Synthesis of Fe-type Layered Double Hydroxide from Biomass Combustion Ash for Removal of Arsenite and Arsenate

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Abstract

In Japan, biomass power generation is being promoted for effective biomass utilization. However, a major problem is the large amount of biomass combustion ash discharged and disposed of as industrial waste. Environmental problems caused by arsenic (As) occur throughout the world, including Japan. In this study, we attempted to synthesize an Fe-type layered double hydroxide (Fe-LDH) from biomass combustion ash for As removal. During this experiment, the combustion ash was added to HCl to dissolve divalent cations, Ca and Mg, in the ash, and then filtrated. Iron chloride hexahydrate (FeCl₃·6H₂O) was added to the filtrate to prepare an acidic liquid mixture with a molar ratio of (Ca+Mg)/Fe = 2-2.5, which was added to 0.3 M NaCl solution and stirred for 6 h to synthesize LDH at 20, 40, and 60°C maintaining a pH 8.5, 10.5, and 12.5, respectively. In addition, the As removal ability of the product was investigated. As a result, the product, including Fe-LDH, prepared from the biomass combustion ash at pH 12.5 at 40°C demonstrated a strong ability to remove arsenite (As(III)) and arsenate (As(V)), and the removal percentage of As(III) using the product was higher than that of As(V).

Keywords: Biomass combustion ash, Layered double hydroxide, Removal of arsenite and arsenate

1. Introduction

In Japan, the Biomass Nippon Strategy has been approved by the cabinet. As part of this strategy, woody biomass power generation has been promoted, and a large amount of biomass combustion ash is generated in power plants. Currently, biomass combustion ash is disposed of as industrial waste, and its processing cost is among the important problems in the promotion of biomass power generation. Effective methods of utilization of biomass combustion ash to reduce processing costs have been attempted. However, it cannot be used as a cement or directly as a fertilizer because biomass combustion ash has high chloride content, and high solubility and contains a limited amount of heavy metals, among other issues.

Heavy metal contamination occurs throughout the world. Among the heavy metals, arsenic (As) is highly toxic, and causes severe health damage, such as skin diseases and carcinogenesis. In some countries, such as Bangladesh and China, environmental pollution caused by arsenite (As(III)) and arsenate (As(V)) is a severe problem. In Japan, strict environmental standards for As have been established. Therefore, removal of As is an urgent task in these countries. Some removal methods include biological treatment, coagulation sedimentation, membrane separation, and ion exchange resin.

A simple treatment method, adsorption using different materials, is generally considered an effective treatment technique for removal of pollutants such as As from water and wastewater. In the adsorption method, selection of the material for removal is important, and Fe-type layered double hydroxides (LDHs) are expected to remove As effectively.
LDH is a nonstoichiometric compound represented by the general formula \([M^{2+},M^{3+}]\left[\text{OH}_{2}\right]\left[\text{As}_{\text{OH}}^{3-}:m\text{H}_{2}\text{O}\right]\). Here, \(M^{2+}\) is a divalent metal ion, such as \(\text{Ca}^{2+}, \text{Mg}^{2+}\) or \(\text{Mn}^{2+}\), and \(M^{3+}\) is a trivalent ion, such as \(\text{Fe}^{3+}\), \(\text{Al}^{3+}\) or \(\text{Cr}^{3+}\). By replacing a part of the divalent metal ions with trivalent metal ions, a positively charged hydroxide basic layer and a laminated structure having an anion in the intermediate layer to compensate for the charge, are adopted. The amount of positive charges in the basic layer results in an anion exchange capacity and the anion in the intermediate layer is an inorganic anion, such as \(\text{Cl}^-, \text{NO}_3^-, \text{OH}^-, \text{CO}_3^{2-}\) or \(\text{SO}_4^{2-}\).

In this study, we attempted to prepare a material, including Fe-LDH, from biomass combustion ash for As removal, with the addition of ineffective FeCl₃.

2. Experimental

2.1 Sample

Biomass combustion ash generated in a domestic power plant was used in this study. All reagents used in this study were purchased from Wako Chemical Co. Ltd. Japan.

2.2 Experimental procedure

The experimental procedure is shown in Fig. 1. Three experiments were conducted: dissolution of biomass combustion ash in HCl, synthesis of Fe-LDH, and evaluation of the obtained product for the removal of As(III) and As(V).

![Fig. 1 Experimental procedure.](Image)

2.2.1 Dissolution

According to a previous study, it is known that the Ca-Mg-Fe-type LDH can be synthesized from an acidic solution with the molar ratio of \((\text{Ca}+\text{Mg})/\text{Fe} = 2-2.5\). To obtain the mixed solution from the dissolution of Ca and Mg from the biomass combustion ash, 0.5-10.0 g of combustion ash was added to 40 mL of distilled water, 0.1 M HCl and 1 M HCl solution, and shaken for 10-60 min. After shaking, filtration was conducted, and then the pH of the solution and the dissolved amounts of Ca and Mg in the solution from the biomass combustion ash were investigated using an atomic absorption spectrometer (AAS, AAnalyst200, Perkin Elmer) and pH meter (LAQUA, F72), respectively. The residue after filtration was dried, and analyzed using a powder X-ray diffraction device (XRD, MiniFlex600, Rigaku). The surface structures of the raw ash and the residue following HCl dissolution were analyzed using a scanning electron microscope (SEM, JEOL, JSM-6510A).

Under the best condition to prepare a mixed solution with \((\text{Ca}+\text{Mg})/\text{Fe} = 2-2.5\), iron chloride hexahydrate \([\text{FeCl}_3\cdot 6\text{H}_2\text{O}\]) was added to 50 mL of the filtrate. The concentrations of Ca, Mg, and Fe in the 50 mL of the mixed solution and the pH of the solution were measured.

2.2.2 LDH synthesis

The obtained mixed solution with \((\text{Ca}+\text{Mg})/\text{Fe} = 2-2.5\) was added to 50 mL of 0.3 M NaCl solution stirred at 20, 40, and 60°C with a hot stirrer at a flow rate of 4 mL/min using a peristaltic pump. During stirring, 4 M NaOH was appropriately added dropwise to maintain the pH of the solution at 8.5, 10.5, and 12.5. After stirring for 6 h, the slurry was filtered, dried, and washed with distilled water to obtain a product. The mineral phases of the product were identified using XRD. For the evaluation of contents of Ca, Mg, and Fe in the product, 0.05 g of the product was completely dissolved in 10 mL of 1 M HCl solution shaking for 1 h, and then centrifuged. The concentrations of Ca, Mg, and Fe in the supernatant were measured using an AAS to calculate the content of each element in the products. The surface structure of the product was analyzed using an SEM.

2.2.3 Evaluation of As removal ability

For the As removal experiment, solutions of As(III) \([\text{H}_2\text{AsO}_3^-]\) and As(V) \([\text{AsO}_4^{3-}\]) with a concentration of 5-50 mg/L were prepared from sodium arsenite (NaAsO₂) and disodium hydrogen arsenate (Na₂HAsO₄), respectively.

100 mg of the product obtained under various conditions was added to 40 mL of As solutions at 50 mg/L and shaken for 12 h. After shaking, the tube was centrifuged, and the removal \((R)\) of As(III) and As(V) was calculated using the following formula (Eq. 1).

\[
R(\%) = \frac{C_0 - C}{C_0} \times 100
\]

where \(C_0\) is the initial concentration of As (mg/L) and \(C\) is the measured concentration of As (mg/L).

100 mg of the product, which was the optimal synthesis condition, was added to 40 mL of As solution at 5-50 mg/L and shaken for 12 h. After shaking, the tube was centrifuged, the pH of the supernatant was measured with a pH meter, and the adsorption amounts \((q)\) of As(III) and As(V) were calculated using the following formula (Eq. 2).

\[
q = (C_0 - C) \times \frac{V}{w}
\]

where \(C_0\) is the initial concentration of As (mg/L) and \(C\) is the measured concentration of As (mg/L), \(V\) is the solution volume (L), and \(w\) is the mass of product added to the solution (g).
3. Results and discussion

3.1 Solubility

Figure 2 shows the dissolved amounts of Ca and Mg from the ash and the pH of the solution using distilled water, 0.1 M HCl and 1 M HCl solution shaking for 12 h. In the case of distilled water after adding the ash, the pH increased to approximately about 11, and the dissolved amounts of Ca and Mg were too small (Fig. 2 (a)). In the case of 0.1 M HCl, the pH of the solution increased because of the dissolution of combustion ash and the dissolved amount of Ca and Mg was small but higher than that using distilled water (Fig. 2 (b)). In the case of the 1.0 M HCl solution, an acidic solution with a pH of approximately 1 was attained with the addition of 0–5.0 g ash, and a solution with total concentrations of Ca and Mg greater than 0.2 mol/L was obtained when more than 6.0 g of combustion ash was added into 40 mL of 1 M HCl solution (Fig. 2 (c)).

The influence of short shaking time was investigated under the condition that 6.0 g of combustion ash was added to 40 mL of 1 M HCl. The dissolution amounts of Ca and Mg into the solution and the pH of the solution after shaking for 10-60 min are shown in Fig. 3. The significant difference in the dissolved amount of Ca and Mg and the pH of the solution was not confirmed during 1 h of shaking. It was confirmed that dissolution sufficiently occurred within 10 min of shaking. It is noted that the pH was always less than 1. From these results, it is considered that dissolution rapidly occurs after adding combustion ash to 1 M HCl and the Ca and Mg sufficiently dissolve into the HCl solution within 10 min of shaking.

Figure 4 shows the XRD patterns of raw ash and the residue after 1 M HCl dissolution. Raw ash contains chloride, carbonate, and sulfate containing calcium and potassium derived from the biomass and quartz (SiO$_2$) used for fluidized bed combustion. After HCl dissolution, peaks for the Ca and Mg compounds nearly disappeared, and the peaks of SiO$_2$ (quartz) and CaSO$_4$·2H$_2$O (gypsum) were remarkably confirmed. These results indicated that the contents of Ca and Mg in the ash can be dissolved in the HCl solution.
Figure 5 shows an SEM photograph of the raw ash and the residue following HCl dissolution. In the raw ash, spherical particles and an agglomerate of some substances were detected (Fig. 5 (a)). In the residue after dissolution in HCl, spherical particles remained and fine substances were detected (Fig. 5 (b)). It is thought that the spherical particles are quartz used for fluidized bed combustion, and agglomerates dissolve to fine substances such as, gypsum.

From these results, a solution was prepared by adding 6.0 g of biomass combustion ash to 40 mL of 1 M HCl solution. After shaking 10 min, iron chloride hexahydrate [FeCl₃·6H₂O] was added into solution to prepare a mixed solution with (Ca+Mg)/Fe = 2–2.5. The composition of the prepared mixed solution is shown in Table 1. The pH of the mixed solution was 1.6, and the molar ratio of the solution was (Ca+Mg)/Fe = 2.3, which is suitable for the synthesis of Fe–LDH.

Table 1 Composition of the mixed solution.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Content (mmol/g)</th>
<th>(Ca+Mg)/Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH 8.5</td>
<td>Ca²⁺ 1.59</td>
<td>Mg²⁺ 0.94</td>
</tr>
<tr>
<td>pH 10.5</td>
<td>Ca²⁺ 0.63</td>
<td>Mg²⁺ 1.53</td>
</tr>
<tr>
<td>pH 12.5</td>
<td>Ca²⁺ 4.02</td>
<td>Mg²⁺ 1.20</td>
</tr>
</tbody>
</table>

3.2 Synthesis of Fe–LDH

Synthesis of Fe–LDH was conducted from a Ca–Mg–Fe mixed solution obtained from biomass combustion ash. XRD patterns of the product synthesized in the solution at pH 8.5, 10.5, and 12.5 are shown in Fig. 6. No peaks of the Fe–LDH and could be confirmed in the product synthesized at pH 8.5 and 10.5, while the peaks of Fe–LDH could be confirmed in the product at pH 12.5. These results indicated that LDH can be synthesized when the pH of the solution is high, because calcium hydroxide precipitates in the solution at a pH value above 10.8.

The compositions of the products obtained at various pH values are shown in Table 2. The amounts of Ca and Mg and the (Ca+Mg)/Fe ratio are small in the products synthesized at pH 8.5 and 10.5. The ratio of the product synthesized for (Ca+Mg)/Fe was 2.27, which means that the contents of Ca²⁺, Mg²⁺, and Fe³⁺ ions in the mixed solution were used for the structure of the product synthesized in the solution at pH 12.5.

Table 2 Composition of the product.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ca²⁺</th>
<th>Mg²⁺</th>
<th>Fe³⁺</th>
<th>(Ca+Mg)/Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH 8.5</td>
<td>1.59</td>
<td>0.94</td>
<td>5.01</td>
<td>0.50</td>
</tr>
<tr>
<td>pH 10.5</td>
<td>2.30</td>
<td>1.53</td>
<td>4.27</td>
<td>0.90</td>
</tr>
<tr>
<td>pH 12.5</td>
<td>4.02</td>
<td>1.20</td>
<td>2.30</td>
<td>2.27</td>
</tr>
</tbody>
</table>

Figure 7 shows the removal of As(III) and As(V) using the products synthesized at pH 8.5, 10.5, and 12.5. With increase in pH, removal of the As(III) and As(V) increased. The removal of 78%, 80%, and 81%, respectively, was achieved for As(III). The removal of 68%, 76%, and 78%, respectively, was achieved for As(V). In each product, the removal of As(III) was higher than that of As(V).

The XRD pattern of the product synthesized from the mixed solution at pH 12.5 at various temperatures is shown in Fig. 8. Peaks of Fe–LDH were confirmed at all temperatures. The highest peak intensity of the Fe–LDH was synthesized at 40°C. At a temperature of 60°C, LDH coexisted with hydroxides, such as Ca(OH)₂, Mg(OH)₂, and Fe(OH)₃.
Fig. 7 Removal of As(III) and As(V) using the products synthesized at pH 8.5, 10.5, and 12.5.

Fig. 8 XRD pattern of the products synthesized at 20, 40, and 60°C.

The compositions of the products obtained at 20, 40, and 60°C are shown in Table 3. It was confirmed that Ca, Mg, and Fe were incorporated into the products by heating at all temperatures. The amount of Ca in the product and the ratio of (Ca+Mg)/Fe increased with a higher temperature.

Table 3 Composition of the product.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Content (mmol/g)</th>
<th>(Ca+Mg)/Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ca^{2+}</td>
<td>Mg^{2+}</td>
</tr>
<tr>
<td>20°C</td>
<td>4.02</td>
<td>1.20</td>
</tr>
<tr>
<td>40°C</td>
<td>4.99</td>
<td>1.03</td>
</tr>
<tr>
<td>60°C</td>
<td>6.15</td>
<td>1.05</td>
</tr>
</tbody>
</table>

Figure 9 shows the removal of As(III) and As(V) using the products synthesized at 20, 40, and 60°C. The removal of 77%, 83% and 80%, respectively, was achieved for As(III). The removal of 78%, 78%, and 65%, respectively, was achieved for As(V). In each product, the removal of As(III) was higher than that of As(V). These results show the best synthesis conditions of the product with As removal ability at pH 12.5 and a temperature of 40°C, which indicated the highest peak intensity of LDH.

3.3 Removal of As(III) and As(V)

Figure 11 shows the adsorption isotherms of the product, which was synthesized in the solution at pH 12.5 and 40°C, for removal of As(III) and As(V), and the pH after removal. With increase in the equilibrium concentration, the adsorption amounts of As(III) and As(V) first increase, and then are nearly constant. The adsorption amount of As(III) was nearly the same as that of As(V) at a low As concentration, while that of As(III) was greater than that of As(V) at a high As concentration. It was noted that the pH of the solution after removal of As(III) and As(V) was approximately 9.0-10.1. This indicated the shape of As(III) as H₂AsO₃⁻ with a size of 2.11Å and As(V) as HAsO₄²⁻ with a size of 2.48Å at pH 9.0-10.1. It is considered that the ion exchange via the interlayer of LDH occurred more in As(III) which is smaller than As(V).

The experimental results obtained in Fig. 11 were analyzed using the Langmuir and Freundlich adsorption models to estimate the As adsorption of the product.
The liner equations of Langmuir (Eq. 3) and Freundlich (Eq. 4) are as follows.

\[
\frac{C_e}{q_e} = \frac{1}{Q_{\text{max}} K_L} + \frac{C_e}{Q_{\text{max}}}
\]

(3)

\[
\ln q_e = \ln K_F + \frac{1}{n} \ln C_e
\]

(4)

where \(q_e\) is the amount of As(III) or As(V) absorbed at equilibrium (mg/g), \(Q_{\text{max}}\) (mg/g) and \(K_L\) (L/mg) are Langmuir constants related to the maximum adsorption capacity corresponding to complete coverage of available adsorption sites and a measure of adsorption energy (equilibrium adsorption constant), respectively. \(K_F\) and \(n\) are Freundlich constants.

The results are shown in Table 4. According to the correlation coefficient, for both As(III) and As(V), the Langmuir equation could be more realistic than the Freundlich equation. The calculated maximum adsorption capacities of the product for As(III) and As(V) using the Langmuir equation are 15.90 mg/g and 10.48 mg/g, respectively.

**Table 4 Results of parameters from the adsorption isotherm.**

<table>
<thead>
<tr>
<th></th>
<th>Langmuir</th>
<th>Freundlich</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(Q_{\text{max}})</td>
<td>(K_L)</td>
</tr>
<tr>
<td>As(III)</td>
<td>15.90</td>
<td>0.28</td>
</tr>
<tr>
<td>As(V)</td>
<td>10.48</td>
<td>0.39</td>
</tr>
</tbody>
</table>

The adsorption amounts of As(III) and As(V) of the product and the adsorbents reported in previous studies (13-17) are shown in Table 5. The product in this work indicated a high adsorption amount compared to that by the adsorbents reported in previous publications. However, it is very difficult to directly compare adsorption capacities because of a lack of consistency in the literature data. Sorption capacities were evaluated at different pH values, temperatures, As concentration ranges, adsorbent doses, and As(III)/As(V) ratios.

**Table 5 Adsorption amount of As(III) and As(V) of the product and the adsorbents reported in previous studies.**

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>As(III) (mg/g)</th>
<th>As(V) (mg/g)</th>
<th>As concentration (ppm)</th>
<th>pH</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca-Mg-Fe LDH</td>
<td>15.9</td>
<td>10.48</td>
<td>5.0 - 50.0</td>
<td>9.0 - 10</td>
<td>This work</td>
</tr>
<tr>
<td>Mono-hydrocalcite</td>
<td>-</td>
<td>1.8</td>
<td>0.6 - 12.0</td>
<td>8.8</td>
<td>13)</td>
</tr>
<tr>
<td>Mg-Fe-Cl LDH</td>
<td>14.59</td>
<td>2.64</td>
<td>0.4</td>
<td>4.0 - 9.0</td>
<td>14)</td>
</tr>
<tr>
<td>Pillared crays</td>
<td>13.0</td>
<td>4.0</td>
<td>20.0 - 100.0</td>
<td>4.0 - 9.0</td>
<td>15)</td>
</tr>
<tr>
<td>Iron hydroxide</td>
<td>28.0</td>
<td>7.0</td>
<td>20.0 - 100.0</td>
<td>4.0 - 9.0</td>
<td>16)</td>
</tr>
<tr>
<td>Anion exchange resins</td>
<td>9.7</td>
<td>28.0</td>
<td>10.0</td>
<td>1.0 - 5.0</td>
<td>17)</td>
</tr>
</tbody>
</table>

4. Conclusion

In this study, a Ca-Mg-Fe-type LDH was synthesized from biomass combustion ash and its removal ability for As(III) and As(V) was examined. As a result, it was possible to obtain an acidic mixed solution with \((\text{Ca} + \text{Mg})/\text{Fe} = 2.3\) using hydrochloric acid and iron chloride. We successfully synthesized a Ca-Mg-Fe-type LDH from this acidic mixed solution using a solution with a pH of 12.5 at 40°C. It was then possible to prepare a product containing a Ca-Mg-Fe-type LDH with a removal ability for As(III) and As(V) from biomass combustion ash.

5. References

8) Y. Lee, I. Um and J. Yoon, Environ. Sci. Technol., 24,