

Relationship between Anion Adsorption and Physicochemical Properties of Aluminum Oxide

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This study investigated the adsorption capacity and adsorption mechanism of phosphate by calcined aluminum oxide (GB) at temperatures of 200 to 1150°C. The results showed that GB and GB calcined at a temperature of 200°C exhibited almost no adsorption capacity, and GB calcined at temperatures of 300 or 400°C exhibited the highest adsorption capacity. After that, adsorption capacity tended to decrease with increasing calcination temperature. The specific surface area and the concentration of surface hydroxyl groups exhibited the highest values in GB calcined at temperatures of 300 and 400°C. From the above facts, it is conjectured that the specific surface area and concentration of surface hydroxyl groups contribute to the adsorption of phosphate in calcined GB. The results of X-ray diffraction showed that the structure of GB changed drastically at temperatures of 200 to 300°C and 900 to 1000°C. Also, it was evident that phosphate was adsorbed selectively even in complex solution systems containing chloride, nitrate, sulfate, hydrogen carbonate and phosphate ions, and that calcined GB is suitable for adsorption of phosphate. For the adsorption of phosphate, it was found that the optimum pH is around 4. When calcined GB is suspended in purified water, it is thought that hydroxyl groups form through dissociative adsorption with water molecules, and that these hydroxyl groups conduct ion exchange with phosphate.

Key words — adsorption, aluminum oxide, eutrophication, calcination, phosphate

INTRODUCTION

In recent years, environmental problems such as air pollution, water pollution and soil pollution have become global in scale. In particular, the occurrence of blue-green algae as water pollution is a cause of foul odors and degradation of scenery.¹⁾ Phosphate has a large impact on the growth of algae, and phosphorus is a more serious problem than nitrogen.^{2, 3)} In closed sea areas and lakes in particular, the phosphate concentration increases, thereby causing eutrophication, which often leads to the occurrence of red tides or blue-green algae blooms. While phosphate is one of the elements comprising DNA, its constituent ratio compared to the other elements comprising living matter (nitrogen and carbon) is very low: P : N : C = 1 : 15 : 80.⁴⁾ The phosphorus concentration that stimulates algae reproduction is

said to be about 0.03 mg/l.²⁾ When this level of phosphate is released into the environment, the result is the abnormal occurrence of phytoplankton.

The decomposition period of phosphate in the ocean is approximately 160000 years,⁵⁾ and the cycle of phosphate in the natural world is said to be extremely slow — approximately 400 million years. Deposits of phosphate rock in the earth are said to be 14 billion tons, and are expected to be exhausted in 2035.⁶⁾ Previously, efforts have been made to develop phosphate removal equipment and to recover phosphorus. For example, there are methods⁷⁾ in which reaction with materials such as calcium, magnesium or iron ions precipitates phosphate, and methods in which phosphate is adsorbed on iron compounds, alumina,⁸⁾ activated alumina (produced through aluminum sulfate treatment),⁹⁾ boehmite,¹⁰⁾ iron hydroxide oxide,¹¹⁾ and yttrium carbonate,¹²⁾ as well as adsorption-based polymer ligand exchange.¹³⁾ There have also been a number of reports on anion removal.^{14, 15)} Using the adsorption method, it is possible to desorb with an alkali aqueous solution after the phosphate has been ad-

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sorbed. At that time, the adsorbent can be reconditioned, and the adsorbate can be recovered as phosphate alkali, which can then be reused. Therefore, this is thought to be a method which is also superior from the perspective of phosphate resource protection.

This research looked at a method by which aluminum oxide (GB) is calcined at different temperatures, and the resulting substance is used to adsorb anions. In this study, the relationship between the physicochemical properties of GB and the adsorption of anions was estimated by the specific surface area or the concentration of hydroxyl groups, the concentration of anions adsorbed at different pH levels, and the adsorption rate.

MATERIALS AND METHODS

Materials—GB (GBH-42M) was purchased from Showa Denko in Japan. Its chemical composition is adhesive moisture 0.23, Al(OH)₃ 99.6, Fe₂O₃ 0.01, SiO₂ 0.01, Na₂O 0.33, and w-Na₂O 0.05. Its average particle size is 1.1 μm, bulk density (light) 0.2 g/cm³, bulk density (heavy) 0.5 g/cm³, specific surface area 5 m²/g, and average moisture absorption capacity 0.90%. In the calcining treatment, 20 g of GB was placed in a porcelain crucible and kept in a muffle kiln at 200 to 1150°C for 2 hr. The specific surface area of GB was measured using Flow SorbII 2300 (Micromeritics, Norcross, GA, U.S.A.). A DTG-60AH automatic differential thermal/thermogravimetry measurement unit (Shimadzu, Kyoto, Japan) was used for differential thermoanalysis of GB, and a RINT2100 V (Rigaku, Tokyo, Japan) was used for X-ray diffraction analysis.

The surface pH of GB was measured as follows: approximately 2.0 g of GB was separately put into 100 ml of deionized water (pH 7.0) for 2 min, and the pH in solution was measured with a digital pH meter (Horiba, Kyoto, Japan).

The concentration of surface hydroxyl groups was found from the amount of fluoride ion adsorption.¹⁶⁾ GB was added to 50 ml of 0.01 mol/l sodium fluoride solution, and shaken at 25°C for 20 hr. The fluoride concentration in the supernatant was measured using DR4000U (HACH, Loveland, CO, U.S.A.) and the amount adsorbed was estimated based on the difference from the initial concentration.

Sodium chloride, sodium sulfate, sodium nitrate

and sodium hydrogen carbonate (Wako Pure Chemical Industries, Osaka, Japan) were used to evaluate the effects of other anions in the adsorption of phosphate.

Adsorption of Phosphate—The adsorption rate of phosphate onto GB was measured as follows: GB (1.0 g) was added to 200 ml of potassium dihydrogen phosphate solution with an initial concentration of 1 mmol/l. After 1, 5, 10, 20, 30, 60, 90, 120, 150 and 180 min, the solution was filtered with 0.45 μm filter paper (Advantec Toyo, Tokyo, Japan). The concentration of phosphate was measured, and evaluation was done by finding the amount adsorbed from the difference with the initial concentration of phosphate. The amount of phosphate adsorbed onto GB was measured by the following method: to 50 ml of 1 mmol/l potassium dihydrogen phosphate solution, 0.1 g of GB or GB calcined at 200 to 1150°C was added and shaken for 15 hr. After that, the solution was filtered with 0.45 μm filter paper. The concentration of phosphate was measured, and the amount adsorbed was found from the difference in phosphate concentration before and after adsorption. The concentration of phosphate was measured using the Phosphate Test (HACH). The amount of phosphate adsorbed onto GB at equilibrium was calculated from Eq. (1).

$$q = \frac{(C_0 - C_e) \cdot V}{1000 \cdot W_s} \quad (1)$$

Here, q is the amount of phosphate adsorbed (mg-PO₄/g), C_0 is the initial concentration (mg-PO₄/l), C_e is the equilibrium concentration (mg-PO₄/l), V is the amount of sample liquid (ml), and W_s is the amount of GB used (g). In order to investigate the saturation amount of phosphate adsorbed onto GB, 0.5 g of GB was added to 50 ml of 12 mmol/l potassium dihydrogen phosphate solution. After shaking for 15 hr at 25°C, the solution was filtered with 0.45 μm filter paper, and the concentration of phosphate was measured.

The solution pH was adjusted to 2–9 using a digital pH meter together with 1 mol/l hydrochloric acid solution, 0.1 mol/l hydrochloric acid solution and 0.1 mol/l sodium hydroxide solution. GB (0.1 g) was added to 50 ml of phosphate solution with an initial concentration of 1 mmol/l after pH adjustment, and after shaking for 15 hr, the solution was filtered with 0.45 μm filter paper, and the concentration of phosphate was measured. This method was used to determine the amount of phosphate adsorbed onto GB in solutions with different pHs.

Selective Adsorption of Anions— In order to evaluate selective adsorption of phosphate onto GB, measurements were taken of the amount of chloride, sulfate and nitrate adsorbed onto 0.1 g of GB and calcined GB. A 1 mmol/l solution of chloride, sulfate and nitrate ions was prepared using sodium chloride, sodium sulfate and sodium nitrate, respectively. GB (0.1 g) was added to 50 ml of the prepared anion solutions, and after shaking for 15 hr, the solutions were filtered with 0.45 μm filter paper, and the concentration of the anion was measured. The concentrations of chloride and sulfate ions were measured using DR4000U (HACH), and the concentration of nitrate was measured using the Nitrate Test (HACH). The removal percentage of anion was calculated from the difference between the initial concentration and the equilibrium concentration.

RESULTS AND DISCUSSION

Properties of Calcined GB

Figure 1 shows the results of differential thermoanalysis of GB. It is evident from the results of differential thermoanalysis that an endothermic reaction and changes in structure occur near a calcination temperature of 300°C. That is, it is conjectured that adsorption water evaporates between 200 and 300°C. The weight also decreases greatly at the same time. The results of X-ray diffraction for calcined GB are shown in Fig. 2. The results show large changes in structure at calcination temperatures between 200 and 300°C. Large changes in structure are also thought to occur in the range 900 to 1000°C. Weller¹⁷⁾ and Peri¹⁸⁾ report that water molecules dissociatively adsorb onto aluminum oxide; dissociative adsorption has also been reported for boehmite.¹⁹⁾ The phases from GB to corundum by calcination were reported by Hill *et al.*²⁰⁾

Table 1 shows the relationship between GB calcination temperature and the specific surface area, the surface pH and the concentration of surface hydroxyl groups. In these results, the specific surface area increased greatly at a calcination temperature of 300°C, reached a maximum at a calcination temperature of 400°C, and then decreased as the calcination temperature rose. Furthermore, the specific surface area decreased greatly at the calcination temperature of 1000°C. The concentration of surface hydroxyl groups was the highest when the calcination temperature was 400°C; above 400°C it decreased with increasing calcination temperature.

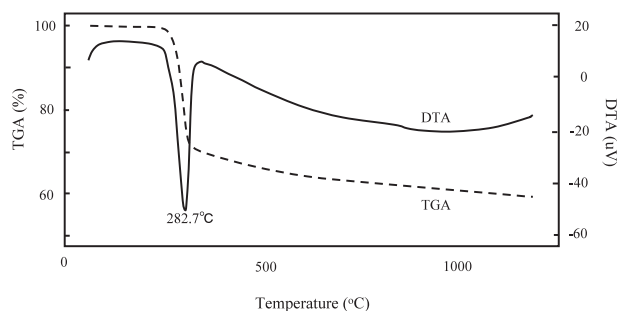


Fig. 1. TG-DTA of GB

Table 1. Specific Surface Area and the Concentration of Hydroxyl Group of GB Calcined at Different Temperatures

Calcination temperatures (°C)	Specific surface area (m ² /g)	Specific pH	Concentration of hydroxyl group (mmol/g)
untreated	4.2	8.7	2.7
200	4.6	9.3	2.8
300	253.9	9.7	4.6
400	295.3	9.8	5.0
500	227.3	9.3	4.8
600	176.1	9.4	4.6
700	147.7	9.6	4.2
800	128.1	9.6	3.8
900	95.4	9.7	3.4
1000	36.8	10.0	1.0
1100	20.8	10.3	1.0
1150	17.7	10.2	1.6

Adsorption of Phosphate

Figure 3 shows the removal percentage of phosphate by GB as time passes. The kinetic constant was calculated to elucidate the adsorption rate using the formula of the first-order reaction. The kinetic constants of GB calcined at 300 and 1000°C measured at 20 min or less were 0.037 and 0.006 min⁻¹, respectively while those at 30 to 180 min were 0.013 and 0.002 min⁻¹, respectively. In the results, the removal percentage of phosphate due to GB showed a striking decrease for the first 30 min for all calcination temperatures; this decrease was more conspicuous as the calcination temperature decreased. After that, there was a smooth decrease as time passed.

Table 2 shows the amount of phosphate adsorbed in a single solution or the saturation amount of phosphate adsorbed onto GB and GB calcined at different temperatures. The results show that GB and GB calcined at 200°C adsorb almost no phosphate. A sudden increase in the amount adsorbed was evident for GB calcined at 300°C. The solu-

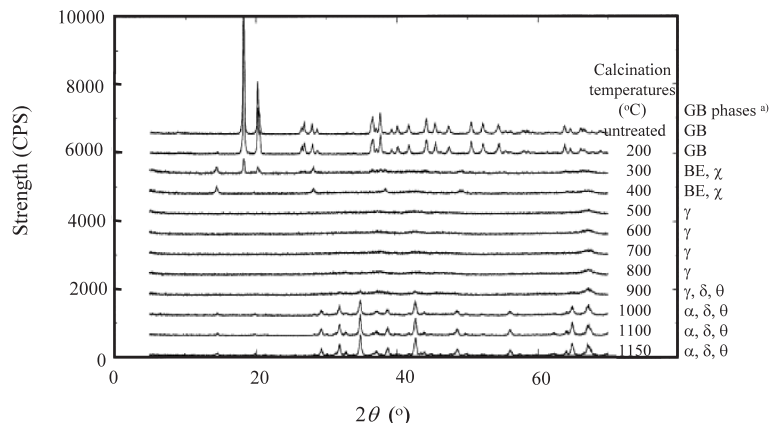


Fig. 2. X-ray Diffraction of GB and GB Calcined at Different Temperatures
a) GB phases: Hill *et al.* reported.

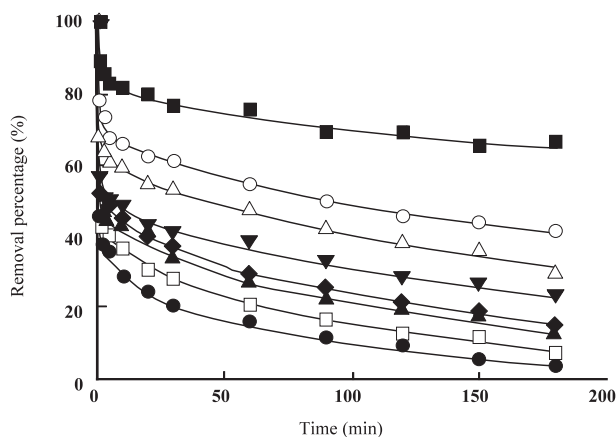


Fig. 3. Removal Percentage of Phosphate onto GB Calcined at Different Temperatures
●: 300°C, □: 400°C, ▲: 500°C, ◆: 600°C, ▼: 700°C, △: 800°C, ○: 900°C, ■: 1000°C.

tion pH after adsorption of phosphate was greater than that before adsorption. This is thought to be due to the surface hydroxyl groups of GB being involved in ion exchange with phosphate. The amount of phosphate adsorbed was the greatest for GB calcined at temperatures of 300 and 400°C; after that, the amount of phosphate adsorbed decreased with increasing calcination temperature. This same trend was evident for the specific surface area and the concentration of surface hydroxyl groups. It has been reported that, in adsorption onto boehmite — which is also aluminum hydroxide oxide — there is dependence on specific surface area and concentration of surface hydroxyl groups,¹⁹⁾ and the specific surface area and the concentration of surface hydroxyl groups are thought to be involved also in the adsorp-

tion of phosphate onto GB.

In terms of the saturation amount of phosphate, that adsorbed onto GB or GB calcined at 200°C was close to none. That onto GB calcined at temperatures of 300 to 500°C was the largest of all, and that onto GB calcined at higher temperatures decreased. The saturation amount of phosphate adsorbed also decreased greatly with calcination temperatures of 900 to 1000°C.

Selective Adsorption of Phosphate

Seawater contains many anions. Hence, for the purpose of phosphate recovery using GB, it is critical to evaluate the effects of other anions on phosphate adsorption. The anions in seawater are chloride and sulfate ions, while the salts contained in seawater are sodium chloride (78%), magnesium chloride (10%), magnesium sulfate (6%), calcium sulfate (4%) and calcium chloride (2%). The amounts of chlorine, nitrate, sulfate and phosphate adsorbed onto GB in complex solution are shown in Table 3. The results show that selectivity in adsorption of anions onto GB increases in the sequence: chloride ion < nitrate ion = sulfate ion < phosphate. From these results, it is evident that GB selectively adsorbs phosphate, and is suitable for recovering phosphate from rivers, lakes and seawater. The amount of phosphate adsorbed in complex solution was evaluated in order to evaluate selectivity in adsorption of phosphate onto GB. It was evident from the results that the amount of phosphate adsorbed onto GB in a complex solution was practically the same as that in a single solution; GB selectively adsorbs phosphate in complex solutions without being affected by other anions.

Table 2. Amount of Phosphate Adsorbed onto Calcined GB at Different Temperatures

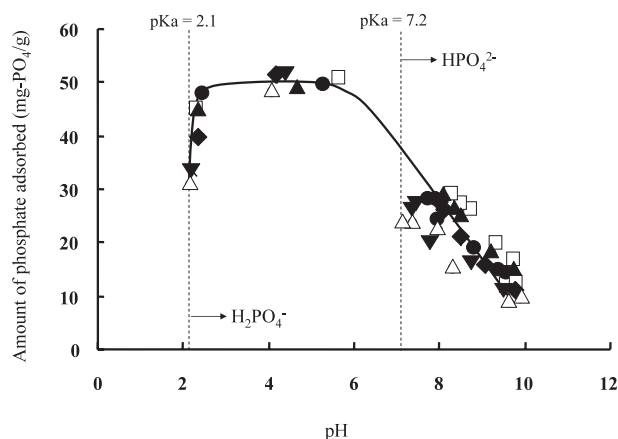
Calcination temperatures (°C)	Amount adsorbed (mg-PO ₄ /g) (Initial concentration: 0.99 mmol/l)	pH in solution after adsorption (pH before adsorption: 4.9)	Amount adsorbed (mg-PO ₄ /g) (Initial concentration: 12 mmol/l)
untreated	1.5	5.8	3.5
200	2.5	6.0	3.0
300	28.3	7.2	56.9
400	30.2	7.4	56.0
500	27.1	7.4	57.0
600	24.6	7.4	51.6
700	22.7	7.4	46.5
800	20.0	7.0	36.4
900	18.1	7.0	33.1
1000	9.6	6.5	14.5
1100	6.6	6.4	9.0
1150	4.5	6.3	6.5

Table 3. Removal Percentage of Chloride, Nitrate, Sulfate and Phosphate Ions by Calcined GB at Different Temperatures

Calcination temperatures (°C)	Removal percentage (%)			
	Chloride ion	Nitrate ion	Sulfate ion	Phosphate ion
untreated	0.0	0.2	1.2	8.6
200	0.0	1.5	0.8	7.7
300	0.1	0.2	5.8	53.6
400	0.0	0.5	2.5	54.5
500	0.0	0.3	5.3	53.2
600	0.1	0.9	1.5	48.6
700	0.0	0.7	1.8	45.9
800	0.0	0.0	1.3	40.9
900	0.0	0.0	0.0	39.5
1000	0.2	0.0	0.3	16.8
1100	0.5	0.0	0.0	16.8
1150	0.0	0.0	0.0	11.8

Amount of Phosphate Adsorbed in Different pH Solution

In general, ion adsorption is affected by pH, and it is important to evaluate phosphate adsorption behavior in aqueous solutions of different pHs. Figure 4 shows the amount of phosphate adsorbed onto GB calcined at temperatures of 300 to 800°C in aqueous solutions with different pHs. In the results, the amount of phosphate adsorbed exhibited its highest value in an aqueous solution with acidic conditions (pH around 4), and decreased as the pH rose. This trend was the same, regardless of differences in calcination temperatures. This is thought to be because phosphate replacement to GB is impossible under alkaline conditions. Xu *et al.*²¹⁾ report

**Fig. 4.** Amount of Phosphate Adsorbed onto GB Calcined at Different Temperatures in Different pH Solutions

●: 300°C, □: 400°C, ▲: 500°C, ◆: 600°C, ▼: 700°C, △: 800°C.

that, when the initial concentration is 0.64 mmol/l, removal of phosphate by aluminum-supported silaszeolite decreases from 80% to approximately 40% from pH 2 to 11. The molecular formula of aluminum supported silaszeolite is Al(OH)₃, the same as GB. Therefore, GB is also thought to be affected by pH.

This research investigated the adsorption mechanism of phosphate onto the surface of GB calcined at temperatures in the range of 200 to 1150°C. The results showed that GB does not exhibit adsorption capacity unless it is calcined at 300°C or higher. The amount of phosphate adsorbed onto GB calcined at temperatures of 300 to 800°C was higher than GB calcined at other calcination temperatures. An adsorbent with adsorption capacity

for phosphate can be fabricated from calcined GB. It was found that GB selectively adsorbs phosphate, and the adsorption rate is extremely fast. Also, the amount of phosphate adsorbed onto GB is affected by pH, and the amount of phosphate adsorbed onto GB is the highest in aqueous solution under acidic conditions; the adsorption capacity decreases in the alkaline state. It was also found that adsorption of phosphate is not affected by the presence of other anions, and that phosphate is adsorbed selectively onto GB compared to chloride, nitrate, sulfate and hydrogen carbonate ions.

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