudo-first-order and pseudo-second-order rate equations. The kinetics data for the adsorption process obeyed pseudo-second-order equation. The equilibrium data were described well by the Langmuir and Freundlich isotherms. The maximum adsorption capacity determined from the Langmuir isotherm was found to be 46.73 mg g**-1** at 303 K. Thermodynamic parameters such as ΔG°, ΔH° and ΔS° were also calculated. The adsorption process was found to be exothermic and spontaneous in nature. The studies showed that HB leaf powder could be used as a good adsorbent material for Pb**+** removal from aqueous solution.

Key words: Rubber leaf powder, adsorption, lead, kinetics, thermodynamic, isotherm

Introduction

Industrialization is one of the major sources of the release of heavy metals in the atmosphere. Industries discharge different types of heavy metals into the environment at an unprecedented and constantly increasing rate. Lead is one of the heavy metals, which is highly toxic to humans, plant and animals. The metal is of special concern because it is non-degradable and therefore persistent. The major sources of lead release into the environment by waste streams are metallurgical industry, electroplating and metal finishing industries, paint manufacture, storage battery manufacture, munitions manufacture, petroleum refining and drainage from ore mines. The environmental impact due to lead toxicity has led to the enforcement of stringent standards for the maximum allowable limits of lead discharge into open landscapes and water bodies. According to the Malaysian standard of effluent, the permissible levels for lead discharges in wastewater are 0.10 mg L**-1** (Standard A) and 0.50 mg L**-1** (Standard B). Among many methods available to reduce heavy metal concentrations from wastewater, the most common are chemical precipitation, filtration, ion exchange, reverse osmosis, ultrafiltration, electrochemical deposition and adsorption on activated carbon. However, the aforementioned methods are not economically feasible for small and medium industries. It is therefore necessary to search for low-cost techniques that may be effective, less environmentally degrading and economical. Adsorption processes using agricultural and industrial waste products are becoming the new alternative for wastewater treatment because they are cheap, simple, sludge free and involve small initial cost and land investment. Some of the agricultural and industrial wastes, which have been used as adsorbent materials for removal of heavy metals from aqueous solution include tree fern (Ho, 2003), sawdust (Yu et al., 2003), fly ash (Gupta et al., 2003), chitosan (Ngah and Fatinathan, 2006; Ngah et al., 2002, 2004), aquatic plant (Keskinkan et al., 2004) and slag (Dimitrova, 2002; Dimitrova and Mekandjiev, 1998). A previous study has been conducted on the potential of HB leaf powder for removal of cadmium from wastewater (Hanafiah et al., 2006). The study found that HB leaf powder was able to remove cadmium at a fast reaction time and the maximum adsorption capacity was reported 3.68 mg g**-1**. Plant waste particularly HB leaf powder was selected as the adsorbent in this study as it is inexpensive and very common in Malaysia due to its relative abundance. The objective of

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RESULTS AND DISCUSSION

Adsorption kinetics: Adsorption kinetics, which describes the solute adsorption rate, is an important characteristic in evaluating the efficiency of adsorption. The adsorption data at different initial Pb²⁺ concentration is shown in Fig. 1. These plots show that for both initial concentrations of lead, the amount of lead adsorbed increased rapidly with time at the beginning and became slow towards the end of the process. For the first 10 min, the adsorption rate was found to be increased for an increase in initial lead concentration from 20 to 50 mg L⁻¹. After 20 min of adsorption, the adsorption rates of lead slowed significantly probably due to saturation on the surface of HB leaf powder. It is clear from the results that the agitation time required to attain equilibrium is dependent on the initial concentration of lead. According to Meena et al. (2005), at lower metal ion concentrations, sufficient adsorption sites are available for adsorption of metal ions. The 20 mg L⁻¹ lead solution is able to attain equilibrium quickly because the lead ions can easily adsorb onto abundantly unhindered or unoccupied sites first. However, at higher concentrations, the number of lead ions is relatively higher compared to availability of adsorption sites. This is the main reason the 50 mg L⁻¹ lead solution took longer time to reach equilibrium due to the proportionally higher number of lead ions present.

The equilibrium adsorption capacity of HB leaf powder was found to increase with increasing initial lead concentration. This indicates that there are plenty adsorption sites in HB leaf powder available for the adsorption of lead. The enhanced adsorption of lead ion with increase in agitation time may be due to the decrease in boundary layer resistance to mass transfer in the bulk solution and an increase in the kinetic energy of hydrated ions. By increasing the agitation time, the boundary layer resistance will be reduced and there will be an increase in the mobility of ions in the solution (Horsfall and Abia, 2003). In order to investigate the controlling mechanisms of adsorption processes, the pseudo-first-order and pseudo-second-order rate equations were used to test the experimental data. The pseudo-first-order rate equation is given as (Lagergren, 1898):

\[
\log (q_e - q_t) = \log q_e - \frac{k_1 t}{2.303}
\]

where \(q_e\) and \(q_t\) are the amount adsorbed (mg g⁻¹) at time \(t\) and at equilibrium and \(k_1\) is the rate constant of the pseudo-first-order adsorption process (min⁻¹). Straight line plots of \(\log (q_e - q_t)\) against \(t\) were used to determine the rate constant, \(k_1\) and correlation coefficients, \(R^2\) for different lead concentrations, as shown in Fig. 2.
Fig. 1: Effect of initial lead concentration on agitation time

Fig. 2: Pseudo-first-order reaction for Pb²⁺ ions adsorbed onto HB leaf powder at different concentrations

The pseudo-second-order equation is expressed as (Ho and McKay, 1999):

\[ \frac{1}{t} = \frac{1}{q_e} + \frac{1}{q_e h} \frac{1}{q} \]  (3)

where \( h = k q_e^2 \) (mg g⁻¹ min⁻¹) can be regarded as the initial adsorption rate at \( t=0 \) and \( k \) is the rate constant of pseudo-second-order biosorption (g mg⁻¹ min⁻¹). The plot \( t/q \) versus \( t \) should give a straight line if pseudo-second-order kinetics is applicable and \( q_e, k \) and \( h \) can be determined from the slope and intercept of the plot, respectively. The plots of the linearized form of the pseudo-second-order reaction at different Pb²⁺ concentrations by HB leaf powder are shown in Fig. 3. The pseudo-first-order and pseudo-second-order rate constants determined from Fig. 2 and 3 are presented in Table 1 along with the corresponding correlation coefficients.

Fig. 3: Pseudo-second-order reaction for Pb²⁺ ions adsorbed onto HB leaf powder at different concentrations

Fig. 4: Influence of temperature on the thermodynamic behavior of adsorption of Pb²⁺ ions on HB leaf powder

A chemical (usually covalent) bond and tend to find sites that maximize their coordination number with the surface. A detail analysis on the pseudo-second-order reveals that the values of the initial adsorption rates (h) increases with decrease in the initial lead concentration. According to Wong et al. (2003), the lower the concentration of metal ions in the solution, the lower the probability of collisions between these species is and hence the faster lead ions could be bonded to the active sites on the surface of the adsorbent. The equilibrium adsorption capacity (q_e) however increased with increase in initial lead concentration due to large number of lead ions are adsorbed at the available adsorption sites. Based on the values of \( R^2 \) obtained from the plots of pseudo-first-order and pseudo-second-order rate equations, it is obvious that with increasing initial concentration of the adsorbate, the correlation of experimental data to the pseudo-second order kinetics model decreases while that to the pseudo-first order model increases. The finding from this study is in complete agreement with the kinetics model developed by Azizian (2004).

**Thermodynamics of adsorption**: For the calculation of thermodynamic parameters, the following equations were used:

\[ K_c = \frac{C_{eq}}{C_e} \]  (4)
Table 1: Comparison between adsorption rate constants, q, estimated and correlation coefficients associated to the pseudo-first-order and to the pseudo-second-order rate equations

<table>
<thead>
<tr>
<th>Pb (mg L⁻¹)</th>
<th>kₜ (min⁻¹)</th>
<th>qₜ (mg g⁻¹)</th>
<th>R²</th>
<th>k₂ (mg g⁻¹ min⁻¹)</th>
<th>q₂ (mg g⁻¹)</th>
<th>b (mg g⁻¹ min⁻¹)</th>
<th>qₑₑ (mg g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0.081</td>
<td>0.248</td>
<td>0.809</td>
<td>2.063</td>
<td>0.973</td>
<td>0.999</td>
<td>1.982</td>
</tr>
<tr>
<td>50</td>
<td>0.055</td>
<td>0.746</td>
<td>0.859</td>
<td>0.380</td>
<td>1.745</td>
<td>0.998</td>
<td>1.157</td>
</tr>
</tbody>
</table>

Table 2: Thermodynamic parameters for adsorption of Pb⁺⁺ ions on HB leaf powder

<table>
<thead>
<tr>
<th>Pb (mg L⁻¹)</th>
<th>-ΔH° (kJ mol⁻¹)</th>
<th>-ΔS° (J mol⁻¹ K⁻¹)</th>
<th>T (K)</th>
<th>-ΔG° (kJ mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>40.44</td>
<td>112.18</td>
<td>363</td>
<td>313</td>
</tr>
</tbody>
</table>

Table 3: Langmuir and Freundlich adsorption isotherms constants and correlation coefficients for removal of Pb⁺⁺ ions on HB leaf powder

<table>
<thead>
<tr>
<th>Langmuir constants</th>
<th>Freundlich constants</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q₀ (mg g⁻¹)</td>
<td>b (l mg⁻¹)</td>
</tr>
<tr>
<td>46.73</td>
<td>0.081</td>
</tr>
</tbody>
</table>

Table 4: The adsorptive capacities of various adsorbents for Pb⁺⁺

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Q₀ (mg g⁻¹)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heves Brasiliensis leaf powder</td>
<td>46.73</td>
<td>This study</td>
</tr>
<tr>
<td>Sago waste</td>
<td>46.64</td>
<td>Quek et al. (1998)</td>
</tr>
<tr>
<td>Phosphoric clay</td>
<td>37.20</td>
<td>Singh et al. (2001)</td>
</tr>
<tr>
<td>Livistonas</td>
<td>35.69</td>
<td>Yan and Viraraghavan (2003)</td>
</tr>
<tr>
<td>NaOH-treated spent grain</td>
<td>35.50</td>
<td>Low et al. (2000)</td>
</tr>
<tr>
<td>Moroccan stevensite</td>
<td>34.16</td>
<td>Berhannou et al. (2005)</td>
</tr>
<tr>
<td>Sawdust Pinar syvdisus</td>
<td>22.22</td>
<td>Taty-Costodes et al. (2008)</td>
</tr>
<tr>
<td>Activated carbon (apricot stone)</td>
<td>22.85</td>
<td>Kobya et al. (2005)</td>
</tr>
<tr>
<td>Carbon nanotubes</td>
<td>16.14</td>
<td>Li et al. (2005)</td>
</tr>
</tbody>
</table>

\[ \Delta G^° = -RT \ln K_c \]  
\[ \log K_c = \frac{\Delta S°}{2.303R} - \frac{-\Delta H°}{2.303RT} \]

where \( K_c \) is the equilibrium constant (unitless), \( C_c \) is the equilibrium concentration in solution (mg L⁻¹) and \( C_m \) is the solid-phase concentration at equilibrium (mg L⁻¹). \( \Delta G°, \Delta H° \) and \( \Delta S° \) are changes in Gibbs free energy (kJ mol⁻¹), enthalpy (kJ mol⁻¹) and entropy (J mol⁻¹ K⁻¹), respectively. \( R \) is the gas constant (8.314 J mol⁻¹ K⁻¹), \( T \) is the temperature (K). The values of \( \Delta H° \) and \( \Delta S° \) were determined from the slope and the intercept of the plots of log \( K_c \) versus 1/T. The \( \Delta G° \) values were calculated using Eq. 5. Adsorption of Pb⁺⁺ on HB leaf powder decreased when the temperature was increased from 303 to 323 K, as shown in Fig. 4. The process was thus exothermic in nature. The plots were used to compute the values of the thermodynamic parameters (Table 2). The values of enthalpy change (\( \Delta H° \)) and entropy change (\( \Delta S° \)) recorded from this work were 40.44 kJ mol⁻¹ and 112.18 J mol⁻¹ K⁻¹, respectively for Pb⁺⁺ concentration of 50 mg L⁻¹. The negative value of \( \Delta S° \) indicates the distribution of Pb⁺⁺ ions in solution was more chaotic compared to Pb⁺⁺ ions bound to HB surface, resulted in a net decrease in entropy.

Spontaneity of the adsorption process was demonstrated by the increase in Gibbs free energy, \( \Delta G° \) (values varied from -6.63 to -4.41 kJ mol⁻¹ in the temperature range 303-323 K). The negative values of \( \Delta G° \) indicate that the equilibrium:

\[ \text{Pb}^{2+} \text{(aqueous)} + \text{HB} \rightarrow \text{Pb}^{2+} \text{-HB} \]

shifts to the right in a spontaneous manner leading to binding of Pb⁺⁺ ions on to surface constituents of HB leaf powder. \( \Delta G° \) values were found to be less negative with increasing temperature, which indicated that the adsorption of Pb⁺⁺ ions on HB leaf powder became less favorable at higher temperature.

Adsorption isotherms: Adsorption data for wide range of adsorbate concentrations are most conveniently described by Langmuir and Freundlich isotherms, which relate adsorption density \( q \), (amount of lead adsorbed in mg g⁻¹) to equilibrium adsorbate concentration in the bulk fluid phase, \( C_e \) (Fig. 5 and 6). To measure the isotherm, initial lead concentrations were varied while the adsorbent weight was kept constant. The linearized Langmuir isotherm is presented as (Langmuir, 1918):

\[ \frac{C_e}{q_e} = \frac{1}{Q^b} + \frac{C_e}{Q^\alpha} \]
It is important to compare the value of maximum adsorption capacity obtained from this study with values from other reported adsorbents, since this will suggest the effectiveness of HB leaf powder as a potential adsorbent for use in the treatment of water containing lead. The adsorption capacity for lead using HB leaf powder is of the same order or higher than other reported adsorbents, as shown in Table 4.

CONCLUSIONS

The adsorption process is exothermic and pseudo-second-order kinetic equation is better obeyed than the pseudo-first-order. Langmuir and Freundlich isotherm models govern the adsorption. This work indicates that HB leaf powder has rapid adsorption rate and high adsorption capacity for lead. HB leaf powder is a non-useful plant waste and could be used as a low-cost adsorbent for small and medium-scale industry in developing countries, hence may enhance the economies of local farmers.

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REFERENCES


