Removal of Arsenic(v) ion from Aqueous solutions by basic Lanthanum Carbonate

M. J. Haron1, W.M.Z. Wan Yunus1, M. A. Sukari1, S. Tokunaga2, and S. A. Wasay1

1Chemistry Department, Universiti Putra Malaysia, 43400 Serdang, Selangor, Malaysia.
2National Institute of Materials and Chemical Research, Higashi, Tsukuba, Ibaraki 305, Japan.

(Received 6 September 2000)

Abstract. A new adsorption process for the removal of As(V) ion from aqueous solutions has been studied using basic lanthanum carbonate (BLC). The compound was effective in removing As(V) ion and decreased its concentration down to < 0.001 mM. The dissolution of BLC was appreciable at initial pH < 4. Kinetic study showed that the As(V) removal was a first-order reaction and the rate constants were varies from 1.8 down to 0.005 h^-1 in acidic and alkaline pH, respectively. The As(V) removal was highly pH-dependent and the optimum pH range was 2-6. The following two mechanisms of removal are proposed: (i) adsorption by exchange of CO_3^{2-} and OH^- groups with As(V) ions in the alkaline to mild acidic pH range where BLC does not dissolve and (ii) precipitation of insoluble lanthanum arsenate in the acid pH range where BLC dissolves.

Materials and Method

Basic lanthanum carbonate (BLC) was prepared by the homogeneous precipitation method [12]. A 3.0 l of mixture containing 0.17 M LaCl_3 and 0.15 M urea was gently heated at boiling temperature until La was not detected in the aqueous solution. The resultant precipitate was recovered by filtration, washed thoroughly with deionized water, and dried at 100°C.

Various methods have been proposed to remove As from water. The conventional methods are precipitation and coagulation processes by converting the As ions to insoluble forms [4]. However these methods may increase salt concentration in the effluent [5]. Adsorption process seems most promising to reduce As concentration to meet the standard. Rare earth compounds have been found to be effective to adsorb some hazardous anions such as fluoride and chromate [6-8]. Our previous study [9] shows that La compounds are effective to remove fluoride ion from aqueous solutions. Lanthanum is one of the cheapest rare earth elements, and can be extracted from bastnaesite and monazite [10]. The authors have attempted to utilise one of the La compounds, which have not been utilised efficiently by the industry in spite of their abundance, as adsorbent. Both As(V) and As(III) ions are found in natural waters [11]. Removal of only As(V) ion has been studied in the present paper since As(III) can be easily oxidised to As(V) by hydrogen peroxide.

Materials and Method

Basic lanthanum carbonate (BLC) was prepared by the homogeneous precipitation method [12]. A 3.0 l of mixture containing 0.17 M LaCl_3 and 0.15 M urea was gently heated at boiling temperature until La was not detected in the aqueous solution. The resultant precipitate was recovered by filtration, washed thoroughly with deionized water, and dried at 100°C. The La content of BLC was determined by the ICP method (ICPS 1000 II; Shimadzu Corp., Kyoto Japan) after dissolving it in HCl solution. The total content of OH and CO_3 groups was determined by acid titration. The CO_3 content was determined by converting it to CO_2 gas by the addition of acid and was recovered in NaOH solution. The surface area of the BLC particles was measured by BET method (Micromeritics Flow Sorb II 2300). The men volume particle size of the compound was determined by a particle size analyzer (Microtrac SRA). The pH of zero surface charge, pH_zpc, was determined from the
titration curve [13]. The characteristics of BLC are summarised in Table 1.

<table>
<thead>
<tr>
<th>Composition</th>
<th>La(OH)(CO₃)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface area, m²/g</td>
<td>0.28</td>
</tr>
<tr>
<td>Mean volume diameter, µm</td>
<td>28</td>
</tr>
<tr>
<td>pH&lt;sub&gt;pzc&lt;/sub&gt;</td>
<td>7.3</td>
</tr>
</tbody>
</table>

A 125 mM stock solution of As(V) was prepared by dissolving dibasic sodium arsenate (Na₂HAsO₄·7H₂O) of analytical grade in deionized water. The stock solution was further diluted to suitable concentrations.

A 0.10 g of the BLC was added to 100 ml of 0.25 mM As(V) solution and the pH was adjusted to 2 to 12. The resultant mixture was shaken at 20°C. At intervals, an aliquot was taken and filtered with a 0.45 µm membrane filter. The filtrate was analyzed for La and As ions by the ICP method.

**Results and Discussion**

**Kinetics of the removal of As(V) ion**

The rate of As(V) removal by the BLC was measured at different pH. In Figure 1, the percentages of As(V) removal are plotted against time for various initial pH values. The As(V) removal rate was significantly affected by initial pH value. The highest As(V) removal rate was obtained at pH 2. The As(V) removal rate decreased with increasing pH. At pH 11, no As(V) removal was observed.

The As(V) removal followed a first-order reaction which can be described as below:

\[ \text{Log}(C_t/C_0) = -(k/2.303)t \]

where \( C_t \) = residual As(V) concentration (mM) at time \( t \); \( C_0 \) = initial As(V) concentration (mM); \( k \) = rate constant (h⁻¹); \( t \) = time (h). The rate constants, \( k \), decrease in the order of increasing pH as shown in Table 2.

**Table 2:** The first-order rate constants for the As(V) removal by the BLC at various pH.

<table>
<thead>
<tr>
<th>pH</th>
<th>( k ), h⁻¹</th>
<th>( r^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0</td>
<td>1.28</td>
<td>0.99</td>
</tr>
<tr>
<td>4.0</td>
<td>0.18</td>
<td>0.91</td>
</tr>
<tr>
<td>5.0</td>
<td>0.11</td>
<td>0.97</td>
</tr>
<tr>
<td>6.0</td>
<td>0.08</td>
<td>0.95</td>
</tr>
<tr>
<td>7.0</td>
<td>0.04</td>
<td>0.96</td>
</tr>
<tr>
<td>8.0</td>
<td>0.01</td>
<td>0.99</td>
</tr>
<tr>
<td>9.0</td>
<td>0.005</td>
<td>0.99</td>
</tr>
</tbody>
</table>

**Effect of pH on the removal of As(V) ion**
The kinetic study shows that the removal of As(V) reaches equilibrium in 24 h after addition of the BLC. In Figure 2 the percentages removal of As(V) and the BLC dissolution are plotted against initial pH. The BLC was effective to remove almost 100% of As(V) which decrease the concentration of the ion down to < 0.001 mM in the pH range of 2 to 6. The adsorption capacity of As(V) at initial pH 4 was found to be 0.25 mmol/g BLC. At initial pH < 4, the dissolution of BLC favoured the precipitation reaction between As(V) and La\(^{3+}\) ions. Although As(V) was removed also in the pH range of > 6, the percentage of the removal was low.

**Mechanism of the As(V) removal by the La compound**

The above results indicated that the mechanism of the As(V) removal consists of (i) precipitation and (ii) adsorption. At initial pH < 4, the BLC dissolves to give La\(^{3+}\) ions. In this pH range, arsenate ion predominantly exists as H\(_2\)AsO\(_4^-\) \[14\], reacts with La\(^{3+}\) ions to form insoluble lanthanum arsenate. The precipitation process can be expressed as follows:

\[
\text{La}^{3+} + \text{H}_2\text{AsO}_4^- \rightarrow \text{LaAsO}_4 + 2\text{H}^+ \quad (1)
\]

In the pH of > 4 where the BLC does not dissolve, it can be concluded that the adsorption process is operating in the As(V) removal. This process includes exchange of CO\(_3^-\) and OH groups with As(V) ions which can be described as follows in the acidic pH range:

\[
\text{La(OH)}\text{CO}_3 + 3\text{H}_2\text{AsO}_4^- \rightarrow \text{La(H}_2\text{AsO}_4)\text{OH}^- + \text{CO}_3^{2-} \quad (2)
\]

In the basic pH range where HAsO\(_4^{2-}\) species is predominant \[14\] the reaction can be written as follows:

\[
\text{La(OH)}\text{CO}_3 + \text{HAsO}_4^{2-} \rightarrow
\]

According to the results of the kinetic study (Table 2), the rate of precipitation (pH 2) is higher than that of adsorption (pH ≥ 4). The precipitation of lanthanum arsenate occurred at pH < 4 can reduce the residual As(V) concentration to meet the effluent standard. However, the disadvantageous is that the dissolution of BLC in acid solution results in the unnecessary existence of La ion in the aqueous phase. Therefore, adsorption process in the pH < 4 is advantageous.

**Conclusion**

Basic lanthanum carbonate (BLC) was effective in removing As(V) ion to decrease the concentration down to < 0.001 mM which meets the effluent standard. The dissolution of this material became appreciable at pH < 4. The highest As(V) adsorption rate where the BLC dissolution is negligible, was obtained at initial pH 4. The As(V) removal was a first-order reaction and the rate constants decreased with increasing initial pH. The optimum initial pH range for the As(V) removal was 2 to 6. Two mechanisms are proposed for the removal of As(V) ion by BLC: (i) adsorption by exchange of CO\(_3^-\) and OH groups with As ions and (ii) precipitation of
insoluble lanthanum arsenate in the low acidic pH range where the BLC dissolves.

**Acknowledgment**

This research was funded by the Environment Agency of Japan.

**References**