Adsorption of Phosphate Ions from Sea Water by Use of Surface-Modified Boehmite[†]

Mineaki KABAYAMA, Naohito KAWASAKI*, Takeo NAKAMURA*,

Toshimitsu TOKIMOTO* and Seiki TANADA*

Tomita Pharmaceutical Co., Ltd., 85-1, Maruyama, Seto-cho, Naruto, Tokushima 771-0360

* School of Pharmaceutical Sciences, Kinki University, 3-4-1 Kowakae, Higashi-Osaka, Osaka 577-8502

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In an attempt to develop materials to remove phosphorus that causes eutrophication or red tide, boehmite (aluminum oxide hydroxide) was surface-treated with sulfuric acid, nitric acid, hydrochloric acid, and sulfates, and the adsorption rates and adsorption isotherms of phosphate ions onto them were measured. The amount of phosphate ions adsorbed onto the boehmite, which was treated with sulfuric acid, was the greatest. This suggests that hydroxyl groups located in the boehmite are exchanged for sulfate groups by the sulfuric acid treatment. When boehmite was surface-treated with sulfuric acid of different concentrations, the amount of phosphate ions adsorbed increase with the increasing concentration of sulfuric acid. This result indicates that the adsorption of phosphate ions can be controlled by the amount of sulfate groups introduced in boehmite. The sulfate group of boehmite could also be introduced by an acidic sulfate solution treatment. When boehmite was treated with sulfuric acid, its capacity to adsorb a low concentration of phosphate ions from sea water increased to approximately 3 times that of the untreated boehmite. This suggests that the boehmite after the treatment of sulfuric acid or an acidic sulfate solution could be utilized for removing phosphate ions from sea water.

1. Introduction

In recent years, eutrophication, which causes red tide and water bloom in the ocean and lakes, has become a serious problem. Water bloom, which is the proliferation of algae, is responsible for the offensive odor and degradation of the landscape,¹⁾ while red tide leads to the extinction of fish and shellfish, and has a major adverse impact on the fish culture business and fishing.²⁾ Nitrogen and phosphorus are the causative agents in eutrophication or red tide, and thus it is desirable to simultaneously remove both in order to prevent eutrophication. Certain kinds of algae help to fix nitrogen, and phosphorous has a greater impact on the growth of algae than nitrogen. Hence, phosphorus is a more serious problem than nitrogen.^{3,4)} It is also known that as little as 0.003 mg/L of phosphate ion is enough for the growth of algae.³⁾ Therefore, it is important to control the concentration of phosphate ion in the water environment

for its protection.

Phosphate ion can be removed by coagulation sedimentation, biological treatment, and adsorption. For removing phosphate ion at a high efficiency by adsorption, both the amount of phosphate ion adsorbed per unit weight of an adsorbent and the adsorption rate should be high. Boehmite (aluminum oxide hydroxide) can be used to adsorb phosphate ion, since it has an adsorption selectivity for phosphate ion.⁵⁾

As part of our attempt to develop adsorbents possessing high capacities to adsorb phosphate ion, we surface-treated boehmite with various acids and sulfates and investigated the adsorption ability and mechanism of phosphate ion.

2. Experimental

2.1 Surface treatment of boehmite by inorganic acids

Boehmite was prepared by adding amorphous aluminum hydroxide to purified water and boiling it at 90-100°C for 1-3 h. As inorganic acids for the surface treatment of boehmite, sulfuric acid, hydrochloric

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E-mail: kawasaki@phar.kindai.ac.jp

ric acid, and nitric acid were used. Before the treatment by each acid, 260 g of boehmite was added to 800 L of purified water, and then the mixture was stirred for 30 min. To this suspension, 260 L of 10 % sulfuric acid, 20 L of 2 mol/L hydrochloric acid, or 21.5 L of 2 mol/L nitric acid was added. The mixture was stirred for 1 h and then filtered. Finally, the residue was thoroughly washed and dried at 90°C for testing.

Boehmite was also treated with different concentrations of sulfuric acid. A 500 g sample of boehmite was mixed with 1.5 L of purified water, and 10 % sulfuric acid was added until the pH was 5.0, 4.0, 3.0, or 1.9. Each mixture was stirred for 30 min and then filtered. Finally, the residue was thoroughly washed and dried at 90°C.

2.2 Surface treatment of boehmite by sulfates

First, 50 g of boehmite was added to 350 mL of purified water, and the mixture was stirred for 30 min, then 40 mL of a 47.1 mmol/L ammonium sulfate solution was added. The mixture was stirred at 96–100°C for 1 h and then filtered. The residue was thoroughly washed and dried at 90°C. The same procedure was repeated with a sodium sulfate solution of the same concentration as the ammonium sulfate solution.

2.3 Measurement of sulfate, chloride, and nitrate contents in boehmite

The sulfate or chloride contents and the nitrate content in boehmite were measured by turbidimetry and colorimetry techniques, respectively. The sulfate content in the surface-treated boehmite (prepared as dried residue) was determined as follows. First, 1.0 g of sample was added to 15 mL of dilute hydrochloric acid, which was heated to dissolve it. Purified water was added to the solution to bring the total volume to 250 mL. This solution was centrifuged, and then 1.0 mL of dilute hydrochloric acid was added to 25 mL of the supernatant liquid. Finally, purified water was added to bring the total volume to 50 mL. The control solutions for calibration were prepared by adding 1.0 mL of dilute hydrochloric acid to predetermined volumes of 0.002 mol/L sulfuric acid and adding purified water to bring the total volume to 50 mL, then following by adding 2.0 mL of barium chloride. The control solutions were used to generate a calibration curve for the nephelometer, which was used to determine the sulfate ion concentrations of the sample solutions subjected to the turbidimetry. Finally, the sulfate content in boehmite was calculated from the sulfate ion concentration.

The chloride content in the surface-treated boehmite was determined as follows. First, 1.0 g of sample was added to 30 mL of dilute nitric acid, which was heated to dissolve it. Purified water was added to the solution to bring the total volume to 100 mL. This solution was centrifuged, and then 6.0 mL of dilute nitric acid was added to 5 mL of the supernatant liquid. Finally, purified water was added to bring the total volume to 50 mL. The control solutions for calibration were prepared by adding 6.0 mL of dilute nitric acid to predetermined volumes of 0.01 mol/L hydrochloric acid and adding purified water to bring the total volume of each solution to 50 mL, then following by adding 1.0 mL of silver nitrate reagent. The control solutions were used to generate a calibration curve for the nephelometer, which was used to determine the chloride ion concentrations of the sample solutions subjected to the turbidimetry. Finally, the chloride content in boehmite was calculated from the chloride ion concentration.

The nitrate content in the surface-treated boehmite was determined according to JIS K 8001. First, 1.0 g of sample was added to 30 mL of dilute hydrochloric acid, which was heated to dissolve it. Purified water was added to the solution to bring the total volume to 100 mL. With 0.01 mg/mL nitric acid solution as the control, the absorbance of each sample solution at a wavelength of 213 nm was measured to determine the nitrate ion concentration, which was used to calculate the nitrate content in the boehmite.

3. Concentration of Phosphate Ion

The concentration of phosphate ion in the sample was measured by the molybdenum yellow method. Two mL of 10 % sulfuric acid and 1.0 mL of 5 % ammonium molybdate solution were added to the sample, and then stirred for 5 min. The absorbance at a wavelength of 389 nm was measured. Likewise, a blank test was performed using purified water. The concentration of phosphate ion in the sample was computed based on a calibration curve prepared beforehand.

4. Adsorption Ability of Phosphate Ion onto Boehmite in Sea Water

The sample was prepared by filtering sea water with a 1 µm membrane filter made of an ester mixed with cellulose, then adding disodium hydrogen phosphate to adjust its phosphate ion concentration to 70 mg/L. A 0.02 g sample of boehmite was added to 800 mL of sea water and this solution was stirred for

30 min, 1 h, 2 h, or 4 h, and filtered. Since the concentration of phosphate ion in sea water was low, it was measured by the molybdenum blue extraction method. Specifically, a filtered sample was poured into a separatory funnel, to which 1.0 mL of sulfuric acid and approx. 30 mL of 1-butanol were added. The funnel was vigorously shaken for 1 min and allowed to stand for 2 h. The supernatant liquid was poured into a 200 mL conical flask with a glass stopper, to which 5.0 mL of an ammonium molybdate solution and 1.0 mL of an L-ascorbic acid solution were added and mixed, and 10 mL 1-butanol was added. The flask was vigorously shaken for 1 min and allowed to stand for 2 h. Finally, the absorbance of the 1-butanol layer at a wavelength of 690 nm was measured. A blank test was performed in the same manner using purified water. The phosphate ion concentration was computed using a previously prepared calibration curve. The amount of phosphate ion adsorbed onto boehmite was calculated from before and after the phosphate ion concentration.

5. Results and Discussion

5.1 Surface treatment of boehmite by inorganic acids

To compare the surface crystal structures of boehmite before and after the sulfuric acid treatment, an X-ray diffraction (XRD) analysis was performed with an RINT 2000 (Rigaku, Tokyo) XRD analyzer under the conditions of 40 kV and 20 mA. The XRD patterns of both the boehmite and boehmite treated with sulfuric acid are shown in Fig. 1. Boehmite has a lamellar structure, each lamella containing hydrogen bonds.⁵⁾ The XRD patterns of the boehmite and

boehmite treated with sulfuric acid were almost identical, which indicated that the surface crystal structure of the boehmite was not changed by the sulfuric acid treatment.

When 260 g of boehmite was added to 800 L of purified water before it was treated by the inorganic acids, the pH of the suspension was 7.5. When the prescribed amount of sulfuric acid was added to the suspension, the pH changed to 1.8. When the prescribed amount of either hydrochloric acid or nitric acid was added, the pH changed to 5.0. In the latter case, when the pH of the suspension was adjusted to 2.0 by adding more hydrochloric acid or nitric acid, the boehmite decomposed and became gelatinous. Therefore, boehmite was treated with hydrochloric acid and nitric acid at pH 5.0.

The aluminum oxide, sulfate, chloride, and nitrate contents in the boehmite treated by inorganic acids are shown in Table 1. The sulfate content in the boehmite treated with sulfuric acid was higher than that of the untreated boehmite, which indicated that sulfate groups could be added to the boehmite treated with sulfuric acid. On the other hand, the chloride and nitrate contents in boehmite treated with either hydrochloric acid or nitric acid were similar to those of the untreated boehmite, which indicated that chloride and nitrate groups could not be added to the boehmite by the treatment with corresponding acids. Furthermore, the amount of phosphate ion adsorbed onto boehmite treated with sulfuric acid was about 3 times that onto the untreated boehmite.

5.2 Boehmite treated with sulfuric acid of different concentrations

Table 2 shows the aluminum oxide and sulfate

Fig. 1. XRD patterns of boehmite and boehmite treated with sulfuric acid.

Table 1. Properties of boehmite and boehmite treated with inorganic acids.

	Boehmite	HC-BE *	HN-BE **	HS-BE ***
Al ₂ O ₃ (%)	64.0	73.9	82.2	66.2
Sulfate (%)	1.3	1.1	1.1	8.8
Chloride (%)	<0.1	<0.1	<0.1	<0.1
Nitrate (%)	<0.1	<0.1	<0.1	<0.1
Amount of phosphate ions adsorbed (mg/g-boehmite)	21.2	22.6	26.4	61.7

*HC-BE: boehmite treated with hydrochloric acid.

**HN-BE: boehmite treated with nitric acid.

***HS-BE: boehmite treated with sulfuric acid.

Table 2. Relationship between pH and properties of boehmite treated with sulfuric acid.

pH	Original (pH 8.7)	5.0	4.0	3.0	1.9
Amount of sulfuric acid used (mL)	0	30	60	80	125
Al ₂ O ₃ (%)	68.3	67.9	65.8	65.8	65.0
Sulfate (%)	1.0	4.2	5.0	7.5	8.3
Sulfate/Al ₂ O ₃ (mole ratio)	0.016	0.065	0.080	0.121	0.136
Amount of phosphate ions adsorbed (mg/g-boehmite)	25.1	44.0	54.3	60.5	65.2

contents in boehmite treated with different concentrations of sulfuric acid and the amounts of phosphate ion adsorbed onto them. As the amount of sulfuric acid added to the boehmite-water suspension increased, the aluminum oxide content decreased and the sulfate content increased. Furthermore, the amount of phosphate ion adsorbed onto the boehmite increased as more sulfuric acid was added to the boehmite-water suspension. This result indicated that hydroxyl groups in the boehmite were substituted by the sulfate groups.

The amount of phosphate adsorbed in different concentration of phosphate ion onto boehmite was measured. In **Fig. 2**, the amount of phosphate adsorbed is the same as the maximum amount of phosphate ion adsorbed. Figure 2 shows the relationship between the sulfate content in the boehmite treated with sulfuric acid and the maximum amount of phosphate ion adsorbed onto it. A positive correlation (correlation coefficient 0.956) was found between the two parameters. This suggests that it is possible to control the amount of phosphate ion adsorbed onto the boehmite by varying its sulfate content.

5.3 Surface treatment of boehmite by sulfate

When 50 g of untreated boehmite was added to 350 mL of purified water, the pH of the suspension was 7.2. When ammonium sulfate and sodium sulfate solutions were added, the pH became 7.2 and 8.5, respectively. **Table 3** shows the aluminum oxide and sulfate contents in boehmite treated with different

Fig. 2. Relationship between sulfate content in boehmite and amount of phosphate ions adsorbed.

sulfates and the amount of phosphate ion adsorbed onto the boehmite. When boehmite was treated with an ammonium sulfate solution, which is acidic, the hydroxyl groups in the boehmite were substituted to sulfate groups, while this was not observed when the boehmite was treated with a sodium sulfate solution, which is neutral. It was thus confirmed that hydroxyl groups in boehmite could be substituted to sulfate groups by treating the boehmite with not only sulfuric acid, but also an acidic sulfate solution.

5.4 Adsorption mechanism of phosphate ion onto boehmite

The adsorption mechanisms of phosphate ion onto untreated boehmite and boehmite treated with sulfuric acid are illustrated in **Fig. 3**. As previously reported by the author, phosphate ion is adsorbed by

Table 3. Properties of boehmite and boehmite treated with sulfate solutions.

	Boehmite	SS-BE *	AS-BE **
Al ₂ O ₃ (%)	64.0	70.0	69.1
Sulfate (%)	1.3	1.5	4.5
Sulfate/Al ₂ O ₃ (mole ratio)	0.021	0.023	0.070
Amount of phosphate ions adsorbed (mg/g-boehmite)	21.2	19.5	37.2

*SS-BE: boehmite treated with sodium sulfate solution.

**AS-BE: boehmite treated with ammonium sulfate solution.

Fig. 3. Adsorption mechanisms of phosphate ions onto boehmite and boehmite treated with sulfuric acid.

the hydroxyl groups in the boehmite, that is, the adsorption mechanism is an ion exchange.⁶⁾ However, it seems that certain hydroxyl groups in boehmite do not undergo ion exchange, and those hydroxyl groups are not exchanged with phosphate ion. This is schematically shown in [I] in Fig. 3. On the other hand, when boehmite is treated with sulfuric acid, hydroxyl groups in it are thought to be substituted by sulfate groups as shown in [II] in Fig. 3. Acidity of sulfuric acid is stronger than that of phosphoric acid. Therefore, when boehmite surface is treated with sulfuric acid, more hydroxyl groups in boehmite would exchange to sulfate groups. Moreover, when the phosphate ion is adsorbed onto boehmite treated with sulfuric acid, sulfate groups in boehmite surface would exchange to phosphate groups. In this scheme, hydroxyl groups bonded to aluminum atoms are removed by the hydrogen groups of sulfuric acid and replaced by sulfate groups, each of which is bonded to two aluminum atoms located in two sites. When

phosphate ions are present, the sulfate groups are exchanged with phosphate ions, because the adsorption selectivity of boehmite for phosphate ion is greater than that for sulfate groups.⁷⁾ This model can explain the present result of the adsorption ability of phosphate ion by boehmite remarkably increased due to sulfuric acid treatment.

5.5 Adsorption of phosphate ion onto boehmite in sea water

Figure 4 shows the amount of phosphate ion adsorbed onto untreated boehmite and boehmite treated with sulfuric acid from sea water with elapsed time. The amounts of phosphate ion adsorbed onto both the untreated boehmite and the boehmite treated with sulfuric acid reached 86 % of their equilibrium values after about 1 h, and reached equilibrium after about 2 h. Moreover, although the sulfuric acid treatment increased by 25 % the equilibrium amount of phosphate ion adsorbed onto the boehmite, it hardly influenced the adsorption rate of the phosphate ion.

Figure 5 shows the adsorption isotherms of phosphate ion onto the untreated boehmite and the boehmite treated with sulfuric acid. They were found to follow Henry's type as the phosphate ion concentration was low. Adsorption of Henry's type is described by the following equation⁸⁾:

$$V = a \cdot C \quad (1)$$

where V (mg/g) is the amount of adsorbate per unit weight of adsorbent, C (mg/L) is the equilibrium concentration, and a is a constant. The constant a is related to the adsorption ability, and the higher the value, the greater the adsorption ability. The values of the constant a of the adsorption isotherms of phosphate ion onto the untreated boehmite and the boehmite treated with sulfuric acid were 0.007 and 0.022, respectively. This suggests that the adsorption ability of phosphate ion onto the boehmite treated with sulfuric acid was approximately 3 times greater than that of the untreated boehmite.

Fig. 4. Adsorption rate of phosphate ions onto boehmite and boehmite treated with sulfuric acid from sea water.

Fig. 5. Adsorption isotherms of phosphate ions adsorbed onto boehmite and boehmite treated with sulfuric acid from sea water.

6. Conclusion

It was determined that hydroxyl groups on boehmite were replaced by sulfate groups due to the sulfuric acid treatment. The sulfuric acid treatment did not change the crystal structure of the boehmite. Sulfate groups could be introduced to the boehmite by a sulfuric acid or an acidic sulfate treatment. Adsorption ability of phosphate ion onto boehmite increased due to sulfuric acid treatment, but it did not change after the hydrochloric acid or nitric acid treatment. The amount of phosphate ion adsorbed onto boehmite was proportional to the sulfate content of the boehmite, which suggested that the adsorption ability could be controlled by this factor. It was demonstrated that boehmite treated with sulfuric acid could be used to adsorb phosphate ion from sea water.

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