Adsorption of Lead(II) Ions using Surface-Modified Chitins

Seoung-Hyun Kim, Hoon Song, Grace Mashate Nisola, Juhyeon Ahn, Melvin Maaliw Galera, Chang hee Lee*, and Wook-Jin Chung+

Department of Environmental Engineering and Biotechnology, Myongji University, Yongin 449-728, Korea
*Korea Environment Institute, Seoul 122-706, Korea

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Abstract: To establish the feasibility of the removal of lead using chitin, adsorption characteristics were investigated at various temperatures and concentrations. The adsorption characteristics of chitin were analyzed by determining its adsorption equilibrium, kinetics, and thermodynamic properties. The data gathered favor the Langmuir over the Freundlich model. The adsorption capacity of the surface-modified natural chitin for Pb(II) removal increased significantly when the adsorbent was treated using the xanthation method. The homogeneous surface diffusion model described the adsorption kinetic data well and can be used to predict the chitin performances; therefore, it could be helpful for design considerations. Under the steady-state reaction conditions, the change in Gibbs free energy (ΔG°) ranged from -19.03 to -21.50 kJ/mol, and the enthalpy (ΔH°) and entropy (ΔS°) changes were 16.54 kJ/mol and 0.124 kJ/mol/K, respectively; i.e., a higher temperature favors a spontaneous Pb(II) adsorption by chitin when using the xanthation method. Thermodynamic calculations indicate that the adsorption of lead on the adsorbents was spontaneous and endothermic. Application of the chitin modified with the xanthation method to the removal of Pb(II) metals from wastewater is expected to be economical and effective.

Keywords: adsorption, lead (II) ion, adsorbent, chitin, xanthation, phosphorylation

Introduction

Heavy metal contamination of various water resources is of great concern because of their toxic effects to human beings and other animals and plants in the environment. The presence of lead in drinking water is known to cause various serious health problems, leading to death in extreme cases. Severe exposure to lead has been associated with sterility, abortion, stillbirths, and neo-natal deaths [1,2]. Lead could exist either in organic or inorganic forms of Pb(II); it is known as a metabolic poison [3].

The several technologies for Pb(II) removal include ion exchange, chemical precipitation with lime, and electrochemical treatment. However, these technologies are often inefficient and/or are very expensive when used for the reduction of Pb(II) ions to very low concentrations [4-6].

The adsorption process plays an important role in removing heavy metals, such as lead, from wastewater. There has been much research into the development of low-cost alternatives to activated carbon; these materials include fly ash, metal oxides, zeolites, peats, chitosans, and activated sludge [7-12].

New methods are required to reduce heavy metal concentrations to environmentally acceptable levels at affordable cost. The adsorption processes are generally among the most effective techniques for the removal of highly toxic metals. Adsorbents that have strong affinities and high loading capacities for targeted metal ions have been developed by modifications of various surfaces with metal-complexing groups [13-15].

Chitin, a natural polymer of acetylated and non-acetylated glucosamine, has been widely postulated as being a cell wall component responsible for metal adsorption [16-19]. To increase the uptake capacity of chitin, the hydroxyl groups of the adsorbent, which has low affinity
for heavy metals, were modified with several functional groups through chemical reactions. Xanthation and phosphorylation are two techniques that could be used to modify chitin to enhance its heavy metal adsorption capacity. Both methods introduce a group that could improve heavy metal uptake. Xanthation has been reported to improve the metal binding capabilities of algae in terms of Pb, Cd, and Zn sequestration [13], while xanthation has been used previously on cellulose and sawdust [20]. Most previous studies have focused on the chitin derivative chitosan. However, chitosan has several drawbacks, such as its solubility in water and the additional cost of the deacetylation step required to yield chitosan from chitin [21]. Furthermore, almost no literature is available regarding the application of phosphorylation and xanthation processes to chitin [21].

For a new set of adsorbents, it is necessary to determine their maximum capacity in order to discern the best approach for optimization. Also, equilibrium and kinetic data are needed, coupled with mathematical tools for data interpretation. In this manner, the system’s behavior could be easily predicted, which is essential for process design. The thermodynamic aspect of the system is also needed to support the equilibrium and kinetic data.

The main rationale of this study was to obtain basic information for the design of an adsorption process, i.e., equilibrium and kinetic data, in batch systems for Pb(II) removal by xanthated and phosphorylated chitin. The xanthate and phosphoryl groups were introduced onto the wall of the biopolymer and their lead adsorption characteristics were compared to that of the control (chitin).

To describe the isotherm mathematically, the experimental data were fitted to the Langmuir and Freundlich equations. Kinetic studies included the effects of the system temperature and the initial Pb(II) concentration. Thermodynamic data were interpreted using Vant Hoff and Clausius Clapeyron equations.

Materials and Methods

Adsorbents

Natural chitin, Undaria Pinnafida, from crushed crab shells (Sigma C-7170) was used throughout this study. Because the purpose of this study was to test the effect of xanthation and phosphorylation, the physical and chemical properties of the purchased chitin were not determined; thereby, the basis of comparison was on the control experiment with the untreated adsorbent. Xanthated and phosphorylated chitins were prepared using xanthation and phosphorylation methods, respectively. These three adsorbents were then compared in this study.

Xanthation of Adsorbents

The xanthation reaction of adsorbents was conducted in two steps, as illustrated in Figure 1. The first step was the hardening of the cell wall structure through a cross-linking reaction using epichlorohydrin. The second step was the introduction of the xanthate group to the hardened cell wall through a chemical reaction with carbon disulphide ($\text{CS}_2$). In the first step, powdered chitin biomass (10 g) was mixed with 600 mL of 0.07 N NaOH for 30 min. Epichlorohydrin (18 mL) was added and the mixture was then heated at 40 °C for 5 h. After cooling, the reaction mixture was filtered through 0.45-µm filter paper (Whatman No. 1) and the residue was washed thoroughly with deionized water. In the second step, the hardened biomass was mixed with 100 mL of 10% (w/v) NaOH for 30 min. $\text{CS}_2$ (10 mL) was added and then the mixture was reacted for 5 h at room temperature. The reaction mixture was filtered and the residue on the filter paper was washed thoroughly with ethanol and stored under a nitrogen atmosphere in the dark in a desiccator.

Phosphorylation of Adsorbents

Figure 2 shows the phosphorylation process of chitin and its expected mechanism for Pb(II) removal. The adsorbent (10 g) was mixed with 5 g each of urea and phosphate [phosphoric acid (2 g); monosodium phosphate (3 g)]. The mixture was left to stand at room temperature
Adsorption of Lead(II) Ions using Surface-Modified Chitins

Figure 2. Chitin phosphorylation process and its mechanism for Pb(II) removal.

Table 1. Calculated Langmuir and Freundlich coefficients

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>T (K)</th>
<th>$q_{\text{max}}$ (mg/g)</th>
<th>b (L/mg)</th>
<th>$r^2$</th>
<th>k (L/mg)</th>
<th>n</th>
<th>$r^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xanthated chitin</td>
<td>288.15</td>
<td>262</td>
<td>1.36E-02</td>
<td>0.997</td>
<td>9.90</td>
<td>1.68</td>
<td>0.996</td>
</tr>
<tr>
<td></td>
<td>298.15</td>
<td>292</td>
<td>1.67E-02</td>
<td>0.996</td>
<td>15.63</td>
<td>1.86</td>
<td>0.993</td>
</tr>
<tr>
<td></td>
<td>308.15</td>
<td>316</td>
<td>2.13E-02</td>
<td>0.996</td>
<td>20.50</td>
<td>1.94</td>
<td>0.992</td>
</tr>
<tr>
<td>Phosphorylated chitin</td>
<td>288.15</td>
<td>248</td>
<td>1.13E-02</td>
<td>0.994</td>
<td>7.21</td>
<td>1.58</td>
<td>0.991</td>
</tr>
<tr>
<td></td>
<td>298.15</td>
<td>249</td>
<td>1.61E-02</td>
<td>0.986</td>
<td>11.69</td>
<td>1.77</td>
<td>0.993</td>
</tr>
<tr>
<td></td>
<td>308.15</td>
<td>258</td>
<td>2.13E-02</td>
<td>0.988</td>
<td>17.37</td>
<td>1.96</td>
<td>0.991</td>
</tr>
<tr>
<td>Natural chitin</td>
<td>288.15</td>
<td>226</td>
<td>1.01E-02</td>
<td>0.989</td>
<td>7.39</td>
<td>1.69</td>
<td>0.991</td>
</tr>
<tr>
<td></td>
<td>298.15</td>
<td>237</td>
<td>1.15E-02</td>
<td>0.997</td>
<td>8.67</td>
<td>1.72</td>
<td>0.992</td>
</tr>
<tr>
<td></td>
<td>308.15</td>
<td>264</td>
<td>1.21E-02</td>
<td>0.985</td>
<td>13.70</td>
<td>1.58</td>
<td>0.980</td>
</tr>
</tbody>
</table>

for 30 min before it was placed in a drying oven at 70 °C for 60 min. The biomass was then mixed with 100 mL of dimethylformamide and reacted for 5 h at 100 °C in a muffle furnace. The phosphorylated biomass was separated by centrifugation and washed with distilled water to remove any excess of unreacted reagents.

Results and Discussion

In principle, the process modifications conducted, xanthation and phosphorylation, imply an ion-exchange mechanism, wherein the light metal sodium salts, which is bound to the bridging functional groups, are displaced during metal uptake. However, T. Davis and coworkers pointed out that the phenomenon of ion exchange in this situation does not explicitly identify the binding mechanism of the system for the reason that the binding mechanisms may range from physical to chemical interactions between the metal and sorbent [23]. In measuring the metal-chitin interaction, theoretically, an ion-exchange mechanism could actually be incorporated with adsorption isotherms [23]. Adsorption isotherms are adapted widely in studies of heavy metal removal through biosorption and adsorption because of the simplicity of the assumptions involved. Nonetheless, ion-exchange models, though they represent a more realistic depiction of the system, are more complex yet still do not accurately

Adsorption Equilibrium, Kinetic, and Thermodynamic Studies

A synthetic lead(II) solution was prepared by dissolving lead nitrate [Pb(NO$_3$)$_2$] (Sigma L-7281) in distilled water. Experiments were conducted in duplicate, using 100 mL Erlenmeyer flasks. For adsorption equilibrium studies, initial metal concentrations were varied between 10 and 30 mg lead(II)/L. Samplings and analyses were halted once the final concentrations of the lead solutions became stable.

Batch adsorption kinetic experiments were performed at initial lead(II) concentrations from 100 to 300 mg/L. The adsorbent (1 g/L) was added in 100 mL solution and shaken for 6 h at 250 rpm. Samples (5 mL) were taken after the addition of the metal solution.

All experiments reported here were investigated at an initial pH of 4 because lead(II) ions gradually precipitate at pH > 5.0 and hydronium ions (H$_3$O$^+$) compete with Pb(II) ions at pH < 4.0 [22].
Adsorption Equilibrium Studies

Equilibrium data can be analyzed using commonly known adsorption isotherms to provide a basis for the design of adsorption systems. The Langmuir equation is valid for monolayer sorption onto a surface having a finite number of identical sites [24]:

\[ q = \frac{q_{\text{max}} b C}{1 + b C} \]  

(1)

This equation represents a practical limiting adsorption capacity when the surface is fully covered with lead. The values of \( q_{\text{max}} \) and \( b \) can be determined from a linear plot.

On the other hand, the Freundlich model [Eq. (2)] is an empirical equation based on sorption on a heterogeneous surface [25]. The Freundlich equation can be linearized, by taking logarithms, so that the constants can be determined.

\[ q = k C^{1/n} \]  

(2)

Experimental equilibrium data were fitted to the Langmuir and Freundlich isotherms, in Figures 3 and 4, respectively; Table 1 presents the corresponding calculated model parameters. The xanthated chitin exhibited the highest adsorption capacity, while natural chitin gave the lowest values. To further understand the higher effectiveness of xanthation, over phosphorylation, for Pb(II) adsorption, activation energies of sulfur and phosphorus were calculated to be 1011.7 and 999.6 kJ/mol, respectively. These values mean that the sulfur ions are more easily ionized to react with Pb(II) metal ions than are phosphorus groups [26].

For the model fitting, we observe that a favorable model depends on the system temperature and the type of adsorbent. Generally, higher temperature enhances the adsorption capacity of a particular adsorbent. However, as the temperature is increased, the behavior of the system tends to deviate from the models, as indicated by the decreased correlation coefficients \( (r^2) \). The experimental results showed a better fit to the Langmuir than to the Freundlich equation, especially for the xanthated and phosphorylated chitins.

Adsorption Kinetics Studies

The material balance in the batch reactor can be described by

\[ \frac{dC_b}{dt} = -\frac{M}{V} \frac{dq}{dt} \]  

(3)

In addition, the homogeneous surface diffusion model [Eqs. (4) ~ (7)] has been used in the study of adsorption kinetics. The homogeneous surface diffusion model consists of a three-step process: (i) the adsorbate diffuses through a stagnant liquid film layer surrounding the carbon particle; (ii) the adsorbate adsorbs from the liquid phase onto the outer surface of the carbon particle; (iii) the adsorbate diffuses along the inner surface of the
Adsorption of Lead(II) Ions using Surface-Modified Chitins

\[ t = 0, \quad q_i = 0 \]  
\[ r = 0, \quad \frac{\partial q_i}{\partial y} = 0 \]  
\[ r = r_m \quad D \frac{\partial q_i}{\partial y} = k_f (C - C_e) \]

The values of $k_f$ and $D_s$ can be computed using the isotherm parameters and the equations above. The batch reactor model was solved numerically by applying the orthogonal collocation method to discretize the equations. Discretization was performed for the spatial variable, resulting in a set of time-derivative ordinary differential equations (ODEs) for the adsorbate concentration. The resulting sets of ODEs were solved using the subroutine LSODA [27].

The adsorption kinetic data obtained from different temperatures and adsorbents were analyzed using a homogeneous surface diffusion model, which was useful for design purposes. This model fits well to the experimental results. The adsorption kinetic experiments were performed using the best adsorbent (xanthated chitin), which was determined from the equilibrium data presented earlier at different temperatures, as shown in Figures 5 and 6.

The lumped effective mass-transfer parameters of the adsorption rate, the external film mass transfer coefficients ($k_f$), and the effective intraparticle surface diffusion coefficients ($D_s$) were derived from the experimental concentration histories through an iterative two-parameter search technique predicted from the minimization of the sum of squares of residuals. To predict the kinetic data, the estimated mass transfer and diffusion coefficients, shown in Tables 2 and 3, were used. We found that increasing the operation temperature improved both the mass transfer coefficient ($k_f$) and the surface diffusion.

### Table 2. Estimated Mass Transfer and Diffusion Coefficients at Various Temperatures

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$k_f$ (m/s)</th>
<th>$D_s$ (m$^2$/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>288.15</td>
<td>9.20E-04</td>
<td>1.45E-11</td>
</tr>
<tr>
<td>298.15</td>
<td>1.10E-03</td>
<td>2.63E-11</td>
</tr>
<tr>
<td>308.15</td>
<td>2.20E-03</td>
<td>3.46E-11</td>
</tr>
</tbody>
</table>

### Table 3. Estimated Mass Transfer and Diffusion Coefficients at Various Concentrations

<table>
<thead>
<tr>
<th>Concentrations (mg Pb/L)</th>
<th>$k_f$ (m/s)</th>
<th>$D_s$ (m$^2$/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>1.63E-03</td>
<td>1.54E-11</td>
</tr>
<tr>
<td>150</td>
<td>1.42E-03</td>
<td>1.97E-11</td>
</tr>
<tr>
<td>200</td>
<td>1.23E-03</td>
<td>2.36E-11</td>
</tr>
<tr>
<td>250</td>
<td>1.13E-03</td>
<td>2.37E-11</td>
</tr>
<tr>
<td>300</td>
<td>1.10E-03</td>
<td>2.63E-11</td>
</tr>
</tbody>
</table>

The above equation can be solved numerically by setting the initial and boundary conditions:

\[ -\frac{\partial q_i}{\partial t} = D_s \left( \frac{\partial^2 q_i}{\partial y^2} + \frac{2}{r} \frac{\partial q_i}{\partial y} \right) \]

**Figure 5.** Adsorption kinetics of lead(II) on the xanthated chitin plotted in terms of the temperature (Co=300 mg Pb / L; V = 1 L; weight of adsorbent = 1.0 g/L; average particle size=500 µm).

**Figure 6.** Adsorption kinetics of lead(II) at different initial concentrations by xanthated chitin (Co=100, 150, 200, 250, 300 mg Pb / L; V = 1 L; weight of adsorbent = 1.0 g/L; average particle size=500 µm).
Table 4. Thermodynamical Parameters for Lead(II) Adsorption

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Temperature (K)</th>
<th>b (L/mol)</th>
<th>ΔG° (kJ/mol)</th>
<th>ΔH° (kJ/mol)</th>
<th>ΔS° (kJ/mol/K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xanthated chitin</td>
<td>288.15</td>
<td>2817.9</td>
<td>-19.03</td>
<td>16.54</td>
<td>0.124</td>
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<tr>
<td></td>
<td>298.15</td>
<td>3460.2</td>
<td>-20.20</td>
<td>23.42</td>
<td>0.146</td>
</tr>
<tr>
<td></td>
<td>308.15</td>
<td>4413.4</td>
<td>-21.50</td>
<td>6.70</td>
<td>0.087</td>
</tr>
<tr>
<td>Phosphorylated chitin</td>
<td>288.15</td>
<td>2341.4</td>
<td>-18.59</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>298.15</td>
<td>3335.9</td>
<td>-20.11</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>308.15</td>
<td>4413.4</td>
<td>-21.50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Natural chitin</td>
<td>288.15</td>
<td>2092.7</td>
<td>-18.32</td>
<td>23.42</td>
<td>0.146</td>
</tr>
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<td>298.15</td>
<td>2382.8</td>
<td>-19.28</td>
<td>6.70</td>
<td>0.087</td>
</tr>
<tr>
<td></td>
<td>308.15</td>
<td>2507.1</td>
<td>-20.05</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The value of ΔG° gives information on the spontaneity of the adsorption process. A higher negative value reflects a more energetically favorable adsorption.

\[
\Delta G^0 = -RT \ln (\ell) \tag{10}
\]

Thermodynamic parameters, namely the Gibbs free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°), were calculated using equations (8), (9), and (10).

The negative values of ΔG° indicate that the adsorption of lead onto the adsorbents was spontaneous under the experimental conditions. As shown in Table 4, the values of ΔH° and ΔS° for the adsorption of lead on xanthated chitin were 16.54 kJ/mol and 0.124 kJ/mol/K, respectively. In the case of phosphorylated chitin, the corresponding values were 23.42 kJ/mol and 0.146 kJ/mol/K, respectively; for natural chitin, they were 6.70 kJ/mol and 0.087 kJ/mol/K, respectively. The positive values of the enthalpy change (ΔH°) indicate that the adsorption of the lead ions onto the biomass was endothermic, while the positive values of the entropy change (ΔS°) reflect the affinity of the biomass for the lead ions and suggest increased randomness at the adsorbent/solution surface.

Conclusions

The adsorption capacity of chitin for Pb(II) increased significantly when it was surface-modified through xanthation. The homogeneous surface diffusion model described the adsorption kinetic data well; it can be used to predict the chitin performances and, therefore, it may be helpful for design considerations. Thermodynamic calculations indicate that the adsorption of lead onto the adsorbents was spontaneous and endothermic. The application of chitin, after modification through xanthation, to the removal of Pb(II) ions from wastewater is expected to be economical and effective.
Acknowledgment

This study was supported by a grant (Code 20050401-034-750-142-01-00) from BioGreen 21 Program, Rural Development Administration, Republic of Korea.

Nomenclature

\[ b: \text{Langmuir adsorption equilibrium constant [L/mg]} \]
\[ C: \text{solute fluid phase concentration [mg/L]} \]
\[ C_b: \text{concentration at the bulk phase [mg/L]} \]
\[ C_s: \text{concentration at the external surface of adsorbent particles [mg/L]} \]
\[ D_s: \text{surface diffusion coefficient [m}^2\text{/s]} \]
\[ k: \text{Freundlich constant [-]} \]
\[ k_f: \text{external mass transfer coefficient [m/s]} \]
\[ M: \text{weight of adsorbent [g]} \]
\[ n: \text{Freundlich constant [L/mg]} \]
\[ q: \text{adsorbed amount [mg/g]} \]
\[ q_t: \text{adsorbed amount with time [mg/g]} \]
\[ q_{\text{max}}: \text{Langmuir adsorption equilibrium constant [mg/g]} \]
\[ R: \text{universal gas constant [8.314 J/mol/K]} \]
\[ r: \text{radical distance [m]} \]
\[ r_p: \text{radius of adsorbent particle [m]} \]
\[ T: \text{temperature [K]} \]
\[ V: \text{volume of the bulk solution in the batch reactor [L]} \]

Greek Letters

\[ \rho_p: \text{apparent density of adsorbent [kg/m}^3\text{]} \]
\[ \Delta G^0: \text{change in Gibbs free energy [kJ/mol]} \]
\[ \Delta H^0: \text{change in enthalpy [kJ/mol]} \]
\[ \Delta S^0: \text{change in entropy [kJ/mol/K]} \]

References