Adsorption of Pb(II) ions by using mangrove-alginate composite beads (MACB): Isotherm, Kinetics and Thermodynamics studies

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ABSTRACT
Present study explored the potential of using mangrove-alginate composite bead (MACB) as adsorbent for the removal of Pb(II) ions from aqueous solution. The batch sorption was studied under different initial concentration (20 to 100 mg/L), contact time (5 to 210 min) and solution temperature (35 to 65°C). The Langmuir, Freundlich, and Temkin isotherm models were used to analyze the experimental equilibrium data and isotherm constants. A comparison of kinetic models applied to the adsorption of Pb(II) ions on MACB beads was evaluated using pseudo-first order and pseudo-second order kinetics models. The experimental data were fitted well with the pseudo-second order kinetic model, means the mechanism of diffusion process is controlled by the adsorption reactions and not depend by the mass transfer during adsorption. Based on thermodynamics parameters, the results show that the adsorption capacity increases with an increase in temperature. The negative value of ΔH° (-1.402 kJ mol⁻¹) and the decreasing k_d value with increasing temperature, which indicate the sorption of Pb(II) onto MACB beads was feasible and an exothermic reaction. The positive value ΔS° (8.256 J mol⁻¹ K⁻¹) reflects good affinity of Pb(II) ions towards the MACB beads. The results described the potential for the MACB beads to be used as adsorbent for the removal of Pb(II) ions from wastewater.
Keywords: Alginate, Composite beads, Adsorption, Modeling, Equilibrium, Kinetics.

1. Introduction

Heavy metals pollution leads to most of the important environmental issue due to its toxic effects and accumulation throughout the food chain and also human body. Lead(II) ion was recognized as one of the toxic heavy metals during the recent years which discharged from batteries and steel industries (Muhammad et al., 2008). The accumulation of toxic lead in human body can cause severe health problem such as hypertension, brain damage and kidney damage (Lalhruaitluanga et al., 2010). It has been reported that excessive intake of lead by human may cause hepatitis and anemia, even at low concentration (Lalhruaitluanga et al., 2010). The existing of conventional methods such as ion exchange, precipitation and reverse osmosis is found to be effective for removal of heavy metals but these methods are costly and inefficient for wastewater with low concentration of metal ions (Li and Bai, 2005a).

In this article, mangrove-alginate composite bead was prepared by immobilized mangrove bark into alginate solution. Alginate, the main component of brown algae which has been reported to have a strong affinity of forming complexes with metal ions due to the abundant of carboxylic acid groups, instead of sulfonic acid and hydroxyl groups (Fourest and Volesky, 1966). In Malaysia, mangrove bark is a waste from timber industry and abundantly available at low cost. The use of mangrove bark as the material for the composite adsorbent is due to high content of tannin in bark which consists of phenolic hydroxyl groups in their structures (Nakano et al., 2001). These barks are inexpensive, abundant and contain polyphenolic compounds that favorable under suitable pH and temperature during adsorption of metal ions (Vazquez et al., 2002). Thus, the main objectives of this paper are: (i) to evaluate the dynamics of adsorption by using the pseudo-first order and pseudo-second order kinetic models (ii) to analyze the equilibrium uptake capacity of the adsorption process from various isotherm models such as Langmuir, Freundlich and Tempkin isotherm equations and (iii) to determine the adsorption feasibility of the MACB beads with the thermodynamic activation parameters such as, standard enthalpy ($\Delta H^\circ$), standard entropy ($\Delta S^\circ$) and Gibbs free energy ($\Delta G^\circ$) using VantHoff equation, respectively.

2. Experimental method

2.1 Preparation of adsorbent

The mangrove bark of *Rhizophora Apiculata* was collected from Kuala Sepetang, Perak, Malaysia. The barks were washed extensively with distilled water before dried under sunlight. After grinding the dried samples into small powder, the bark powder was sieved using 250 μm mesh size. The barks were then acid-treated according to ratio 37% formaldehyde and 0.2 N sulfuric acid at (5/20 v/v) followed by washing with distilled water and oven-dried at 60°C for 24 hrs. For alginate solution, 4 g of sodium alginate was dissolved into 160 mL deionised water under vigorously stirring. Then, 2 g of treated mangrove bark was slowly added into 100 mL of sodium alginate solution and stirred continuously at 200 rpm. For bead formation, the composite solution then was rapidly dropped into a 200 mL of 2 M calcium chloride solution using syringe pump at flow rate 3 mL min⁻¹. The beads were hardened in the solution for 24 h,
then the beads were washed using distilled water repeatedly till pH of bead neutral. The beads were dried at room temperature for 48 h and assigned as mangrove-alginate composite bead (MACB) for further experiment.

3. Results and discussion

3.1. Adsorption isotherms

Isotherm models were used to describe the distribution of adsorbate molecules between the liquid and the solid phase on the adsorbent surface at equilibrium (Sureshkumar, 2010). For isotherm studies, 0.35g of MACB beads was added in 50 ml of Pb(II) solution as the initial concentrations were varied (20 –100 mg/L) and agitates at 200 rpm, at ambient temperature of 25°C, pH 5 for 180 minutes. The equilibrium data were analyzed using three different adsorption isotherm models, Langmuir, Freundlich and Tempkin models respectively.

3.1.1. Langmuir isotherm

The Langmuir isotherm is based on the assumption that adsorption process occurs on a homogeneous surface (Hall et al., 1966) either by physical or chemical interactions. The interaction of adsorbate ion via Van der waals is known as physisorption while via covalent bond is known as chemisorptions. The linear form of the Langmuir adsorption isotherm equation is:

$$q_e = \frac{Q_o(K_L)C_e}{1 + K_LC_e}$$  \hspace{1cm} (1)

where $q_e$ (mg g$^{-1}$) is the amount of metal adsorbed per gram of the adsorbent at equilibrium, $C_e$ (mg L$^{-1}$) is the equilibrium concentration of adsorbate ion, $q_o$ is the maximum monolayer capacity (mg g$^{-1}$) and $K_L$ is the Langmuir isotherm constant (L mg$^{-1}$). The plot of 1/$q_e$ against 1/$C_e$ show a straight line with slope of 1/$Q_o$ and intercepts 1/$Q_oK_L$.

The characteristics of the Langmuir isotherm can be defined in terms of a dimensionless equilibrium parameter ($R_L$) and expressed as:

$$R_L = \frac{1}{1 + K_LC_0}$$  \hspace{1cm} (2)

where $K_L$ is the Langmuir constant and $C_0$ is the initial metal concentration (mg/L). $R_L$ values indicate the type of isotherm: to be irreversible ($R_L = 0$), favorable (0 < $R_L < 1$), linear ($R_L = 1$), or unfavourable ($R_L > 1$) (Gopalakrishnan et al., 2013). The $R_L$ values calculated from each initial metal concentration are tabulated in Table 2.0.
3.1.2. Freundlich isotherm

The Freundlich isotherm described the adsorption process occurs on a heterogeneous surface and expressed by:

\[
\log Q_e = \log K_F + \frac{1}{n} \log C_e 
\]  

(3)

where \( Q_e \) is the quantity of solute adsorbed at equilibrium (mg of adsorbate per g of adsorbent). \( C_e \) is the concentration of adsorbate at equilibrium (mg/L). \( K_F \) and \( n \) are the Freundlich constants related to adsorption capacity and adsorption intensity of the adsorbent respectively. The plot of \( \log q_e \) against \( \log C_e \) gives a straight line with slope of \( 1/n \) and intercept of \( \log K_F \).

3.1.3. Tempkin isotherm

Tempkin isotherm describes that the adsorption heat of all molecules decreases linearly with the increase in coverage of the adsorbent surface, which can be determine based on uniform distribution of binding energies during the process (Piccin et al., 2011). The linear form of the Tempkin isotherm can be described as:

\[
q_e = B \ln A_T + B \ln C_e 
\]  

(4)

where \( A_T \) is the isotherm equilibrium binding constant (L/g), \( b_T \) is the Temkin isotherm constant while \( R \) and \( B \) are the universal gas constant (8.314 J/mol/K/T) and heat of sorption (J/mol). The plot of \( q_e \) against \( \ln C_e \) for the Tempkin isotherm gives a straight line with slope of \( B \) and intercept of \( B \ln A_T \). The calculated isotherm values are presented in Table 1.0.

**Table 1** Summary Results of Isotherms Model

<table>
<thead>
<tr>
<th>Isotherm models</th>
<th>Parameters</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>( q_o = 10.84 \text{ mg g}^{-1} ) \n( K_L = 0.0247 \text{ L mg}^{-1} )</td>
<td>0.9473</td>
</tr>
<tr>
<td>Freundlich</td>
<td>( n = 0.528 ) \n( K_f = 0.026 \text{ mg g}^{-1} )</td>
<td>0.9888</td>
</tr>
<tr>
<td>Tempkin</td>
<td>( A_T = 0.1235 \text{ L g}^{-1} ) \n( B = 8.7818 \text{ mg L}^{-1} ) \n( b_T = 282.13 )</td>
<td>0.8587</td>
</tr>
</tbody>
</table>
Table 2 $R_L$ values for different initial concentrations

<table>
<thead>
<tr>
<th>Initial Pb(II) concentration, Co(mg/L)</th>
<th>20</th>
<th>40</th>
<th>60</th>
<th>80</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_L$</td>
<td>0.669</td>
<td>0.503</td>
<td>0.403</td>
<td>0.336</td>
<td>0.288</td>
</tr>
</tbody>
</table>

Based on the correlation coefficients ($R^2$) obtained, the adsorption process was found to fit well on Freundlich isotherm model rather than other isotherm models. Thus, the adsorption of Pb(II) ions by MACB beads occurred heterogeneously on adsorbent surface. The maximum adsorption capacity was 10.84 mg/g. The values of $R_L$ for each initial concentration shows a favorable occurrence of monolayer adsorption as the range of $R_L$ values between $(0 < R_L < 1)$. Thereby, the adsorption of Pb(II) ions using MACB beads was considered to be a favorable adsorption process.

3.2. Kinetic studies
To evaluate the adsorption kinetics data of Pb(II) ions by MACB beads, the pseudo-first order and pseudo-second order models were used in this study. Both of these kinetic models were determined when 0.35 g of MACB beads was suspended in 50 ml of known concentration Pb(II) solution with the contact time varied from 5 to 100 min, agitates at 200 rpm at room conditions. The correlation coefficients ($R^2$) values and comparison of experimental adsorption capacity, $q_e$ were used to predict the fitness of the kinetic models of this adsorption process.

3.2.1. Pseudo-first order
To evaluate the mechanism of kinetic for MACB beads, the pseudo first order (Lagergen, 1898) and pseudo-second order (Ho and McKay, 1999) were applied to determine the validity of the models based on plot of log ($q_e - q_t$) vs t and $(t/q_t)$ vs t, respectively. Pseudo-first order described the rate of change of solute uptake with time is directly proportional to the difference in saturation concentration and the amount of solid uptake with time (Khaled et al. 2009). A linear form of pseudo-first order can be expressed as:

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

(5)

where $q_e$ and $q_t$ are the adsorbed metal in mg/g on the adsorbent at equilibrium, time, $t$, and $k_1$ is the constant of first-order adsorption (min$^{-1}$).

3.2.2. Pseudo-second order
The pseudo-second order assumes that the rate limiting steps depend on the chemical forces of attraction and resemble the whole of adsorption process. The mathematical expression of pseudo-second order can be expressed as:
\[
\frac{1}{q_f} = \frac{1}{k_2q_e^2} + \frac{1}{q_e}
\]  
(6)

where \(k_2\) is the rate constant of second-order adsorption (g mg\(^{-1}\) min\(^{-1}\)), \(q_e\) is the amount of metal ions adsorbed at equilibrium and \(q_e^2\) is the pseudo-second order adsorption rate constant. The constants and \(R^2\) values obtained were summarized in Table 3.0.

### Table 3 Summary Results of Kinetics Models

<table>
<thead>
<tr>
<th>Kinetics models</th>
<th>Parameters</th>
<th>(R^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pseudo-first</td>
<td>(q_e = 0.1320) (mg/g)</td>
<td>0.9579</td>
</tr>
<tr>
<td></td>
<td>(k_1 = 0.00484) (min(^{-1}))</td>
<td></td>
</tr>
<tr>
<td>Pseudo-second</td>
<td>(q_e = 0.2019) (mg/g)</td>
<td>0.9887</td>
</tr>
<tr>
<td></td>
<td>(k_2 = 2.6084) (min(^{-1}))</td>
<td></td>
</tr>
</tbody>
</table>

The rate constant and the correlation coefficients (\(R^2\)) of the two kinetic models are summarised in Table 3.0. Based on the results, the kinetics data were fitted well with the pseudo-second order kinetic model than the pseudo-first order kinetic model. This indicates that overall of the adsorption process was controlled by chemisorptions process, which involves the exchange of electrons between the adsorbent and the adsorbate ions (Ho and McKay, 1999).

### 3.3. Thermodynamics studies

Temperature is one of the important parameters for the sorption of metal ions related to the thermodynamics parameters during adsorption process. Generally, the two common types of thermodynamic reaction, endothermal and exothermal sorption process can be determine based on the increase or decrease in the temperature during the process. The thermodynamic parameters change in Gibb’s free energy (\(\Delta G^\circ\)), change in enthalpy \(\Delta H^\circ\), and change in entropy \(\Delta S^\circ\) for the adsorption of Pb(II) ions using MACB beads cab be determined by using the following equation:

\[
\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ
\]  
(7)

The values of \(\Delta H^\circ\) and \(\Delta S^\circ\) are calculated from the slope and intercepts of the linear plot of \(\ln k_d\) vs \(1/T\). According to Table 4.0, the negative values of \(\Delta H^\circ\) and \(\Delta G^\circ\) indicate that the adsorption process is spontaneous and an exothermic reaction in nature. The positive value of \(\Delta S^\circ\) described the increased in randomness at the solid/solution interface during the sorption process, thus causing an increase in the disorderness of the system (Ajmal et al., 2003).
Table 4 Summary Results of Thermodynamic Model

<table>
<thead>
<tr>
<th>Temperature(K)</th>
<th>$k_d$</th>
<th>$\Delta G^0$ (KJ/mol)</th>
<th>$\Delta H^0$ (KJ/mol)</th>
<th>$\Delta S^0$ (JK$^{-1}$mol$^{-1}$)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>308</td>
<td>41.1215</td>
<td>-9.5170</td>
<td>-1.402</td>
<td>8.256</td>
<td>0.9576</td>
</tr>
<tr>
<td>318</td>
<td>45.3002</td>
<td>-10.0818</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>328</td>
<td>55.5161</td>
<td>-10.9534</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>338</td>
<td>60.1933</td>
<td>-11.5147</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

4. Conclusion

The adsorption of Pb(II) ions by MACB bead was carried out under different experimental conditions. The adsorption equilibrium data were fitted to Langmuir, Freundlich, and Tempkin isotherms and the equilibrium data was fitted well to Freundlich isotherm model, with the maximum monolayer adsorption capacity of 10.84 mg g$^{-1}$ respectively. The kinetic model was found to follow pseudo-second order kinetic model compare to pseudo-first order model as evident in their correlation coefficients ($R^2$) values. The negative values of $\Delta H^0$ and $\Delta G^0$ indicate the adsorption process is spontaneous and an exothermic reaction in nature. Hence, the results indicate that the MACB beads is suitable as a potential adsorbent for adsorption of Pb(II) ions from aqueous solutions.

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References


