Kinetic, Equilibrium, and Thermodynamic Studies of the Biosorption of Pb(II) from solution by Calymperes erosum.

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ABSTRACT

In this study, the batch removal of Pb(II) from dilute aqueous solution using Calymperes erosum as the biosorbent has been investigated. The Pb(II) uptake was dependent on the initial pH, contact time, initial metal ion concentration and temperature. The residual Pb(II) in the solution was determined using Atomic Absorption Spectrophotometer (AAS). The optimum pH range for the biosorption was pH 4. Maximum biosorption was obtained after 75 min of the process. Kinetic study showed that the pseudo-second-order rate equation described the biosorption process better than the pseudo-first-order kinetics. The adsorption isotherms obtained fitted well into the Freundlich and Langmuir isotherm. The Freundlich equation obtained was log $\Gamma = 0.8348 \log C_e + 1.0629$ while the Langmuir equation obtained was $1/\Gamma = 0.0881/C_e + 0.0047$. The correlation factors obtained were 0.9987 and 0.9923, respectively. The standard deviation values are 0.102 and 0.001, respectively. The free energy change obtained for the biosorption of Pb(II) at 300K, initial Pb(II) concentration of 100mgL$^{-1}$ and pH 4 was $-5.4775$ kJmol$^{-1}$. The thermodynamic study showed that the increase in temperature led to decrease in the amount of the metal ion biosorbed. These results indicate that Calymperes erosum has potential for the uptake of Cd(II) from industrial effluents.

(Keywords: Calymperes erosum, lead(II), biosorption, equilibrium, thermodynamics)

INTRODUCTION

Toxic heavy metal contamination has been described as a worldwide environmental problem (Seker et al., 2008). Biosorption of heavy metals from solution has gained much attention in the recent years due to its merit of being a safe and cost effective process. It has therefore, been found to be a better and an alternative ‘technology’ for treatment of effluents containing these metals. The mechanism of the biosorption process has been reported to be very complex and it may involve the combination of diffusion, adsorption, chelation, complexation, co-ordination, or micro-precipitation mechanisms depending on the specific biosorbent (Veglio and Beolchini, 1997). Therefore, biosorption can be affected by many chemical and physical variables such as pH, ionic strength, biomass dosage and presence of other metal ions. All these factors must be investigated in order to have a better understanding of the phenomenon.

Lead was chosen for this biosorption studies due to its wide use in industry and potential pollution impact. It is extensively used in many industrial applications, such as storage battery manufacturing, printing pigments, fuels, photographic materials, and explosive manufacturing (King et al., 2007). Lead has been known for its toxicity for a long time as one of the most toxic heavy metals, which may cause health problems such as behavioral anomaly, learning disabilities and seizures (Bulut and Baysal, 2006). Different biological materials have been used for the biosorption of lead(II) from aqueous solutions (Klic et al., 2006, Green-Ruiz et al., 2008, Panda et al., 2008, Pandey et al., 2008, Romera et al., 2008 Ziagova et al., 2007). These include algae (Seker et al., 2008; Hanni et al., 2007; Sari et al., 2007; Vilar et al., 2008; Apiratikul and Pavasant , 2008; Uluozlu et al., 2008; Romera et al., 2007) seaweed (Tsui et al,
2006), passion-fruit shell (Jacques et al., 2007), rice husk (Krishmani, 2008), bacteria (Burnett et al., 2007), pectin-rich fruit (Schiewer and Patil, 2008), and maize leaf (Babarinde et al., 2008a). The use of bacteria, algae and fungi or their separated components as biosorbents has been reported widely. In this study, we evaluated the biosorption capacity of the dried moss, Calymperes erosum, which is a nonvascular green plant that produces spores instead of seed for removal of Pb(II) from aqueous solution.

MATERIALS AND METHODS

The plant (Calymperes erosum) used as the biosorbent was obtained on a palm tree trunk in dry form from a farm settlement in Apoje, Ogun State, Nigeria. It was kept in a dry place until the time of usage.

Preparation of metal solution

The lead salt used for this study was analytical grade of Pb(NO3)2. Stock solution of 1000 mgL\(^{-1}\) of Pb\(^{2+}\) was prepared from the salt. The initial pH of each solution was adjusted to the desired pH by drop wise addition of 0.1M HNO\(_3\) and/or 0.1M NaOH solution. Fresh dilution of the stock solution was done for each biosorption study.

Biosorption Studies

The methods used for the biosorption studies are similar to those earlier reported (Babarinde et al., 2008b). Each of the batch biosorption studies was carried out by contacting 0.2g of the Calymperes erosum with 25ml of 100mgL\(^{-1}\) Pb(II) solution in a glass tube.

Effect of contact time on biosorption

The biosorption of Pb(II) by Calymperes erosum plant was studied at various time intervals (5-300 min). A constant concentration of 100 mgL\(^{-1}\) was used. 0.2g of Calymperes erosum (biomass) was weighed into each glass tube and 25ml of Pb(II) solution at pH 4 was introduced into it.

Effect of initial Pb(II) concentration on biosorption

Batch biosorption study was carried out using a concentration range of 10 – 100 mg L\(^{-1}\). 0.2g of the Calymperes erosum was introduced into each of the glass tube employed and 25ml of Pb(II) solution at pH 4 was added to the tubes. The biosorption mixture was then maintained in a thermostated water bath in order to maintain the temperature at 27\(^{0}\)C for optimum contact time required to reach equilibrium time. The biosorbent was removed from the solution and the concentration of residual Pb(II) ion in each solution was determined.

Effect of temperature on biosorption

The biosorption of Pb(II) by Calymperes erosum was studied at temperatures between 21\(^{0}\)C and 37\(^{0}\)C with a constant concentration of 100 mgL\(^{-1}\) of the Pb(II) solution used. 0.2g of the Calymperes erosum was introduced into each of
the glass tubes employed and 25ml of Pb(II) solution at pH 4 was added to the tubes. The biosorption mixture was then left in a thermostated water bath to maintain the temperature for optimum time. The biosorbent was removed from the solution by centrifuging and the concentration of residual Pb(II) ion in each solution was determined.

**Statistical analysis**

The curve fittings of all the data obtained were performed using Microcal Origin 6.0® software.

**RESULTS AND DISCUSSION**

**Effect of pH on biosorption**

Preliminary study on the effect of pH was carried out to determine the optimum pH for maximum lead(II) uptake by the biosorbent before investigating the kinetic, equilibrium and thermodynamic studies on the biosorption. The optimum pH has been reported to be closely related to the chemical speciation of metal ion, speciation of the functional groups on the biosorbent, and the nature of interaction of the metal ion with the biosorbent functional groups (Seker et al., 2008). The optimum pH is different for each type of metal ion and biosorbent for efficient biosorption (Veglio and Beolchini, 1997). The pH of the solution significantly affects the cell wall of the biosorbent as well as the solution chemistry.

The biosorption of metal ion (represented as M\(^{2+}\) for a divalent metal ion) from the liquid phase to the solid phase, the biosorbent with lone pair of electron (represented as \(\hat{A}\)), can be considered as a reversible reaction with an equilibrium being made between the two phases as schematically shown below:

\[
\hat{A} + M^{2+} \rightleftharpoons A-M
\]  

The pH of the solution therefore controls the biosorption process. A decrease in pH to the acidic range makes the biosorbent to be highly protonated hence the amount of the metal ions biosorbed is reduced. This is because the metal ions are prevented from binding to the functional groups on the biosorbent. On the other hand, increase in pH to the basic range enhances the biosorption process by the lone pair of electrons. In other words, the net charge on the biosorbent is determined by the pH and this will determine the amount of metal ions biosorbed.

The result of this study is presented in Figure 1 where optimum pH is pH 4. The amount of the metal ions biosorbed was lower at other pH values but much lower at pH 1 due to high protonation of the cell wall of the biosorbent and the competition between hydrogen ion and lead ions for the same binding sites in the biosorbent at that pH value.

![Figure 1: Effect of pH on the biosorption of Pb(II) using Calymperes erosum.](http://www.akamaicaiuniversity.us/PJST.htm)

**Kinetics of the biosorption**

The effect of contact time on the biosorption of is shown in Figure 2. This shows that optimum biosorption was obtained within 75 of the biosorption process. The pseudo-first-order, pseudo-second-order and the intra-particle diffusion rate equations were applied to the kinetic study as shown below in the following equations:

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

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}
\]  

\[
\log R = b \log t + \log K_s
\]
where $k_1$ is the Lagergren rate constant of the biosorption (min$^{-1}$); $k_2$ is the pseudo-second-order rate constant (g mg$^{-1}$ min$^{-1}$); $q_e$ and $q_t$ are the amounts of metal ions biosorbed (mg g$^{-1}$) at equilibrium and at time $t$, respectively. $R$ is the percent metal biosorbed, $t$ is the contact time of the biomass with the metal ions (min), $b$ is the gradient of linear plots and $K_s$ is the intra-particle diffusion constant.

The pseudo-second-order plot gave a better result than the pseudo-first-order plot. However, the biosorption does not support the intra-particle diffusion equation. The pseudo-second-order model is considered to be the best correlation for this biosorption process. Figures 3 and 4 show the results of the pseudo-first-order and pseudo-second-order correlations, respectively. These plots were constructed using the model parameters obtained from the linear regression analyses. The linear regression plots of $\log(q_e-q_t)$ versus $t$ for the biosorption of Pb(II) ions on the biomass at initial concentration of 100 mg L$^{-1}$ obey the pseudo-first-order reversible kinetics as shown in Figure 3. The overall rate constant of the biosorption ($k_1$) was calculated from the slope of the plot. The linear regression of $t/q_t$ against $t$ gave the rate constant, $k_2$, which are given in Table 1, together with $q_e$ and the linear correlation coefficients, $R$.

### Isotherm models of the biosorption

The isotherm models are mathematical models describing the distribution of metal ions between the solid and liquid phases that are in contact. The Freundlich and Langmuir isotherms are the most commonly used (Kilic et al., 2008; Sari et al., 2007; Uluözlu et al., 2008; Bueno et al., 2008; Demirbas, 2008).

<table>
<thead>
<tr>
<th>Freundlich Parameters</th>
<th>$N$</th>
<th>$K_f$</th>
<th>$R$</th>
<th>S.D</th>
</tr>
</thead>
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<tr>
<td>1.1979</td>
<td>11.5585</td>
<td>0.9987</td>
<td>0.102</td>
<td></td>
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</table>

<table>
<thead>
<tr>
<th>Langmuir Parameters</th>
<th>$b_m$</th>
<th>$Γ_m$</th>
<th>$R$</th>
<th>S.D</th>
</tr>
</thead>
<tbody>
<tr>
<td>11.3507</td>
<td>212.77</td>
<td>0.9846</td>
<td>0.001</td>
<td></td>
</tr>
</tbody>
</table>
The Freundlich model can be applied for non-ideal sorption on heterogeneous surfaces and multiplayer sorption. The Freundlich model (Freundlich, 1906) is:

\[ \log \Gamma = \frac{1}{n} \log C_e + \log K_f \]  
(5)

where \( K_f \) is a constant relating the biosorption capacity and \( \frac{1}{n} \) is an empirical parameter relating the biosorption intensity, which varies with the heterogeneity of the biomass.

The isotherm is presented in Figure 5. Linear regression of the model gave the Freundlich equation as \( \log \Gamma = 0.8348 \log C_e + 1.0629 \) with correlation coefficient (R²) of 0.9987. The R² value indicated that the biosorption of Pb(II) on *Calymperes erosum* fitted well the Freundlich model.

The Langmuir model (Langmuir, 1918) assumes that biosorption occurs at specific homogenous sites on the biosorbent and is used successfully in many monolayer biosorption processes. The model in its linear form is written as:

\[ \frac{1}{\Gamma} = \frac{1}{b_m C_e} + \frac{1}{\Gamma_m} \]  
(6)

where \( \Gamma \) and \( C_e \) are the equilibrium metal ion concentrations on the biosorbent (mg g\(^{-1}\)) and in the solution (mg l\(^{-1}\)), \( b_m \) the monolayer biosorption capacity of the biosorbent (mg g\(^{-1}\)) and \( \Gamma \) is the Langmuir biosorption constant (L mg\(^{-1}\)) relating the free energy of biosorption, respectively. The isotherm is presented in Figure 6. Linear regression of the isotherm gives the Langmuir equation as \( 1/\Gamma = 0.0881/C_e + 0.0047 \) with correlation coefficient (R²) of 0.9846. The values of the correlation coefficients for the two isotherms show that the Freundlich model better represents the biosorption process. The values of the parameters for the two models are presented in Table 1.

![Figure 5](image_url)

**Figure 5:** Freundlich Isotherm for the Biosorption of Pb(II) from Aqueous Solution using *Calymperes erosum* at 27°C and pH 4.

The same data was employed in the calculation of biosorption efficiency given as:

\[ E = 100 \left( \frac{C_i - C_e}{C_i} \right) \]  
(7)

where \( C_i \) and \( C_e \) are the concentrations of the metal ions at initial and equilibrium times, respectively.

The efficiency plot is presented in Figure 7. The result shows that the efficiency of the biosorbent decreases with increase in the initial concentration of the metal ion. This was due to the fixed number of binding sites on the...
biosorbent. The increase in the initial concentration only led to increase in the amount of the metal ions left in solution.

**Figure 7**: Removal Efficiency of Pb(II) by *Calymperes erosum* at 27°C and pH 4.

**Thermodynamics of the biosorption**

In order to describe the thermodynamics of the biosorption of Pb(II) by *Calymperes erosum* from aqueous solution, thermodynamic parameters such as the change in free energy (Δ\(G^\circ\)), enthalpy (Δ\(H^\circ\)) and entropy (Δ\(S^\circ\)) were calculated from equations 8-12.

\[
\Delta G^\circ = -RT \ln K_c 
\]

(8)

where Δ\(G^\circ\) is the standard Gibbs free energy change for the biosorption (Jmol\(^{-1}\)), R is the universal gas constant (8.314 Jmol\(^{-1}\)K\(^{-1}\)), and T the temperature (K).

The distribution ratio, \(K_c\), is defined as:

\[
K_c = \frac{C_{ad}}{C_c} 
\]

(9)

\(K_c\) reflects the extent of distribution of the Pb(II) ions between the biomass (mg g\(^{-1}\)) and liquid (mgL\(^{-1}\)) phases at equilibrium.

The free energy change obtained for the biosorption of Pb(II) at 300K, initial Pb(II) concentration of 100mgL\(^{-1}\) and pH 4 was -5.4775 kJmol\(^{-1}\). The thermodynamic study showed that the increase in temperature led to decrease in the amount of the metal ion biosorbed.

The entropy and enthalpy parameters were estimated from the following equations:

\[
\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} 
\]

(10)

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

(11)

\[
\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} 
\]

(12)

The plot of Δ\(G^\circ\) against T shown in Figure 8 gives a linear fit with slope of -Δ\(S^\circ\) and intercept of Δ\(H^\circ\). The entropy and enthalpy values obtained from the plot are -44.468 Jmol\(^{-1}\)K\(^{-1}\) and -18.244 KJmol\(^{-1}\), respectively. The decrease in Δ\(G^\circ\) values with increase in temperature shows a decrease in feasibility of biosorption at higher temperatures. The negative Δ\(S^\circ\) value suggests a decrease in the randomness at the solid/liquid interface during the biosorption of Pb(II) ions onto *Calymperes erosum*. The negative Δ\(H^\circ\) value indicates the endothermic nature of the biosorption process within the temperature range of our study.

**Figure 8**: Thermodynamics Plot for the Biosorption of Pb(II) on *Calymperes erosum*.

**CONCLUSIONS**

In this study, the ability of *Calymperes erosum* to bind Pb(II) ions from aqueous solutions was investigated. The biosorption process has been shown to be affected by pH, contact time, initial metal ion concentration and temperature. The optimum pH range for the biosorption was pH 4. Optimum biosorption was obtained after 75 min.
of the process. Kinetic study showed that the pseudo-second-order rate equation described the biosorption process better than the pseudo-first-order kinetics. The adsorption isotherms obtained fitted well into the Freundlich and Langmuir isotherm. Increase in temperature led to increase in the biosorption of Pb(II) indicating and endothermic process.

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