Adsorption of Lead Ions from Synthetic Wastewater Using Oyster Shell

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Abstract

The objective of this work was to study the adsorption ability of various Pb²⁺ ion concentrations by oyster shell (Crassostrea commercialis). Oyster shells were prepared by 2 different methods. For the first method, oyster shell was washed with distilled water, dried in the oven at 105°C, then, crushed and sieved to particle size of 75-106 µm in diameter. This was called OSA. For the second method, oyster shell was crushed and burnt in furnace at 850°C for 2 hr, then, sieved to particle size of 75-106 µm in diameter. This was called OS-B. The results of the adsorption experiment showed that adsorption reached equilibrium within 120 min with eighty four percent of Pb²⁺ was removed from 100 mg/L initial concentration. Moreover, Langmuir and Freundlich adsorption isotherms were used to fit the experimental data. The results showed that both Langmuir and Freundlich adsorption isotherms fitted the experimental data very well with high correlation coefficient (R²). The high Kᵢ value implied that the Pb²⁺ ions adsorption capacities of both OSA and OS-B were high. The maximum Pb²⁺ adsorption capacity (qₑ) of OSA and OS-B obtained from Langmuir adsorption isotherm were 196 and 233 mg-mg⁻¹-metal-adsorbent, respectively.

Keywords: Adsorption, Lead, Oyster shell, Adsorption Isotherm

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Introduction

Wastewater containing heavy metal ions is often encountered in chemical industries such as electroplating, tannery and textile dyeing, etc. Heavy metals such as lead, cadmium and mercury are highly toxic and not biodegradable. When accumulating in living organisms, they cause diseases\(^8\). Heavy metal ions treatment techniques such as chemical precipitation, solvent extraction, electrolytic processes, membrane separation and ion-exchange, etc. are not suitable for low contaminated heavy metal ions in wastewater because of high operating cost\(^8\).

Adsorption is one of the most efficient methods for the removal of heavy metal ions from low-contaminated industrial effluents. The research for low-cost adsorbents that have high adsorption capacities has intensified and materials locally available in large quantities such as natural materials, agricultural waste or industrial by products can be utilized as low-cost adsorbents.

The objective of this work was to study the adsorption ability of various Pb\(^{2+}\) ion concentrations by oyster shell (Crassostre commericais).

Materials and Methods
Preparation of synthetic Pb\(^{2+}\) ion solution

The synthetic Pb\(^{2+}\) ion solution at concentration of 1,000 mg-metal/L was prepared by dissolving Pb(NO\(_3\))\(_2\) in deionized water and adding 5 ml of concentrated nitric acid (concHN\(_3\))\(_3\) for 1 L of solution. The stock solution was kept in refrigerator at 4°C and was diluted to the concentrations of 50, 60, 70, 80, 90, 100 ppm to be used for the experiment.

Preparation of adsorbent

Crassostre commercialis was collected from Chonburi province, Thailand. Oyster shells were prepared by 2 different methods. For the first method, oyster shell was washed with distilled water, dried in the oven at 105°C, then, crushed and sieved to particle size of 75-106 \(\mu\)m in diameter. This was called OS-A. For the second method, oyster shell was crushed and burnt in furnace at 850°C for 2 hr, then, sieved to particle size of 75-106 \(\mu\)m in diameter. This was called OS-B.
Adsorption experiment

The experiments were performed by mixing 0.1 g oyster shell in 500 ml erlenmeyer flasks containing 200 ml of Pb\(^{2+}\) ion solution. The Pb\(^{2+}\) ion solution was prepared by dilution of stock solution to the concentration 50, 60, 70, 80, 90, 100 ppm and adjustment with 0.1 mol NaOH solution for pH 6. The mixtures were mixed in a shaker at the rate of 200 rpm. The 2 ml mixtures was collected at each time (0, 5, 10, 15, 30, 60, 120 and 180 min) and filtered with filter paper (Whatman No. 1), immediately. The filtrates were added with 0.05 ml conc HNO\(_3\). The amount of lead ions in filtrates were determined by Flame Atomic Absorption Spectrophotometer (AAS) following standard methods.

Calculation for percentage of removal and adsorption capacity

The percentage of lead ion removal was calculated as follows:

\[
\text{% Removal} = \frac{C_i - C_e}{C_i} \times 100 \tag{1}
\]

where,
\[
C_i = \text{initial concentration (mg/L)} \\
C_e = \text{equilibrium concentration (mg/L)}
\]

The amount of Pb\(^{2+}\) ion uptake per unit mass of adsorbent (Adsorption capacity, \(q_e\)) was calculated as follows:

\[
q_e = \frac{(C_i - C_e)v}{w} \tag{2}
\]

where,
\[
q_e = \text{The amount of Pb}^{2+}\text{ ions uptake per unit mass of adsorbent at equilibrium (mg/g)} \\
C_i = \text{initial concentration (mg/L)} \\
C_e = \text{equilibrium concentration (mg/L)} \\
v = \text{volume of solution (L)} \\
w = \text{amount of adsorbent (g)}
\]

Adsorption isotherm

Langmuir and Freundlich adsorption isotherm were used to fit the experimental data. Langmuir adsorption isotherm was presented in Equation 3

\[
q_e = \frac{K_L q_m C_e}{1 + K_L C_e} \tag{3}
\]

The linear form of this model is given below:

\[
\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{1}{q_m} C_e \tag{4}
\]

where,
\[
q_m = \text{The amount of Pb}^{2+}\text{ ions uptake per unit mass of adsorbent at equilibrium (mg/g)} \\
C_e = \text{equilibrium concentration (mg/L)}
\]

Freundlich adsorption isotherm was presented in Equation 5

\[
q_e = K_F C_e^{1/n} \tag{5}
\]
The linear form of this model is given below:

$$\log q_e = \log K_F + \left(\frac{1}{n_F}\right) \log C$$  \hspace{1cm} (6)

where,

- $K_F$ = the Freundlich constant related to the adsorption capacity of the sorbent (mg/g/L/mg$^{1/n_F}$)
- $1/n_F$ = the Freundlich constant related to the energy heterogeneity of the system and the size of the adsorbed molecule.

Result and Discussion
Characterization of the adsorbent

Characterization of the adsorbent was investigated by X-ray Fluorescence Spectrometer (XRF), BET (Brunauer, Emmett, and Teller) surface area analysis and Scanning Electron Microscopy (SEM) investigations.

The OS-A has a high percentage of calcium carbonate (CaCO$_3$) about 80%. The latter, which is OS-A, has silica oxide (SiO$_2$) and alumina oxide (Al$_2$O$_3$). The OS-B has a high percentage of calcium oxide (CaO) about 69%. The latter, which is OS-B, has 18% of silica oxide (SiO$_2$) and 2.4% of magnesium oxide (MgO) (Table 1). The OS-B has a high percentage of CaO because CaCO$_3$ was converted to CaO at 850°C in pretreatment process. The calcination reactions were shown in Equation 7.

$$\text{CaCO}_3(s) \rightarrow_{\Delta} \text{CaO}(s) + \text{CO}_2(g)$$  \hspace{1cm} (7)

The BET surface area of the OS-A (9.47 m$^2$/g) was higher than that of the OS-B (1.73 m$^2$/g). Moreover, the pore size of OS-A and OS-B were 10.08 and 9.89 μm, respectively (Figure 1).

The chemical composition and surface area affect on the adsorption capacity of adsorbent. High percentage of CaO and high surface area of adsorbent provided high adsorption capacities, accordingly.

### Table 1. Chemical composition of OS-A

<table>
<thead>
<tr>
<th>Chemical composition</th>
<th>Wt. %</th>
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<tbody>
<tr>
<td>SiO$_2$</td>
<td>17.67</td>
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<tr>
<td>Al$_2$O$_3$</td>
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<tr>
<td>CaO</td>
<td>68.99</td>
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<tr>
<td>MgO</td>
<td>2.43</td>
</tr>
<tr>
<td>Fe$_3$O$_4$</td>
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</tr>
<tr>
<td>TiO$_2$</td>
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<tr>
<td>MnO$_2$</td>
<td>0.01</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>0.04</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>0.53</td>
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</table>

### Table 2. BET surface area of adsorbent

<table>
<thead>
<tr>
<th></th>
<th>OA</th>
<th>OB</th>
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</thead>
<tbody>
<tr>
<td>Surface area</td>
<td>9.47</td>
<td>1.73</td>
</tr>
<tr>
<td>porosity (%)</td>
<td>70.83</td>
<td>75.96</td>
</tr>
<tr>
<td>Pore size (μm)</td>
<td>10.08</td>
<td>9.89</td>
</tr>
<tr>
<td>Loss on incineration</td>
<td>8.93</td>
<td></td>
</tr>
</tbody>
</table>
Figure 1. SEM micrograph of the particles of adsorbent (1,000 x)

Effect of reaction time

The variation of adsorbed amount of Pb\(^{2+}\) ion on OS-B according to time was examined by using 0.5 g/L adsorbent dosage and 100 ppm Pb\(^{2+}\) ions synthetic wastewater. At the initial stage of adsorption, the removal rate of Pb\(^{2+}\) was high during the first 5 min. After 5 min, the removal rates of Pb\(^{2+}\) slowly declined and adsorption reached equilibrium within 120 min with 84% Pb\(^{2+}\) removed from 100 mg/L initial concentration (Figure 2). Initially, the active adsorption sites are open and the metal ions interacts easily with the sites and hence a higher rate of adsorption is observed. Further, the driving force for adsorption (the concentration difference between the bulk solution and the solid-liquid interface) is higher initially and this results a higher adsorption rate. However, after the initial period, slow adsorption may be due to slower diffusion of solute into the interior of the adsorbent\(^6\).

Figure 2. The percentage on the removal of Pb\(^{2+}\) ions OS-B according to time
Effect of initial concentration

In Figure 3, when the initial Pb\textsuperscript{2+} ions concentration increased from 50 to 100 mg/L, Pb\textsuperscript{2+} adsorption removal of OS-A and OS-B decreased from 78% to 65.7% and 92% to 84%, respectively. The higher percentage of removal at low concentration is attributed by the availability of greater surface area with active centers on the adsorbent for lesser amounts of adsorbate ions\textsuperscript{9}.

![Figure 3. Effect of initial concentration to removal efficiency (adsorbent dosage 0.5 g/L)](image1)

In Figure 4, when the initial Pb\textsuperscript{2+} ion concentration increased from 50 to 100 mg/L, the adsorption capacity of OS-A and OS-B increased from 71 to 124.6 mg/g and 84 to 160 mg/g, respectively. The higher initial concentration provided increasing driving force to overcome all mass transfer resistance of metal ions between the aqueous and solid phases resulting in higher probability of collision between Pb\textsuperscript{2+} ions and sorbents. This results in higher metal uptake\textsuperscript{9}.

![Figure 4. Effect of initial concentration on the adsorption capacity (adsorbent dosage 0.5 g/L)](image2)
Adsorption isotherm

The adsorption of Pb²⁺ ions was carried out at different initial Pb²⁺ ion concentrations ranging from 50 to 100 mg/L, at equilibrium time (120 min). The linearized Freundlich and Langmuir adsorption isotherm of each sorbent were shown in Figures 5 and 6. Langmuir and Freundlich adsorption isotherm parameters were shown in Table 3.

![Figure 5. Langmuir adsorption isotherm of OS-A and OS-B](image)

![Figure 6. Freundlich adsorption isotherm of OS-A and OS-B](image)
The both Langmuir and Freundlich adsorption isotherm fitted the experimental data very well with high correlation coefficient ($R^2$). Freundlich parameters ($K_F$ and $n$) indicates whether the nature of adsorption is either favorable or unfavorable. The intercept is an indicator of adsorption capacity and the slope is an indicator of adsorption intensity. A high value of the intercept, $K_F$, is indicative of a high adsorption capacity. A relatively slight slope ($1/n$) indicates that adsorption intensity is good (or favorable) over the entire range of concentrations studied, while a steep slope ($n > 1$) means that adsorption intensity is good (or favorable) at high concentrations but much less at lower concentrations. The $K_F$ value of OS-A and OS-B were 22.68 and 46.60, respectively.

The $K_L$ parameter is the adsorption equilibrium constant, which not only gives information on adsorption rate compared to desorption rate of the system, but also was used to the heat of adsorption. For exothermic reaction, $K_L$ should decrease with increasing temperature of the system. The maximum $\text{Pb}^{2+}$ adsorption capacity ($q_m$) of OS-A and OS-B obtained from Langmuir adsorption isotherm were 196 and 233 mg-adsorbent, respectively (Table 3). The maximum $\text{Pb}^{2+}$ adsorption capacity ($q_m$) of various adsorbents (30-796 mg/g) were shown in Figure 7.

Table 3. Langmuir and Freundlich adsorption isotherm parameters

<table>
<thead>
<tr>
<th>Type of adsorbent</th>
<th>Langmuir Adsorption Isotherm</th>
<th>Freundlich Adsorption Isotherm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$q_m$ (mg/g)</td>
<td>$K_L$ (L/mg)</td>
</tr>
<tr>
<td>OS-A</td>
<td>196</td>
<td>18.20</td>
</tr>
<tr>
<td>OS-B</td>
<td>233</td>
<td>6.40</td>
</tr>
</tbody>
</table>

Figure 7. The maximum adsorption capacity ($q_m$) of various adsorbent.
The maximum adsorption capacity of OS-B was higher than maximum adsorption capacity of OS-A because main composition of OS-B was calcium oxide (CaO) that removed Pb²⁺ ions well although surface area of OS-A was more than surface area of OS-B about 5.5 times. In this case, the result showed that chemical composition was important effect to adsorption.

Conclusion

Oyster shells were prepared with 2 different methods for using as low-cost adsorbents for removal of Pb²⁺ ions from aqueous solutions. The removal rate of Pb²⁺ was high during the first 5 min. At 5 min, Pb²⁺ ions were removed from 100 mg/L initial concentration by OS-B about 76% and adsorption reached equilibrium within 120 min with 84% Pb²⁺ removal. Langmuir and Freundlich adsorption isotherm fitted the experimental data very well with high correlation coefficients (R²). The Kₜ value of OS-A and OS-B were 22.68 and 46.60, respectively. The maximum adsorption capacity (q) of OS-A and OS-B obtained from Langmuir adsorption isotherm were 196 and 233 mg-metal/g-adsorbent, respectively. The maximum adsorption capacity of OS-A and OS-B were moderately high when compared with the maximum adsorption capacity of various adsorbents that were between 30 to 796 mg-metal/g-adsorbent.

References


