

Original Paper

## A Novel Anion Exchanger Composed of Formate Hydrotalcite for Sorptive Recovery of Phosphorus

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### Abstract

Feasibility of a renewable sorbent for phosphorus was determined by testing the anion-exchange ability of hydrotalcite, which holds formate ions in its interlayer. The formate hydrotalcite, successfully prepared by reacting raw hydrotalcite with a formic acid/1-propanol solution, exhibited high performance for phosphorus removal and collection based on a stoichiometric anion-exchange principle. It was estimated that the collected orthophosphate ions existed as poly-anion forms of  $\text{HPO}_4^{2-}$  and  $\text{PO}_4^{3-}$  with a ratio of 67.6:32.4 in the interlayer after the sorption. The formate hydrotalcite is also able to revert to the starting hydrotalcite after the sorption, when treated with  $\text{Na}_2\text{CO}_3$  aqueous solution, demonstrating that it can be an attractive alternative to the conventional chloride or nitrate hydrotalcite as an anion exchanger.

**Key words:** Formate hydrotalcite, Anion exchange, Orthophosphate ion, Sorbent

### 1. Introduction

Phosphorus is an important resource, because it is an essential element for living beings and is also used industrially in manure. Since there is no process available that allows the simultaneous industrial application of phosphorus and its regeneration after use, it is important to secure stable phosphate resources. A method to secure phosphate resources is sorption from discharged and/or environmental water by using an anion exchanger such as hydrotalcite (HT). HT is a typical mineral with layered double hydroxides (LDHs), which are known as anion-exchange materials<sup>1,2</sup>. HT consists of positively charged brucite-like octahedral layers formed by partial substitution of Al for Mg and interlayer carbonate ion, and is represented by the chemical formula  $\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$ . HTs are commonly synthesized in industrial fields for use in products such as resin additives and antacids for the stomach<sup>3-5</sup>, and LDHs are often studied for application as scaffolds for immobilizing functional organic

species<sup>6-8</sup>. The sorption of phosphate ions with LDHs from aqueous solution is an attractive method to secure phosphate resources and has been studied by many researchers<sup>9-18</sup>. In general, these anion-exchange reactions are conducted by using LDHs with chlorate or nitrate ions in the interlayer, because it is difficult to exchange carbonate ions incorporated on the LDH structure with external anions because of the strong affinity of carbonate anions toward the brucite-like layer<sup>19,20</sup>. However, the chlorate ion might release harmful trihalomethane, and the nitrate ion is detrimental to water treatments; therefore, an alternative to chlorate- or nitrate-LDHs is necessary to develop an anion-exchange technology for securing phosphorus resources.

In the present work, we focused on HT with incorporated formate ions in the interlayer for the removal of orthophosphate ions in aqueous solutions. The formate ion is the smallest carboxylate ion and has a very simple structure like that of carbonate, chlorate, and nitrate ions. The loading of short-chain carboxylate ions such as the formate ion into LDHs is regarded as difficult in aqueous media<sup>21-23</sup>, implying that formate-HT, wherein the incorporated anion has low affinity

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toward the brucite-like layers, will exhibit high performance as an anion exchanger. Although the chemical structure of formate-HT was reported from the viewpoint of the delamination of brucite-like layers<sup>24-26</sup>, the anion-exchange property was not studied in this process. Anion-exchange tests were conducted to investigate the stoichiometry of the anion exchange process and the feasibility of the phosphorus sorbent.

## 2. Experimental

### 2.1 Reagents

Special grade reagents were obtained from Tokyo Chemical Industry Co., Ltd., and Wako Pure Chemical Industries, Ltd., Japan, and were used as-received without further purification. Distilled water used in this work was purified by the water passing through an Advantec GS-200 AQUARIUS automatic water distillation apparatus. The commercially available HT was used as the starting material (DHT-6 with the theoretical composition  $\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$ , Kyowa Kagaku Kogyo Co., Ltd).

### 2.2 Sample preparation

The typical preparation of formate-HT was conducted using the batch technique as follows. The reaction was performed in a 1-propanol solution of formic acid<sup>27-31</sup>. The HT powder was dispersed in 50 cm<sup>3</sup> of a formic acid/1-propanol solution adjusted to the prescribed concentration of formic acid, which was equivalent to 98% of the anion-exchange capacity of the added HT, with a concentration of 80 g·dm<sup>-3</sup>, in a capped glass bottle, and the mixture was stirred for 4 h. The suspension was centrifuged, and the precipitate was washed with 1-propanol and dried under vacuum at room temperature. The resulting powder was referred to as formate-HT.

Subsequently, the formate-HT powder (0.5 g) was dispersed in a single-anion aqueous solution (50 cm<sup>3</sup>) containing 100 mmol·dm<sup>-3</sup> of KNO<sub>3</sub>, KF, KCl, KBr, or KI in a capped Erlenmeyer flask. The flasks were shaken for the prescribed time at 25°C in a constant-temperature bath. Additionally, a similar method was conducted using a 10 mmol·dm<sup>-3</sup> of K<sub>2</sub>HPO<sub>4</sub> aqueous solution in order to investigate the removal behavior for phosphorus. Furthermore, the HT powder, which incorporates orthophosphate ions, was dispersed in a 10 mmol·dm<sup>-3</sup> of Na<sub>2</sub>CO<sub>3</sub> aqueous solution in the same manner in order to check the stoichiometry of the elimination of phosphorus from the HT in conjunction with re-carbonation of HT. The resulting suspension was centrifuged, and the

supernatant was analyzed.

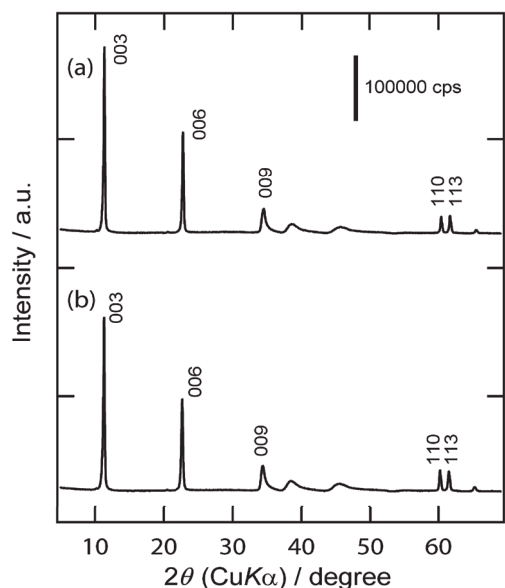
### 2.3 Equipment

X-ray powder diffraction (XRD) patterns were measured on a Rigaku Ultima IV diffractometer attached to a D/teX Ultra semiconductor detector with Ni-filtered Cu-K $\alpha$  radiation, using an operating voltage and current of 40 kV and 40 mA, respectively. Fourier transform infrared (FTIR) spectra were measured on a Shimadzu IR Prestige-21 Fourier transform infrared spectrometer equipped with an AIM-8800 automatic infrared microscope by accumulating 40 scans at 4 cm<sup>-1</sup> resolution using a diamond cell. The anions in aqueous solutions were analyzed by an ion chromatograph system equipped with a Waters 432 conductivity detector, 515 HPLC pump, and Shodex NI-424 column using the eluent composed of 8 mmol·dm<sup>-3</sup> 4-hydroxybenzoic acid, 2.8 mmol·dm<sup>-3</sup> bis(2-hydroxyethyl)imino-tris(hydroxymethyl)methane, 2 mmol·dm<sup>-3</sup> phenylboronic acid, and 0.005 mmol·dm<sup>-3</sup> trans-1,2-diaminocyclohexane-N,N,N',N'-tetraacetic acid aqueous solution. A Seiko Instruments Inc. SPS3100 inductively coupled plasma-atomic emission spectrometer and a Kyoritsu Chemical-Check Lab. TOC-UVA total organic carbon analyzer were used to analyze the aqueous solutions and validate the ion chromatography results.

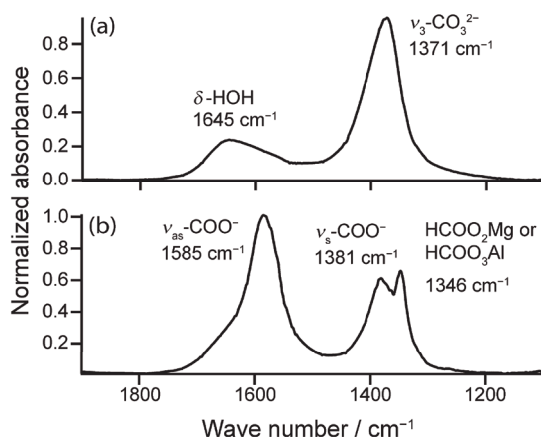
## 3. Results and discussion

### 3.1 Preparation of formate-HT

The XRD patterns and FTIR spectra of the prepared samples are shown in Fig. 1 and Fig. 2, respectively. The XRD pattern of formate-HT displayed typical diffraction peaks indexed with rhombohedral symmetry for the starting HT<sup>32</sup>, indicating that the crystal structure of HT were maintained after the formate acid/1-propanol treatment. In contrast, the intensity of the absorption bands attributed to the interlayer carbonate ion ( $\nu_3\text{-CO}_3^{2-}$ : 1371 cm<sup>-1</sup>) decreased in formate-HT, and the absorption bands attributed to carboxylate antisymmetric ( $\nu_{\text{as}}\text{-COO}^-$ : 1585 cm<sup>-1</sup>) and symmetric ( $\nu_{\text{s}}\text{-COO}^-$ : 1381 cm<sup>-1</sup>) stretching were observed<sup>24-26,30</sup>. This observation is evidence of the substitution of carbonate ions (CO<sub>3</sub><sup>2-</sup>) by formate ions (HCOO<sup>-</sup>). For the reasons stated above, the formate ion was considered successfully loaded on to the interlayer of HT. A sharp peak other than the ones listed above was observed at 1346 cm<sup>-1</sup> in the spectrum of formate-HT. This peak could be assigned to magnesium or aluminum formate, because of dissolution and reprecipitation of the brucite-like layer by the reaction



**Fig. 1** XRD patterns of (a) HT as received and (b) formate-HT. The prime miller indices are assigned in each pattern to a rhombohedral system.

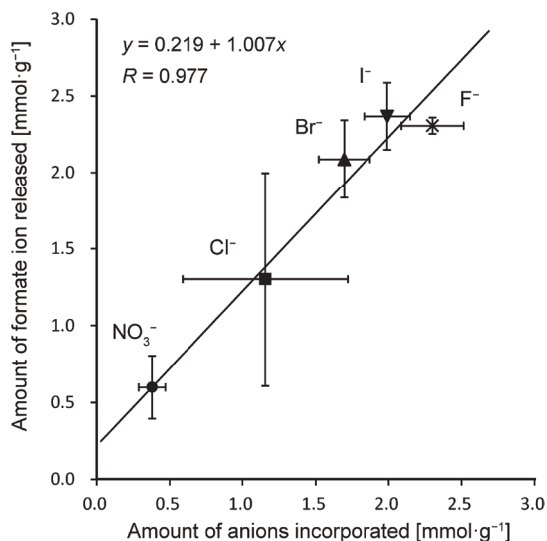


**Fig. 2** FTIR spectra of (a) HT as received and (b) formate-HT. The prime assignment is shown in each spectrum.

with formic acid in 1-propanol medium<sup>33-35</sup>.

### 3.2 Stoichiometry for anion exchange

Stoichiometry for the anion-exchange reaction of monovalent anions on formate-HT is shown in Fig. 3. The correlation between the amount of the formate ions released and the anions incorporated was tested by correlation coefficient (*R*) and orthogonal linear regression methods<sup>36</sup>. The relationship had a strong positive correlation (*R* = 0.977), and the slope of the regression line was 1.007, which is close to 1. These values indicate

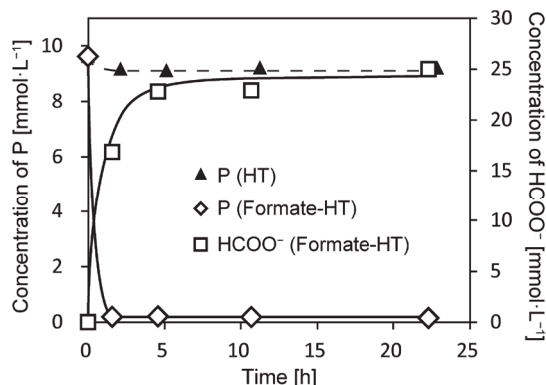


**Fig. 3** Relationship between the amounts of formate ions released from formate-HT and anions sorbed to them. Data represent mean  $\pm$  standard deviation.

that the amounts of formate ions released from the hydrotalcite were in fair agreement with that incorporated to hydrotalcite, irrespective of the species of the monovalent anions. Therefore, the correlation demonstrates that formate-HT can work as an anion-exchanger. Meanwhile, the intercept of the regression line was 0.219, i.e., the amount of formate ions released was slightly larger than that expected from stoichiometry. This value indicates that a little amount of magnesium or aluminum formate formed during the preparation of formate-HT in 1-propanol dissolved into the aqueous solution. Fig. 3 also shows an approximate order of the monovalent anion selectivity for formate-HT through anion exchange, which is  $F^- > I^- > Br^- > Cl^- > NO_3^-$ . However, this order does not conform to that shown by the chlorate-, nitrate-HT, and Ni-Al-type formate-LDHs ( $F^- > Cl^- > Br^- > NO_3^- > I^-$ )<sup>19,20,26</sup>. Although the reason for the change in sequence is under investigation, we believe that the phenomena is interesting and might be owing to the hydrated or non-hydrated structure of the interlayer formate ions.

### 3.3 Removal behavior for phosphorus

The time course of orthophosphate and formate ion concentrations after the dispersion of formate-HT in the  $K_2HPO_4$  aqueous solution is shown in Fig. 4. Formate-HT could remove phosphorus with the release of the formate ions within 2 h of dispersion, whereas carbonate-HT could remove little. As mentioned before, the anion-exchange reaction is perhaps the expected mechanism of the

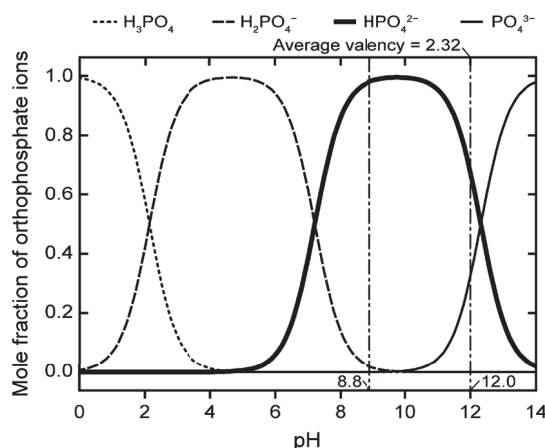


**Fig. 4** Time dependences of P and  $\text{HCOO}^-$  concentration after the dispersion of formate-HT (0.5 g) in  $\text{K}_2\text{HPO}_4$  aqueous solution ( $10 \text{ mmol}\cdot\text{dm}^{-3}$ ,  $50 \text{ cm}^3$ ,  $25^\circ\text{C}$ ).

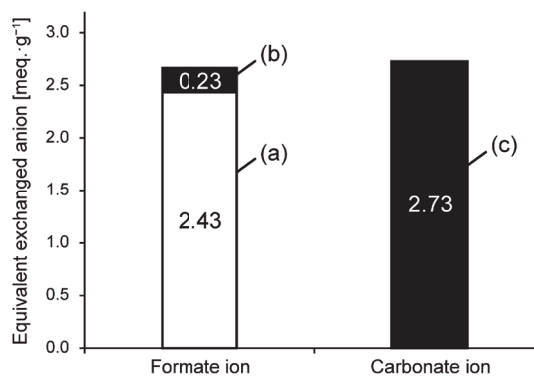
removal. The subsequent change in the valency of the orthophosphate ion might be of interest to researchers. The typical speciation of the orthophosphate ions is depicted in Fig. 5. The ratio of  $\text{HPO}_4^{2-}$  to  $\text{PO}_4^{3-}$  in the starting solution at pH 8.8 was estimated to be 97.4:0.01, by solving the simultaneous equations involving acid dissociation constants and mass balance<sup>37</sup>. Meanwhile, the  $\text{HPO}_4^{2-}:\text{PO}_4^{3-}$  ratio of 67.6:32.4 in the interlayer of HT was estimated in the following way. First, the net amount of formate ions contributing toward anion exchange ( $2.14 \text{ mmol}\cdot\text{g}^{-1}$ ) was calculated by subtracting the intercept of Fig. 3 ( $0.22 \text{ mmol}\cdot\text{g}^{-1}$ ) from the amount of formate ions released from formate-HT ( $2.36 \text{ mmol}\cdot\text{g}^{-1}$ ). Second, the average valency of the incorporated orthophosphate ions (2.32) was calculated by dividing the net exchanged anions amount by the amount of incorporated phosphorus ( $0.92 \text{ mmol}\cdot\text{g}^{-1}$ ). Third, the ratio of orthophosphate ions ( $\text{HPO}_4^{2-}:\text{PO}_4^{3-}=67.6:32.4$ ) was estimated by applying the average valency to the system depicted in Fig. 5. This change in the ratio indicates that deprotonation of the interlayer species may proceed through an anion-exchange reaction, since the interlayer surface of the hydroxide layer of HT is basic, possibly corresponding to pH 12.0. Further work is in progress to investigate the valency of the orthophosphate ion in the interlayer. In Addition, formate-HT is expected to incorporate orthophosphate ions up to an anion-exchange capacity of  $3.2 \text{ meq}\cdot\text{g}^{-1}$ . Based on the above facts, it can be suggested that formate-HT could serve as a rapid remover of phosphorus.

### 3.4 Regeneration of sorbent

Stoichiometry was investigated for the elimina-

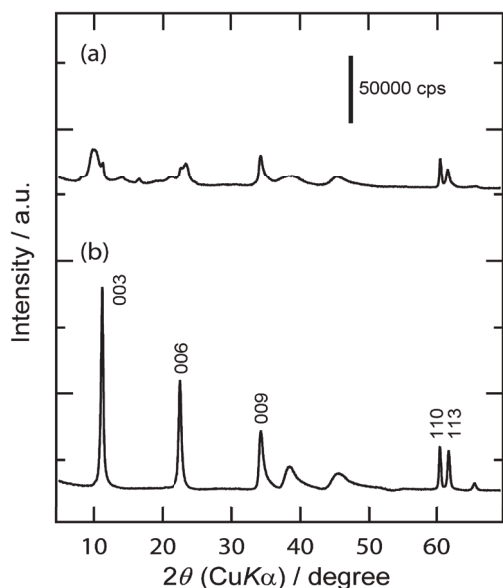


**Fig. 5** Speciation of orthophosphate ions at various pH. This graph is drawn by solving the simultaneous equations of acid dissociation constants and mass balance. The acid dissociation constants of orthophosphate ions are  $K_{a1} = 7.5 \times 10^{-3}$  ( $\text{p}K_{a1} = 2.1$ ),  $K_{a2} = 6.2 \times 10^{-8}$  ( $\text{p}K_{a2} = 7.2$ ), and  $K_{a3} = 4.8 \times 10^{-13}$  ( $\text{p}K_{a3} = 12.3$ ).



**Fig. 6** Equivalent exchanged anions: (a) formate ion released from formate-HT when testing removal for orthophosphate ion, (b) formate ion released when testing the reaction with sodium carbonate, and (c) carbonate ion removed when testing the reaction with sodium carbonate.

tion of phosphorus from phosphate-HT in conjunction with re-carbonation of HT. The amount of phosphorus was  $0.80 \text{ mmol}\cdot\text{g}^{-1}$  for the incorporation and  $0.92$  for the elimination after dispersion of phosphate-HT in the  $\text{Na}_2\text{CO}_3$  aqueous solution. Then, the equivalent exchanged anions other than phosphate through the incorporation and elimination test are shown in Fig. 6. The amount of formate ions released when testing the incorporation and elimination for phosphorus ( $2.66 \text{ meq}\cdot\text{g}^{-1}$ ) was comparable to that of carbonate ions consumed when testing the elimination ( $2.73$



**Fig. 7** XRD patterns of (a) phosphate-HT and (b) re-carbonated HT. The prime miller indices are assigned in the pattern of re-carbonated HT to a rhombohedral system.

meq·g<sup>-1</sup>). These facts indicate that the formate and orthophosphate ions incorporated in HT can be easily and stoichiometrically eliminated by the reaction with CO<sub>3</sub><sup>2-</sup>, which has a strong affinity toward the brucite-like layer. The crystal structures of HTs were checked both before and after the reactions using XRD patterns shown in Fig. 7. The crystal structure nearly reverted to the starting HT structure after the elimination, showing that the material is able to regenerate the starting state. Based on this observation, formate-HT is expected to be suitable as a renewable anion-exchange material for the removal and collection of phosphorus. Furthermore, both sodium phosphate and formic acid might be regenerated by distilling the mixed aqueous solution of formate, orthophosphate ions, and sodium carbonate after the elimination.

#### 4. Conclusion

A novel anion exchanger, hydrotalcite with formate ions in the interlayer (formate-HT), was investigated. This material showed the ability to remove phosphorus based on an anion-exchange principle. Furthermore, the phosphorus incorporated in HT can be collected and the formate-HT can be renewed as the starting HT. Because of the unique feature that allows formate ions to be easi-

ly eliminated from aqueous solution by volatilization or oxidative degradation, formate-HT is expected to be an interesting substitute for chloride- and nitrate-HT, which are commonly used as anion exchangers. Further work is in progress to explore the removal and collection of harmful and/or recyclable anions using formate-HT.

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