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Synthesis of Fe-Type Layered Double Hydroxide from Biomass Combustion Ash for Removal of Phosphorus

A. Suhara and T. Wajma

Abstract—**In this study, we attempted to synthesize Fe-type layered double hydroxide (LDH) from biomass combustion ash for phosphorus removal.**

In Japan, biomass power generation is being promoted for effective biomass utilization, and there is a big problem that a large amount of biomass combustion ash is discharged to dispose at landfill as industrial wastes. On the other hand, water pollution caused by anions, such as eutrophication with phosphoric acid (PO_4^{3-}) in wastewater, has become a problem. As a simple treatment method, adsorption method using anion removal material is focused. In the adsorption method, it is important to select the adsorbent, and Fe-based LDH are expected as phosphorus-removing materials.

In this experiment, the combustion ash was added to HCl to dissolve divalent cations, Ca and Mg, in the ash, iron chloride hexahydrate ($FeCl_3$ $6H_2O$) was added to prepare acidic liquid mixture with a molar ratio of (Ca + Mg)/Fe = 2 - 3, and the mixture stirred to synthesize the product including LDH at 40 ^oC for 6 h with keeping pH 12.5. The product was analyzed by scanning electron microscope (SEM), energy dispersive X-ray spectrometer (EDS) and powder X-ray diffraction (XRD), and the phosphorus removal ability of the product was investigated.

As the result, Ca-Mg-Fe LDH was successfully synthesized from biomass combustion ash with addition of $FeCl_3$, 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.

Index Terms—**Biomass combustion ash, layered double hydroxide, phosphorus removal, $FeCl_3$.**

I. 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 [1]. 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 [2], [3], 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 [4], [5].

Worldwide depletion of phosphate resources, which are used in 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 [6], [7]. A simple treatment method, adsorption using different materials, is generally considered as an effective treatment technique for removal of phosphorus 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 phosphorus effectively [8]. LDH is a nonstoichiometric compound represented by the general formula $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2][A_{x/n}^{n-} \cdot mH_2O]$. Here, M^{2+} is a divalent metal ion, such as Ca^{2+}, Mg^{2+} or Mn^{2+}, and M^{3+} is a trivalent ion, such as Fe^{3+}, Al^{3+} or 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 generally an inorganic anion, such as Cl^-, NO_3^-, OH^-, CO_3^{2-} or SO_4^{2-}. Among LDH, Ca-Fe type LDH ($M^{2+} = Ca^{2+}$, $M^{3+} = Fe^{3+}$, $M^{2+}/M^{3+} = 2$ and 3) is expected to recover phosphorous from aqueous solution and then be directly used as fertilizer [9].

In this study, we attempted to prepare a material, including Ca-Fe LDH, from biomass combustion ash for phosphorus removal, with addition of inexpensive $FeCl_3$ and the phosphorus adsorption ability of the product was examined.

II. EXPERIMENT

A. Sample

Biomass combustion ash used in this study was collected from one of the biomass power plant, which burns the cedar pellets using fluidized bed reactor, in Japan. The elemental composition of the ash analyzed by X-ray fluorescence (XRF, Epsilon1, PANalytical) is shown in Table I. The ash contains a large amount of divalent metal ion, Ca, but the amount of trivalent metal ions, Fe and Al, are low, indicating that $M^{2+}/M^{3+} > 2$. All reagents used in this study were purchased from Wako's Chemical Co. Ltd., Japan.

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TABLE I: ELEMENTAL COMPOSITIONS OF BIOMASS COMBUSTION ASH AND PRODUCTS

Content (wt%)	Ash	Product-S1	Product-S2
Mg	3.08	2.13	3.20
Al	3.09	0.89	3.69
Si	9.86	3.77	13.06
P	2.00	0.81	2.42
S	2.98	0.48	0.15
Cl	10.83	0.55	0.35
K	13.08	0.35	2.46
Ca	41.69	44.77	38.89
Mn	1.19	0.74	1.32
Fe	11.36	44.89	32.63
Cu	0.15	0.14	0.19
Zn	0.27	0.23	0.34
As	0.02	0.01	0.01
Pb	0.03	0.01	0.04
Others	0.12	0.24	1.17
Total	100	100	100

B. Synthesis

The experimental procedure is shown in Fig. 1. According to the past literature, it is known that the Ca-Mg-Fe type layered double hydroxide can be synthesized from the acidic solution with the molar ratio of (Ca+Mg)/Fe = 2 - 3 [8]. In order to obtain the mixed solution from the dissolution of Ca and Mg from biomass combustion ash, 6.0 g of combustion ash was added into 40 mL of 1 M HCl solution, and shaken for 1 min [10]. After shaking, filtration was carried out (S1) or filtration was not carried out (S2), and then iron chloride hexahydrate [$FeCl_3 \cdot 6H_2O$] was added into the solutions to prepare a mixed solution with (Ca+Mg)/Fe = 2 - 3. The concentrations of Ca, Mg and Fe in the mixed solution and the pH of the solution were measured using atomic absorption spectrometer (AAS, AAnalyst200, PerkinElmer) and pH meter (LAQUA, F 72), respectively.

Synthesis method of S1 and S2 were as follows;

S1 : The obtained mixed solution with (Ca+Mg)/Fe = 2 - 3 was added into 50 mL of 0.3 M NaCl solution stirred at 40 °C with a hot stirrer with the flow rate of 4 mL/min using a peristaltic pump. During stirring, 4 M NaOH solution was appropriately added dropwise to keep the pH of the solution at 12.5.

S2: The obtained mixed solution with (Ca+Mg)/Fe = 2 - 3 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 was identified using X-ray diffraction (XRD, MiniFlex600, Rigaku), and the surface structure of the product was analyzed using scanning electron microscope (SEM, JEOL, JSM-6510A).

For the contents of Ca, Mg, Fe, Cl and SO_4 in the product, the obtained product (0.05 g) was dissolved in 1 M CH_3COOH solution (10 mL) by shaking for 1 h, and centrifuged. The concentrations of Ca, Mg and Fe in the supernatant were measured by AAS and these of Cl^- and SO_4^{2-} were analyzed by ion chromatograph (SHIMADZU, CTO-10A) to calculate the content of each element in the product.

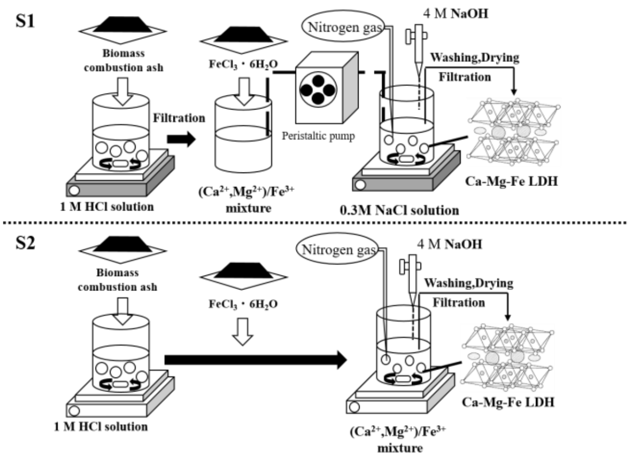

Fig. 1. Experimental procedure of S1 and S2.

C. Phosphorus Removal

For phosphorus removal experiment, the phosphorus solution with concentration of 0.1 - 10 mmol/L were prepared from dihydrogen potassium phosphate (KH_2PO_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),

$$q = (C_0 - C) \times V/W \tag{1}$$

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 added to the solution (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, JEOL, EX-94300S4L1Q).

III. RESULTS AND DISCUSSION

A. Synthesis of Fe-LDH

The compositions of the prepared mixed solution for synthesis of S1 and S2 are shown in Table II. The pH of the mixed solution was acidic and the molar ratio of the solution is (Ca+Mg)/Fe = 2 - 3, which was suitable for the synthesis of Fe–LDH.

Fig. 2 shows the XRD patterns of raw ash and the products synthesized from the mixed solution. Raw ash contains chloride, carbonate, and sulfate containing calcium and potassium derived from the biomass and quartz (SiO_2) used for fluidized bed combustion. Product-S1 and product-S2 showed different mineral phases. In product-S1, the peaks of Fe-LDH can be confirmed, while in product-S2, the peaks of Fe-LDH cannot be confirmed. It is considered that the peak of SiO_2 is high, and the weak peak of Fe-LDH cannot be confirmed. It is noted that SiO_2 mineral would be fluidized bed sand used in fluidized bed furnace.

TABLE II: COMPOSITIONS AND PHS OF THE MIXED SOLUTIONS

	Concentration (mol/L)				Molar ratio	pH
	Ca	Mg	Ca+Mg	Fe	(Ca+Mg)/Fe	
S1	0.23	0.05	0.28	0.13	2.2	1.6
S2	0.22	0.06	0.28	0.12	2.4	1.4

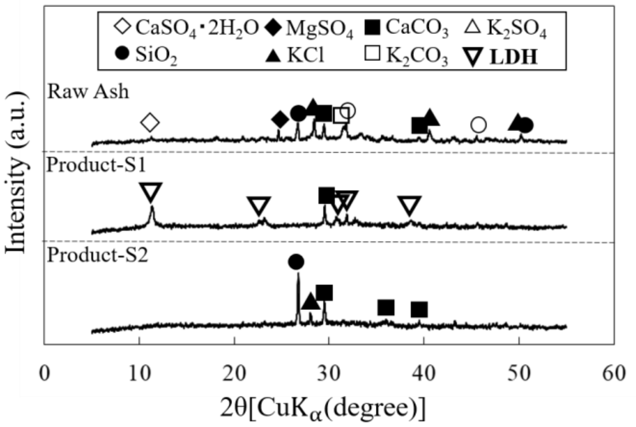

Fig. 2. XRD patterns of raw ash, product-S1 and product-S2.

Fig. 3 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.

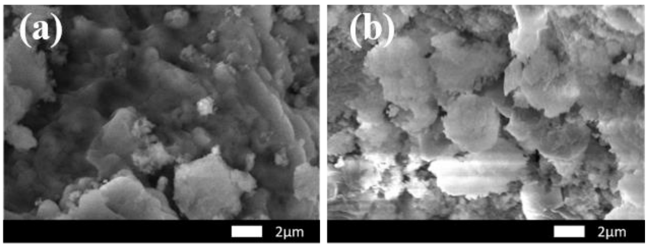

Fig. 3. SEM photographs of the (a) product-S1 and (b) product-S2.

The elemental compositions of the obtained products are shown in Table I and Table III. The ratio of the product for (Ca+Mg)/Fe is 2.6 and 2.5 respectively, which means that almost contents of divalent metal ion and trivalent metal ion in the mixed solution are used for the product structure.

TABLE III: ELEMENTAL COMPOSITIONS OF THE PRODUCTS

	Content (mmol/g)			
	Ca	Mg	Ca+Mg	Fe
Product-S1	3.6	1.0	4.6	1.8
Product-S2	1.7	0.8	2.5	1.0

The amount of Si including in Product-S2 is higher than that including in Product-S1due to the content of SiO_2 minerals.

B. Removal of Phosphorus

Fig. 4 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 (SiO_2) having no phosphorus removal.

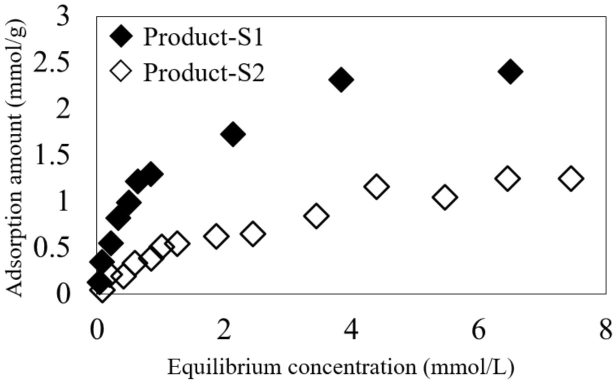

Fig. 4. Adsorption isotherms after removal of phosphorus using product-S1 and product-S2.

The experimental results obtained in Fig. 4 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,

$$C_e/q_e = (q_{max}\,K_L)^{-1} + C_e/q_{max} \tag{2}$$

$$ln q_e = ln K_F + n^{-1} \cdot ln C_e \tag{3}$$

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 IV. 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 2.69 mmol/g and 1.69 mmol/g, respectively.

TABLE IV: RESULTS OF PARAMETERS FROM THE ADSORPTION ISOTHERM

	Langmuir			Freundlich		
	q_{max}	K_L	R^2	n^{-1}	K_F	R^2
Product-S1	2.69	0.11	0.99	0.54	1.21	0.93
Product-S2	1.69	0.98	0.93	0.67	0.39	0.92

The important feature of the Langmuir isotherm can be written in form of a dimensionless quantity known as separator factor (R_L) which is given by (4)

$$R_L = (1 + K_L C_{0,\,max})^{-1} \tag{4}$$

where K_L and $C_{0,max}$ are the adsorption equilibrium constant of Langmuir model and maximum initial concentration, respectively.

The value of R_L determines nature of the isotherm shape. It can either be favorable ($0 < R_L < 1$), unfavorable adsorption ($R_L > 1$), liner ($R_L = 1$) and irreversible adsorption ($R_L = 0$). The obtained values of R_L for product-S1 and product-S2 to be 0.55 and 0.11, respectively, for phosphorus adsorption, suggesting that the process is favorable.

In addition, the value of the Freundlich constant (n) indicates the affinity adsorbed ($0.1 < n^{-1} < 1$), or difficulty adsorbed ($n^{-1} > 2$) [11]. The obtained value of n^{-1} for product-S1 and product-S2 to be 0.54 and 0.67, respectively, for phosphorus adsorption, suggesting that the process has affinity.

The XRD patterns of the products after removing phosphorus when 20 mg of the product was added into 40 mL of phosphorus solution with 1 mmol/L are shown in Fig. 5. After removing, the peaks of LDH could not be confirmed in both product-S1 and product-S2. It is indicated that the phosphorus removal is not mainly dependent on ion exchange of LDH, and is considered to be removed by the formation of amorphous phosphates.

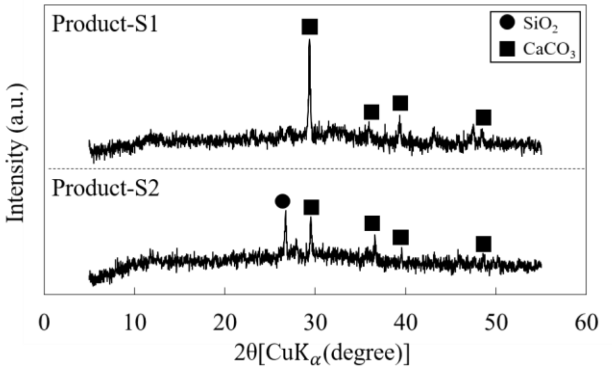

Fig. 5. The XRD patterns of product-S1 and product-S2 after removing phosphorus.

Fig. 6 shows SEM photographs of the products after removing phosphorus. In both products, particulates on the surface of the product can be observed.

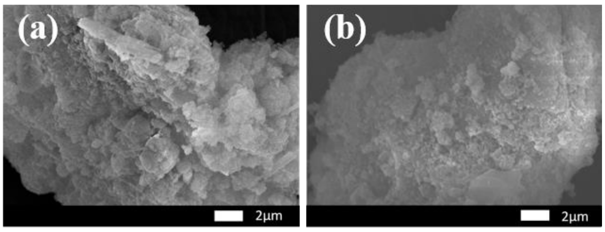

Fig. 6. SEM photographs of (a) product-S1 and (b) product-S2 after removing phosphorus.

Chemical compositions of the structure of product-S1 and product-S2 after removing phosphorus are shown in Table V. Phosphorus content can be detected on the surface of the product after phosphorus removal. It is considered that phosphorus was present on the surface of the products by formation of particulates.

TABLE V: CHEMICAL COMPOSITIONS OF THE PRODUCT-S1 AND PRODUCT-S2 AFTER REMOVING PHOSPHORUS

	C	O	Ca	Mg	Fe	P
Product-S1	16.1	56.6	7.4	1.8	4.7	6.5
Product-S2	30.4	44.5	6.4	1.3	5.9	4.1

From these results after removing phosphorus, it is considered that main mechanism for removing of phosphorus by the product is the reaction between phosphorus in aqueous solution and dissolved elements from Fe-LDH.

IV. CONCLUSION

In this study, a Ca-Mg-Fe-type LDH was synthesized from biomass combustion ash, and its removal ability for phosphorus was examined. As a result, we successfully synthesize the product containing Ca-Mg-Fe-type LDH with removal ability for phosphorus from biomass combustion ash.

The calculated maximum adsorption amount for product-S1 and product-S2 were 2.69 mmol/g and 1.69 mmol/g, respectively.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

AUTHOR CONTRIBUTIONS

A. Suhara conducted the research, analyzed the data and wrote the paper, T. Wajima revised the manuscript and all authors had approved the final version.

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