Synthesis of layered double hydroxide from biomass combustion ash and coal fly ash for phosphate removal

T Wajima* and A Suhara

Department of Urban Environment Systems, Graduate School of Engineering, Chiba University, 1-33, Yayoi-cho, Inage-ku, Chiba 263-8522, Japan

*E-mail: wajima@tu.chiba-u.ac.jp

Abstract. In this study, we attempted to synthesize layered double hydroxide (LDH) from biomass combustion ash and coal fly ash for phosphorus removal. There is a big problem that a large amount of these ashes are discharged to dispose at landfill as industrial wastes due to the shortage of landfill sites in Japan. On the other hand, water pollution caused by anions, such as eutrophication with phosphoric acid (PO\textsubscript{4}^{3-}) in wastewater, has become a problem. In this study, the biomass combustion ash and coal fly ash were added to HCl to dissolve cations, Ca\textsuperscript{2+}, Mg\textsuperscript{2+}, Fe\textsuperscript{3+} and Al\textsuperscript{3+}, in the ash to prepare acidic liquid mixture with a molar ratio of (Ca\textsuperscript{2+} + Mg\textsuperscript{2+}) / (Fe\textsuperscript{3+} + Al\textsuperscript{3+}) = 5.2, and the mixture stirred to synthesize the product including LDH at 40 °C for 6 h with keeping pH 12.5. As the result, Ca-Mg-Fe-Al LDH was successfully synthesized from the solution extracted from biomass combustion ash and coal fly ash using HCl, and the obtained product showed high phosphorus removal ability. From Langmuir and Freundlich adsorption models to estimate the phosphorus adsorption of the product, Langmuir equation could be more realistic than the Freundlich’s equation, and the calculated maximum adsorption capacity is 2.33 mmol/g.

1. Introduction

In Japan, the Biomass Nippon Strategy aiming to reduce greenhouse gas emissions using alternative energy by producing from livestock, food waste, wood, and organic materials, has been approved by the cabinet in 2002. As a part of this strategy, woody biomass power generation has been promoted, and a large amount of biomass combustion ash is generated in power plants. Biomass combustion ash is an industrial waste. The ash with heavy metal concentrations exceeding a certain value are classified as specific hazardous industrial wastes and need to be landfilled at a block-type final disposal site. Even if the concentration of heavy metals is within the allowable value, the ash after appropriate intermediate treatment will be disposed of in landfills at a managed final disposal site [1, 2], and its processing cost is one of the important problems in the promotion of biomass power generation. Effective 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 [3, 4].

Coal is one of the energy sources having an advantage in terms of abundant deposits, compared with the other energy sources. In 2012, the percentage of electric power generation in coal power plants in Japan occupies about 23.4 % to all amount of electric power [5]. By increasing coal demand, the discharge amount of coal ash is also estimated to increase. According to the law relating recycling in Japan, the coal ash derived from thermal power plant is especially designated as specified by-product, and the effective usage of this coal ash is strongly required. Recently, the reuse and recycle of coal ash are tried to proceed aggressively, and the percentage and amount of effective usage in 2014 reach about
98 % and 9.4 million tons/year, respectively. However, more than 200000 ton/year of coal ash must be deposited in the landfill treatment still. Furthermore, since the Great East Japan Earthquake on March 11, 2011, the focus of energy production in Japan has shifted from nuclear power toward coal-generated power. The fly ash generated at coal-fired power plants was mostly wasted before the earthquake, and more fly ash is expected to be generated in the future. However, the lack of landfill space is anticipated in Japan, so new recycle technologies for coal ash are also desired to develop [6-9].

Worldwide depletion of phosphate resources for fertilizer production and other industrial applications has become a major concern. Phosphorous is known to be a main cause of eutrophication, and phosphorous removal is an important issue in sewage treatment from wastewater with high phosphorous concentration [10, 11]. A simple treatment method, adsorption using different materials, is generally considered as an effective treatment technique for removal of phosphorus from water and wastewater with low phosphorous concentration. Coagulation methods using AlCl₃, Al₂(SO₄)₃, FeCl₃, Fe₃(SO₄)₃ and so on are one of the popular methods for phosphate removal, but it is very complicated the phosphate recovery from the generated sludge containing phosphate is very difficult, and the complicated process is necessary to reuse as phosphate resources. In the adsorption method, selection of the material for removal is important, and layered double hydroxide (LDH) is expected to remove phosphorus effectively [12]. LDH is a nonstoichiometric compound represented by the general formula [Mₓ/n⁺Mₙ⁻(OH)₂]((Aₓ/n)⁺mH₂O). Here, M²⁺ is a divalent metal ion, such as Ca²⁺, Mg²⁺ or Zn²⁺, and M³⁺ is a trivalent ion, such as Fe³⁺, Al³⁺ or Cr³⁺. 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 generally an inorganic anion, such as Cl⁻, NO₃⁻, OH⁻, CO₃²⁻ or SO₄²⁻. Among LDH, Ca-Fe type LDH (M²⁺ = Ca²⁺, M³⁺ = Fe³⁺, M²⁺/M³⁺ = 2 and 3) is expected to recover phosphorous from aqueous solution and then be directly used as fertilizer [13]. It is expected to reuse the removing phosphate as resources using simple process with LDH.

In this study, we attempted to prepare a material, including Ca-Fe LDH, from the solution with Ca²⁺ and Fe³⁺ extracted from biomass combustion ash and coal fly ash using HCl, and the phosphorus adsorption ability of the product was examined.

2. Materials and methods

2.1. Samples

Biomass combustion ash (BCA) and coal fly ash (CFA) were collected from one of the power plants in Japan, respectively. The elemental composition of the ashes analyzed by X-ray fluorescence (XRF) (Epsilon1, PANalytical) is shown in Table 1. BCA contains a large amount of divalent metal ion, Ca, but the amount of trivalent metal ions, Fe and Al, are low, while CFA contains a large amount of trivalent metal ions, Fe and Al, but the amount of divalent metal ions, Ca and Mg, are low, indicating that the solution with M²⁺/M³⁺ > 2 can be prepared by extracting metal ions from these ashes.

| Table 1. Chemical compositions of BCA and CFA. |
|-----------------------------------------------|
| Content (%) | Ca  | Mg  | Fe  | Al  | Si  | K   | Ti  | P   |
| BCA       | 71.8 | 2.5 | 1.3 | -   | 3.2 | 15.4| -   | 1.8 |
| CFA       | 6.8  | -   | 17.9| 22.0| 43.2| 2.2 | 3.5 | 1.5 |

Mineralogical compositions, analysed using X-ray diffraction (XRD) (MiniFlex600, Rigaku), of BCA and CFA are shown in Figure 1. BCA mainly composed of calcium compounds, such as calcite (CaCO₃), larnite (Ca₂SiO₄), portlandite (Ca(OH)₂) and lime (CaO), periclase (MgO) and quartz (SiO₂) used for fluidized bed combustion. CFA consists of quartz, mullite (Si₂Al₂O₇) and hematite (Fe₂O₃), with amorphous phases indicating the broad hump between 20 - 30°.
2.2. Synthesis

The experimental procedure is shown in Figure 2. In order to obtain the mixed solution with Ca$^{2+}$, Mg$^{2+}$, Fe$^{3+}$ and Al$^{3+}$, 10 g of CFA was added into 40 mL of 5 M HCl solution, then stirred for 1 h, 2 g of BCA ash was added into this solution, and stirred for 10 min. After stirring, the solution was centrifuged, and the concentrations of Ca, Mg, Fe and Al in the supernatant and the pH of the supernatant were measured using atomic absorption spectrometer (AAS) (AAnalyst200, PerkinElmer) and pH meter (LAQUA F 72, Horiba), respectively.

Synthesis was carried out with (S1) or without filtration (S2) as follows; The solution with or without filtration stirred at 40° C with a hot stirrer. During stirring, 4 M NaOH solution was appropriately added dropwise to keep the pH of the solution at 12.5. After stirring for 6 h, the slurry was filtered, dried and washed with distilled water, and dried to obtain a product. The mineral phases of the product were identified using X-ray diffraction (XRD) (MiniFlex600, Rigaku), and the surface structure of the product was analyzed using scanning electron microscope (SEM) (JSM-6510A, JEOL).

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2.3. Phosphorous removal
For phosphorus removal experiment, the phosphorus solution with concentration of 0.1 – 8.0 mmol/L were prepared from dihydrogen potassium phosphate (KH$_2$PO$_4$). For effect of initial phosphorus concentration on phosphorus removal of the product, 20 mg of the product was added to 40 mL of phosphorus solution with 0.1 – 8.0 mmol/L, and shaken for 12 h. After shaking, the tube was centrifuged, and the concentration of phosphorous in the supernatant was measured using molybdenum blue method, and the adsorption amounts ($q$) of phosphorus were calculate using the following formula (1),

$$ q = \frac{(C_0 - C) V}{W} $$

where $C_0$ is the initial concentration of phosphorus (mmol/L), $C$ is the measured concentration of phosphorus (mmol/L), $V$ is the solution volume (L), and $W$ is the mass of product (g).

The mineral phases of the products after removing phosphorus were identified using XRD. The surface structure of the products after removing phosphorus were observed using SEM, and the chemical compositions of the surface of the products after removing phosphorus were analyzed by energy dispersive X-ray spectrometer (EDS) (EX-94300S4L1Q, JEOL).

It is noted that all analytical errors for the data in this paper are less than 10%.

3. Results and discussion

3.1. Synthesis of LDH
The composition of the solution prepared from BCA and CFA for synthesis of the product is shown in Table 2. It is noted that the pH of the solution was strongly acidic (< 1). The divalent and trivalent cations can be extracted into the solution from the ashes, and the molar ratio of the solution is $(Ca+Mg)/(Fe+Al) = 5.17$, which is possible for the synthesis of LDH ($> 2$).

Table 2. Chemical compositions of the solution prepared from BCA and CFA.

| Concentration (mol/L) | (Ca+Mg)/(Fe+Al) molar ratio |
|-----------------------|-----------------------------|
| Ca        | Mg  | Fe  | Al  | 5.17 |
| 0.22      | 0.08| 0.01| 0.05|      |

Figure 3. XRD patterns of the Product-S1 and Product-S2.
Figure 3 shows the XRD patterns of the products synthesized from the solution prepared from the ashes with and without filtration. It is noted that Product-S1 and Product-S2 indicates the product synthesized from the solution with filtration process (S1) and without filtration process (S2), respectively. Product-S1 and Product-S2 showed different mineral phases. In Product-S1, the peaks of LDH can be confirmed, while in Product-S2, the peaks of LDH cannot be confirmed and those of quartz and mullite, which are originated from the raw ashes, are confirmed.

Figure 4 shows SEM photographs of Product-S1 and Product-S2. Both products showed agglomerates of plate-like hexagonal crystals like LDH crystals, indicating that LDH can be synthesized in both products. It is considered that the peaks of quartz and mullite are high, and the weak peak of LDH cannot be confirmed.

3.2. Removal of phosphorous

Figure 5 shows the adsorption isotherms of Product-S1 and Product-S2 for removal of phosphorus. It is indicated that the phosphorus removal ability of Product-S1 is higher than that of Product-S2, because Product-S2 contains some impurities, such as quartz and mullite, having no phosphorus removal.

Figure 4. SEM photos of (a) Product-S1 and (b) Product-S2.

Figure 5. Isotherm of phosphorous adsorption using Product-S1 and Product-S2.
The experimental results obtained in Figure 5 were analyzed using the Langmuir and Freundlich adsorption models to estimate the phosphorus adsorption of the product.

The liner equations of Langmuir (2) and Freundlich (3) are as follows,

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

where \( q_e \) is the amount of phosphorus absorbed at equilibrium (mmol/g), \( q_{max} \) (mmol/g) and \( K_L \) (L/mmol) 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 3. According to the correlation coefficient \( R^2 \), for both Product-S1 and Product-S2, the Langmuir equation could be more realistic than the Freundlich’s equation. The calculated maximum adsorption capacities of the Product-S1 and Product-S2 for phosphorus using the Langmuir equation are 2.33 mmol/g and 0.60 mmol/g, respectively.

Table 3. Langmuir and Freundlich parameters in the adsorption for phosphorous using Product-S1 and Product-S2.

|           | Langmuir | Freundlich |
|-----------|----------|------------|
|           | \( q_{max} \) | \( K_L \) | \( R^2 \) | \( n \) | \( K_F \) | \( R^2 \) |
| Product-S1 | 2.33     | 0.53       | 0.977     | 2.35     | 1.19     | 0.974     |
| Product-S2 | 0.60     | 0.33       | 0.950     | 7.47     | 0.45     | 0.476     |

The XRD patterns of the Product-S1 after removing phosphorus when 20 mg of the product was added into 40 mL of phosphorus solution with 0.5 mmol/L and 5 mmol/L are shown in Figure 6. After removing, the peaks of LDH could be confirmed in both solutions. It is indicated that the phosphorus removal is mainly dependent on ion exchange of LDH, without destructing the structure of LDH, regardless of phosphorous concentrations.

Figure 6. XRD patterns of Product-S1 after removing phosphorous from the solution with (a) 0.5 mmol/L and (b) 5 mmol/L of phosphorous.
4. Conclusions
In this study, a Ca-Mg-Fe-Al type LDH was synthesized from biomass combustion ash and coal fly ash, and its removal ability for phosphorus was examined. As a result, we successfully synthesize the product containing Ca-Mg-Fe-Al type LDH with removal ability for phosphorus from biomass combustion ash and fly ash. The calculated maximum adsorption amount for Product-S1 and Product-S2 were 2.33 mmol/g and 0.60 mmol/g, respectively. These results suggest that it is possible to produce a product containing LDH with phosphate removal ability from industrial waste ashes for using as fertilizer.

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