Synthesis of Hydrotalcite from Bittern, and Its Removal Abilities of Phosphate and Nitrate

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Abstract-In this study, hydrotalcite was synthesized from bittern solution with addition of AlCl₃ (Mg/Al molar ratio of the solution = 3), and its removal abilities of phosphate and nitrate from aqueous solution were examined. Hydrotalcite can be synthesized from bittern and seawater, and the product from bittern is higher content of hydrotalcite than that from seawater. The product from bittern has a removal abilities of phosphate and nitrate, which were higher than commercial hydrotalcite. The equilibrium adsorption capacity of the product for phosphate and nitrate ions were measured and extrapolated using Langmuir and Freundlich isotherm models, and experimental data are found to fit Langmuir than Freundlich. In the solution with 1 mM of phosphate or nitrate ions, adsorption of phosphate on the product was saturated within 30 min and almost constant after 30 min, while that of nitrate increase within 15 min and then gradually decrease, due to the ion exchange reaction of chlorine and sulphate in the product.

Index Terms—Hydrotalcite, bittern, removal of phosphorus and nitrate, anion exchange.

I. INTRODUCTION

The hydrotalcite (HT) is classified as a layered double hydroxide (LDH) composed of metal complex hydroxide: $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{x+}[(A^{n-})_{x/n}\cdot nH_2O]^{x-}$ (x = 0.2 - 0.33), where M^{2+} and M^{3+} are divalent and trivalent metal ions, respectively, and A^{n-} is anionic species [1]. The structure of HTs consists of a positive charged brucite-like octahedral layer and a negatively charged interlayer containing anions and water molecules [2]. The positively charged layer is formed by partial substitution of a trivalent metal for a divalent one. The layers can be stacked, and the balancing interlayer anions can be exchanged with other anions.

HT have received increasing attention in recent years as ion-exchanger [3]-[8], catalyst [9], [10], precursor for catalyst [11]-[13] and antacids [14]-[16] in medical application. Extensive studies have been made on the method of preparation and the physicochemical properties of HT compounds [17]-[21].

Eutrophication is a water enrichment in nutrients that generally leads to symptomatic changes when the production of algae and other aquatic vegetations are increased, degradation of fisheries and deterioration of water quality as well as all its uses in general. Eutrophication is a peculiar form of water pollution, causing major alterations: abnormal water colorations, loss of transparency and toxicity by the presence of certain algae products [22]. The eutrophication process is caused by the increase in nutrients levels, particularly phosphorus and nitrogen, which exceeds the limiting threshold of the primary production and, consequently, ecosystem control mechanisms are not used [23]. In order to prevent eutrophication, it is considered to reduce the load of phosphorus and nitrate to water environment. One method is the removal of phosphate and nitrate ion by HT [24]-[28]. However, HT is an expensive material used as antacid, etc., and it is necessary to develop a new process for inexpensive HT.

The bittern was the by-product from the refinement process of salt. Though the bitterns are regarded as waste material, several kinds of ions (Mg^{2+} , Ca^{2+} , K^+ , Na^+) are rich in bittern. Especially, magnesium ion is the most abundant cation species in bittern.

In this study, HT was synthesized using bittern in consideration for the utilization of plant-producing $Mg(OH)_2$, and the characteristics of removal for phosphate and nitrate by the HT was examined for the application of water purification.

II. MATERIALS AND METHODS

A. Seawater and Bittern

Seawater and two bittern samples were used in this study. Seawater was collected from the surface layer of Imari bay, Saga prefecture, Japan. Two bittern was obtained from two Japanese salt making plants with different processes. Chemical compositions and pHs of these samples are shown in Table I. The contents of Na⁺, K⁺, Mg²⁺, Ca²⁺, Cl⁻, Br⁻ and SO₄²⁻ in samples were determined by ion chromatography (DX-120, Dionex), and pHs of the sample were measured by pH meter (MA-130, Mettler toledo).

TABLE I: CHEMICAL COMPOSITIONS AND PHS OF SEAWATER AND BITT	ERNS
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	Seawater	Bittern-1	Bittern-2		
Contents (g/L)					
Na^+	9.7	103.5	30.7		
\mathbf{K}^+	0.4	5.4	35.0		
Mg^{2+}	1.3	14.8	43.9		
Ca^{2+}	0.4	N.D.	24.6		
Cl	18.5	204.1	250.8		
Br	N.D.	N.D.	18.3		
SO_4^{2-}	4.4	43.0	N.D.		
pH	7.7	7.4	6.8		
-		N.D. Not detected			

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B. Synthesis of Hydrotalcite

1 M AlCl₃ solution was added to 100 mL of seawater or bittern to adjust the Mg/Al molar ratio of 3 in the mixed solution, and stirred at 50 °C for 24 h. During stirring, pH of the solution was maintained at 10.5 by dropping10 w/v% NaOH solution. After stirring, precipitates were filtered, washed with distilled water, and then dried at 80 °C to obtain the product. The products were identified using X-ray diffraction (XRD) (RINT-2500, Rigaku), and was observed by scanning electron microscope (SEM) (S-2400, Hitachi). To determine chemical composition of the products, 25 mg of the product was perfectly dissolved in 10 mL of 0.1 M HNO₃ solution, the contents of Mg^{2+} and Al^{3+} were measured by inductively-coupled plasma spectrometers (ICP-AES) (SPS3000, Seiko instruments), and those of Cl⁻ and SO₄²⁻ were determined using ion chromatograph. The content of CO₃ in the product was analyzed by carbon/sulfur analyzer (EMIA1200, Horiba). Differential thermal analysis (DTA) / thermogravimetry (TG) (TG8120, Rigaku) was carried out in the temperature range 20 - 800 °C at a heating rate of 10 °C \min^{-1} in flowing air.

C. Removal Tests of Phosphate and Nitrate

Isotherm experiments of removals for phosphate and nitrate using the product from bittern-1 were performed as follows: 0.1 g of the product was added to 20 mL of the solution of NaH_2PO_4 or $NaNO_3$ with 1 - 25 mM in 50 mL of centrifuge tube, and the slurry was shaken with reciprocal shaker for 12 h. After shaking, the tube was centrifuged, and the concentrations of phosphate and nitrate in supernatant were measured using ion chromatograph.

The adsorption amounts of phosphate and nitrate per sample were calculated using the following equation;

$$q = (C_0 - C) \bullet V / w \tag{1}$$

where C_0 and C are the initial and final concentrations of phosphate and nitrate in the solution (mmol/L), respectively, V is the solution volume (L), and w is the mass of sample added to the solution (g).

Kinetics of removal reaction for phosphate and nitrate using the product were determined as follows; 50 mg of the product was added to 100 mL of the solution of NaH_2PO_4 or $NaNO_3$ with 1 mM in 200 mL baker, and the slurry was stirred with magnetic stirrer for 120 min. During stirring, 2 mL of aliquot was removed, and then filtered to obtain the filtrate, and the concentrations of phosphate, nitrate, chloride and sulfate in the filtrate were measured using ion chromatograph.

III. RESULTS AND DISCUSSION

Fig. 1 shows XRD diffraction patterns of the products from (a) bittern-1, (b) bittern-2 and (c) seawater. It is clear that from Fig. 1 that the HT can be formed as a main reaction product with addition of AlCl₃. The single peak pattern of HT is identified in both products from bitterns, while the product from seawater is the mixture of HT, calcite and brucite. The order of peak intensities for HT is the product from bittern-1 > that from bittern-2 > that from seawater.



Fig. 1. X-ray diffraction patterns of the products from (a) bittern-1, (b) bittern-2 and (c) seawater.

Table II shows chemical compositions of the products and commercial hydrotalcite. As the HT has positive charged sites based on the Al^{3+} in double hydroxide layer [21], the intercalated amount of anion should be theoretically equal to the Al^{3+} amount in the HT. Namely, the amount of Al^{3+} should be in accord with the anion exchange capacity of the HT. The anion exchange capacities of the products were estimated to be 2.7 - 2.8 mmol/g, and that of commercial HT are also considered to be 2.0 mmol/g. Generally speaking, 1 mmol/g or more of anion exchange capacity should be required as a standard for the practical use. So these exchange capacities may be adequate large as an anion exchanger.

The amount of exchangeable anions in commercial HT is 2.1 mmol/g as CO₃, which is almost same as anion exchange capacity of commercial HT (2.0 mmol/g). It is considered that exchangeable anion in HT present as monovalent HCO₃⁻. The exchangeable anions in the products are mainly Cl⁻, SO₄²⁻ and HCO₃⁻, and the total amounts of exchangeable anions are 2.9 mmol/g in the product from bttern-1 and 3.0 mmol/g in the product from bttern-2, respectively, which are almost same as anion exchange capacities of the products. Therefore, these three anions are mainly exchangeable anions in the product. It is noted that the product from seawater is low content of Cl and high content of CO₃, due to the present of calcite in the product.

The Mg/Al molar ratios of the products indicate 3.5 - 3.6, and they may be higher than 3.0 of the set value in the HT preparation. It may be caused by the nature of the solution with different concentration of Mg²⁺ and some coexisting ions. It is noted that Mg/Al molar ratio of commercial HT is 4.4.

TABLE II: CHEMICAL COMPOSITIONS OF THE PRODUCTS AND COMMERCIAL HYDROTALCITE

	Chemical composition (mmol/g)				Mg/Al	
	Mg	Al	Cl	SO_4	CO ₃	molar ratio
The product from bittern-1	9.8	2.8	1.6	0.3	0.7	3.5
The product from bittern-2	9.4	2.7	1.9	0.1	0.9	3.6
The product from seawater	8.3	2.8	0.1	0.4	2.2	3.0
Commercial HT	8.7	2.0			2.1	4.4

The DTA and TG curves of the product from bittern-1 are shown in Fig. 2. The DTA curve shows two endothermic peaks at 210 and 370 °C. Corresponding to these peaks, the TG curve shows two step mass losses of 11.1 mass% by 230 °C and 18.0 mass% between 350 and 400 °C. The first step, around 210 °C, with a weight loss of 11.1 % is due to the loss of physically adsorbed and interlayer water molecules. The second step, around 370 °C, with sum weight losses of 18.0 % can be ascribed to the dehydroxyration of structural water (hydroxyl group in the brucite-like layer) and the elimination of anions (Cl⁻ and CO₃²⁻). These reactions give rise to the destruction of the layered structure to form calcined hydrotalcite. These curves of the product resemble that given for hydrotalcite-like compounds in the literature [29], [30]. This suggests the nature of bittern has little effect on the final structure and thus thermal degradation of the HT.



Fig. 2.TG-DTA curves of the product from bittern-1.

Fig. 3 illustrates the SEM photograph of the product. The particles of the product have smooth surface, and consists of an aggregate of primary particles.

The removal isotherms of (a) phosphate and (b) nitrate using the product and commercial HT are shown in Fig. 4. With increasing equilibrium concentration, the adsorptions of phosphate and nitrate increase to approximately 0.6 mmol/g and 0.4 mmol/g, respectively, and both becomes almost constant, while the adsorption of commercial HT for phosphate and nitrate are 0.18 mmol/g and zero, respectively. The product has better adsorption capacities of phosphate and nitrate than commercial HT.



Fig. 4. Isotherm for adsorption of (a) phosphate and (b) nitrate using the product and commercial HT.



Fig. 3. SEM photograph of the product from bittern-1.

The removal behaviors of the product for phosphate and nitrate are determined by the isotherm models. Several isotherm models are available to describe the equilibrium sorption distribution with the Langmuir and Freundlich models being commonly used to fit experimental data. The linear forms of the Langmuir and Freundlich models are given by:

$$C_e / q_e = 1/(Q_{\text{max}} \bullet K_L) + C_e / Q_{\text{max}}$$
(2)

$$\ln(q_e) = \ln(K_F) + (1/n) \bullet \ln(C_e)$$
(3)

where q_e is the amount of phosphate or nitrate adsorbed at equilibrium (mmol/g); Q_{max} (mmol/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 values of Langumuir and Freundlich constants and regression coefficients for phosphate and nitrate removal were given in Table III. For both phosphate and nitrate, the correlation regression coefficients (R^2) of Langmuir model indicate a better fitting than the Freundlich model, and the maximum adsorption capacity of the product for PO₄³⁻ and NO₃⁻ calculated from Langmuir model is 0.59 mmol/g and 0.43 mmol/g, respectively.

TABLE III: ISOTHERM PARAMETERS FOR ADSORPTION OF POHSPHATE AND NITRATE ON THE PRODUCT

	Langmuir			Freundlich		
	Q_{max}	K_L	R^2	n	K_F	R^2
Phosphate	0.59	5.14	1.000	5.04	0.39	0.691
Nitrate	0.43	0.93	0.999	2.99	0.18	0.901

The removals of phosphate and nitrate during the reaction and the release of chloride and sulfate from the product are shown in Fig. 5. In the case of phosphate (Fig. 5 (a)), the removal of phosphate increases rapidly and reaches an equilibrium value within 20 min, while the release of chloride into the solution increases and reaches equilibrium value within 20 min and that of sulphate are always zero, which means that phosphate in the solution can be rapidly removed by ion exchange reaction of chloride in the product. In the case of nitrate (Fig. 5 (b)), the removal of nitrate increases rapidly within 10 min and gradually decreases after 20 min, while the releases of chloride and sulphate into the solution increases and reaches equilibrium value within 10 min. In first stage by 20 min, nitrate in the solution can be rapidly removed by ion exchange reaction of chloride and sulphate in the product, but in the second stage, the nitrate in the product released into the solution by ion exchange, such as CO_3^{2-} , because the uptake of monovalent nitrate ion by HT is weaker than that of divalent ion.



Fig. 5. The removal of (a) phosphate and (b) nitrate during the reaction and the release of chloride and sulfate from the product.

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