



## Research paper

## Phosphate recovery by generating hydroxyapatite via reaction of calcium eluted from layered double hydroxides



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## ABSTRACT

Ca/Fe ( $[\text{Ca}^{2+}]/[\text{Fe}^{3+}]$ )-based layered double hydroxides (CF-LDHs) were designed and synthesized with the aim of developing an adsorbent that can recover phosphorous from aqueous solution and then be directly used as fertilizer. Fundamental properties of phosphate recovery and reaction mechanisms between CF-LDHs and phosphate were investigated. The adsorption isotherm of CF-LDH was fit by the Langmuir isotherm at a low Ca/Fe molar ratio (= 1). However, CF-LDHs exhibited a larger adsorption volume of phosphate at high Ca/Fe molar ratios (= 2 and 3) than low Ca/Fe molar ratios or conventional Mg/Al ( $[\text{Mg}^{2+}]/[\text{Al}^{3+}]$ )-based LDHs. At high Ca/Fe molar ratios, CF-LDH reacted with phosphate through a reaction mechanism different from that of the conventional LDHs. Whereas ion exchange is the primary mechanism of the reaction between the conventional LDHs and phosphate, CF-LDHs released calcium into aqueous solution and the reaction of calcium and phosphate generated hydroxyapatite. The amount of phosphate recovered depended on the amount of calcium that eluted from CF-LDH and on pH, which is affected by the hydroxyl groups of CF-LDH. Hydroxyapatite was generated more efficiently under alkaline conditions, indicating the involvement of a supersaturated state in hydroxyapatite generation.

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## 1. Introduction

Phosphorous is known to be a main cause of eutrophication, making phosphorous removal an important issue in sewage treatment. At the same time, worldwide depletion of phosphate resources, which are used in fertilizer production and other industrial applications, has become a major concern. Since the main phosphate-producing countries, including China and the United States, have implemented export control measures, the international market price of phosphate rock has soared in the past several years. Some researchers have predicted that phosphate rock reserves could be exhausted within 50 years (Gilbert, 2009). Methods for collecting and reusing consumed phosphates are therefore urgently needed.

In Japan, the amount of phosphorus that flows into sewers is estimated to correspond to 35% of the country's annual phosphate rock imports (Matsubae et al., 2008), but very little of that phosphorus is collected and reused. Thus, technology for recovering phosphorus from wastewater in a form that can be reused as a resource is in high demand. Although many techniques, such as crystallization and adsorption, have been investigated previously (Ames and Dean, 1970; Hano et al., 1997; Suzuki and Fuji, 1987; Tanaka and Shimamura, 2005; Yee, 1966), phosphorus recycling remains difficult due to the imbalance between the recovery cost and market price of the collected phosphorus,

resulting in few examples of its utilization. Because most phosphate rock is consumed in the production of fertilizer, one way to simplify processing and lower recovery costs is to collect phosphorus in a form that can be directly used as fertilizer.

In many previous studies (Ookubo et al., 1993, 1994; Shin et al., 1996), layered double hydroxides (LDHs) (Cavani et al., 1991; Khan and O'Hare, 2002; Miyata, 1975, 1980) have shown promise as phosphorous adsorbents. The general chemical formula of these compounds is  $[\text{M}^{2+}_{1-x}\text{M}^{3+}_x(\text{OH})_2]\text{A}^{n-}_{x/n} \cdot m\text{H}_2\text{O}$ , where  $\text{M}^{2+}$  represents a divalent cation ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ),  $\text{M}^{3+}$  represents a trivalent cation ( $\text{Al}^{3+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Ga}^{3+}$ ),  $x$  is defined as the ratio  $[\text{M}^{3+}]/([\text{M}^{2+}] + [\text{M}^{3+}])$ , and A is an anion of valence  $n$ .

LDHs have a lamellar structure of brucite-like layers, which are positively charged by partial substitution of  $\text{M}^{3+}$  for  $\text{M}^{2+}$ . The overall system is electrically neutral because the interlayer space is negatively charged, and thus the structure is stable and the interlayer space is capable of anion exchange. The anion exchange capacity of an LDH depends on the number of negatively charged sites, and corresponds to the number of positively charged sites in the brucite-like layer. Generally, the structure of LDHs is stable in the range  $0.17 \leq x \leq 0.33$  (Ookubo et al., 1994), and the highest anion exchange capacity is obtained at  $x = 0.33$ . The anion exchange capacity in the interlayer space is governed by the charge density of the brucite-like layer and anionic species, the distance between brucite-like layers, and the ionic radius of the anion. Therefore, the anion exchange function is altered by the species of cations in the brucite-like layer and anions in the interlayer space, and by the ratio

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between the anions and cations. Furthermore, dehydration destroys the LDH structure, but it can be reconstructed with intercalating anions in water. This characteristic can also contribute to the anion adsorption mechanism (Koilaraj et al., 2013). In this study, Ca/Fe-based LDHs (CF-LDHs) were designed and synthesized as candidate adsorbents for use as fertilizer after phosphorus recovery, and the fundamental properties of the phosphate recovery and reaction mechanism of the adsorbent were investigated.

## 2. Materials and methods

### 2.1. Sample preparation

All chemicals used as starting materials were of reagent grade, and all solutions were prepared using deionized water. CF-LDHs were synthesized as follows: A sodium hydroxide solution (2.0 M) was added dropwise to a mixed solution of calcium chloride and iron chloride (Ca/Fe molar ratio = 0.75, 1, 2, or 3, corresponding to  $x = 0.57, 0.5, 0.33,$  or  $0.25,$  respectively) to adjust the pH to 11. The reaction was run with the mixture kept at 70 °C for 4 h under vigorous stirring. The precipitate that formed was collected by filtration and rinsed several times with deionized water. The compound was dried at 80 °C for 2 days and crushed into a powder. It should be noted that the starting materials were chosen with the aim of using elements and ions that are used in the manufacture of fertilizer.

Mg/Al-based LDH (MA-LDH) (Mg/Al = 2), which is the most well-known type of LDH (Miyata, 1983), was also synthesized for comparison.

### 2.2. Characterization of samples

The cationic and anionic composition of LDHs were measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES; SPS-400, SII Nano Technology Inc.) and ion chromatography (IC; Alliance, Waters), respectively. The concentration of carbon in the LDHs was measured by high-frequency induction heating followed by infrared spectroscopy (CS-444LS, LECO).

The LDHs were analyzed by powder X-ray diffraction (XRD; M18XHF22, MAC Science) using CuK $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ) at 100 mA and 40 kV, and at a scanning rate of  $2^\circ \text{ min}^{-1}$ . Raman spectroscopy (Almega, Thermo Fisher Scientific) was performed using the 532 nm line of a Nd:YAG laser.

### 2.3. Recovery properties of sample

Phosphate solutions were prepared from Na<sub>2</sub>HPO<sub>4</sub>. All the tests were performed in a 50 mL polypropylene centrifuge tube at room temperature (around 25 °C). The concentrations of phosphate and cations in the solutions were measured by IC and ICP-AES, respectively. Changes in concentration were calculated by mass balance.

Adsorption isotherms were obtained by the batch equilibration technique. LDH (20 mg) was placed in a series of 50 mL phosphate solutions, ranging in concentration from 20 to 100 mg P/L. Each mixture was stirred for 2 h and filtered with a membrane filter (0.2  $\mu\text{m}$ ). The concentrations of ions in the filtrate were then analyzed.

The desorption properties of phosphate from LDH were examined using a CF-LDH (Ca/Fe = 2) that had been saturated with phosphate by using 100 mg P/L solution. The pH of the desorption solution was varied from acidic to alkaline by using hydrochloric acid or sodium hydroxide. LDH (20 mg) was placed in a 50 mL desorption solution and stirred for 10 h. The concentration of phosphate in the solution was analyzed, with the desorption proportion defined as the ratio of desorbed phosphate to phosphate retained in the sample.

## 3. Results and discussion

### 3.1. Characterization of LDHs

The chemical compositions of LDHs are listed in Table 1. The cationic ratio of an LDH depends on the molar ratio of the starting materials. The small amount of carbon observed is attributed to carbonate introduced during the synthesis.

XRD patterns of LDHs are shown in Fig. 1. All the samples exhibited the characteristic patterns of LDH (Kovanda et al., 2005; Zhang et al., 1995). The reflections of the (003) and (006) faces of CF-LDH, that is, the basal reflections of the LDH structure, were very strong and sharp compared with those of MA-LDH. In other words, the crystal quality of CF-LDH was higher than that of MA-LDH. However, the interlayer distances ( $d$ -value) calculated from the (003) reflection and the Bragg equation were not markedly different between CF-LDH (7.72  $\text{\AA}$ , Ca/Fe = 2) and MA-LDH (7.78  $\text{\AA}$ ; Mg/Al = 2). Other phases thought to be Ca(OH)<sub>2</sub>, Fe(OH)<sub>3</sub>, and CaCO<sub>3</sub> were evident in XRD profiles of CF-LDH, whereas MA-LDH consisted of a single phase of LDH.

The above results indicate that the basal structures of CF-LDH and MA-LDH are fundamentally similar. Although both materials certainly exhibit the LDH structure, CF-LDH has higher crystal quality and more secondary phases in comparison with MA-LDH.

### 3.2. Reaction mechanism

Fig. 2 shows the adsorption isotherms of CF-LDHs and MA-LDH. The maximum adsorption volume of CF-LDH was extremely large at high Ca/Fe molar ratios (= 2 and 3), and the adsorption behavior differed from that at low Ca/Fe molar ratios (= 0.75 and 1) and that of MA-LDH. These results indicate that CF-LDH reacts with phosphate not by a single mechanism but by two or more mechanisms.

The equilibrium data for Ca/Fe = 1 was fit with the Langmuir equation (Fig. 3), which is given by

$$C_{eq}/W = 1/(K_1K_2) + C_{eq}/K_2$$

where  $C_{eq}$ ,  $W$ ,  $K_1$ , and  $K_2$  are the equilibrium concentration of phosphate in solution, the phosphate uptake into the sample, the adsorption coefficient, and the saturated adsorption volume for phosphate, respectively. A straight line fit the data fairly well, indicating that the adsorption behavior of Ca/Fe = 1 with phosphate follows the Langmuir isotherm. Although the equilibrium data for Ca/Fe = 0.75 did not conform to the Langmuir equation, the adsorption behavior of Ca/Fe = 0.75 was similar to that of Ca/Fe = 1.

As mentioned above, ion exchange is a dominant adsorption mechanism for typical LDHs, such as MA-LDH. In the case of LDH with Ca/Fe = 0.75 and 1 ( $x = 0.57$  and  $0.5$ ), the reaction mechanisms cannot be satisfactorily explained by ion exchange because the stoichiometry of CF-LDHs deviates from that in which the LDH structure is stable ( $0.17 \leq x \leq 0.33$ ). However, the curve follows the Langmuir equation, which demonstrates the existence of a clear interaction (Das et al., 2004; Ookubo et al., 1993) between CF-LDH and phosphate. We therefore suggest that it is attributable to surface adsorption, which is already known as the one of the

**Table 1**  
Chemical composition of LDHs.

Synthesized compound	Molar ratio (Fe is set to 1.00)			
	Ca	Fe	Cl	C
Ca/Fe = 0.75	0.75	1.00	0.30	0.09
Ca/Fe = 1	1.02	1.00	0.29	0.09
Ca/Fe = 2	1.80	1.00	0.72	0.05
Ca/Fe = 3	3.09	1.00	0.67	0.10

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